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Photopyroelectric Monitor of Olive Oil Quality and Olive Fruit Oil Content During the Ripening Period.

Yasser Ibrahem EL-Sarahneh.

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By:

Yasser Ibrahem EL-Sarahneh.

(B.Sc. Physics, 1995, Bethlehem University, Palestine)

Supervisor: Dr. M. I. Abu - Taha

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By:

Student Name: Yasser Ibrahem El-Sarahneh.

Registration No: 20310011

Supervisor: Dr. Mohammad Abu-Taha.

Master thesis submitted and accepted, Date: 8 / 8 / 2005.

The names and signature of the examining committee members are as follow:

1- Dr. Mohammad Abu-Taha   Head of Committee.   Signature…………….

2- Dr. Imad Barghouthi   Internal Examiner.   Signature…………….

3- Dr. Zeid Naeim Qamhieh   External Examiner.   Signature…………….

Al-Quds University

2005

Declaration:

I certify that this thesis submitted for the degree of Master is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed: …………………

Name: Yasser Ibrahem Ahmad El-Sarahneh.

Date: 8 / 8 / 2005.

DEDICATION

To the memory of my mother

To my father

To my wonderful wife

To my beloved family

Acknowledgements

Thank God the Merciful the Graceful, who granted me the capability, ability and courage to finish up this work.

I am greatly indebted to the kindness, assistance, and patience of my advisor Dr. Mohammad Abu-Taha, for his great help, guidance and assistance during the research and the preparation of this dissertation that made the present work possible. In addition I would like to sincerely thank those who have contributed their efforts to this study.

Special thanks and deep gratitude and appreciation go to my wife for her support and encouragement throughout the period of study and work on the thesis. Last, but in no way least, my heartfelt thanks go to my parents specially to the soul of my mother, sons Btool, Alma and Osaid, and to my brothers, sisters, suns of my cousin and cousin in law, for their lightened with love every step toward the complication of this work.

Abstract

The new findings about olive oil healthy virtues have increased interest and consumption of this material. Virgin olive oil quality depends on many factors related to our care in the olive tree such as cultivation, harvesting, storage and olive processing steps, as well as fertilization and irrigation of olive trees. The moment of picking olive fruits is vital, although not the only factor ensuring a good quality of the olive oil. Mature olives fruit may reach an oil content of (20%) on fresh weight basis in about (6-8) months after full bloom. In the course of ripening the color of olives changes from green, spotted, purple and finally ends up in black. The characteristics of the olives differ at different stages of ripening. Olive's cultivation at the right time is of great importance in insuring the best oil quality and maximizing the year yield of harvest. Taking the above factors into consideration this study is aimed to investigate olive oil properties dependant on some storage parameters and the approximate ripening time of olives by monitoring olives composition by the detection of a photopyroelectric (PPE) signal of fresh olives at different period of maturation. The pyroelectric effect is well known and it has good potential for use to measure the temperature change related to infrared absorption from a wideband pulsed source. It is rather important to establish a simple method to estimate the best ripening time for picking olives by monitoring fresh olive juice using

wideband infrared (IR) absorption which depends mainly on its composition as ripening time passes.

Results have shown that the PPE method is suitable and sensitive technique which gave results comparable to sophisticated techniques especially for oil accumulation in olives during maturation. The method was also used for olive oil adulteration and investigation of oil storage condition.

ملخص:

أن النتائج الجديدة حول خصائص زيت الزيتون الصحية   أدت إلى زيادة الاهتمام والاستهلاك لهذه المادة. تعتمد النوعية النقية لزيت الزيتون على عدة عوامل   : منها ما يتعلق بطريقة العناية بشجرة الزيتون من تسميد، ري، طريقة زراعة والوقت المناسب للحصاد.

كما تعتبر طريقة تخزين الزيت عاملاً مهما في الحفاظ على صفات الجودة المحبذة للمستهلك.

في الواقع؛ النوعية الجيدة لزيت الزيتون تعتمد اعتماداً أساسيا على وقت الحصاد المناسب أي مدى نضج الثمار، لكن ليس هذا العامل الوحيد الذي يضمن جودة زيت الزيتون. النضوج الفعلي لحبة زيت الزيتون يستمر من (6 – 8) شهور بعد نضوج الزهرة الكاملة، وقد تصل نسبة الزيت في حبة الزيتون (20 %) من وزن الحبة ، كما انه خلال فترة النضوج يتغير لون حبة الزيتون من الأخضر إلى المنقط والأرجواني ثم الأسود. خصائص زيت الزيتون ومكوناته تختلف أثناء المراحل المختلفة من النضج، إن قطف الزيتون في الوقت المناسب يعد ذا أهمية كبيرة في تأمين أفضل نوعية زيت، ناهيك عن أنه يزيد محصول السنة من الإنتاج آخذاً بالاعتبار كل العوامل السابقة . لا بد من إيجاد طريقة تساعد في تحديد الوقت التقريبي لنضج ثمار زيت الزيتون ولإيجاد أفضل ظروف لتخزين الزيت ليصل لاحقاً للمستهلك محتفظاً بصفاته وخصائصه الغذائية والصحية على حد سواء.

اعتمد البحث على طريقة تدعى فوتوبايروالكتريك (PPE) لفحص عصير طازج مستخدم من حبات الزيتون في مراحل مختلفة من النضج لمراقبة مدى احتواء الحبة على زيت الزيتون. وقد استخدم مصدر متردد من الأشعة تحت الحمراء لدراسة امتصاص عصير الزيتون الطازج في الحزمة من   2–15 ميكرون. وبالطريقة ذاتها تم فحص زيت زيتون من مناطق جغرافية محلية مختلفة وضعت في عبوات زجاجية وبلاستيكية تحت ظروف تخزين مختلفة أيضاً، لقد وجد أن الطريقة المقترحة سهلة التنفيذ وذات دقة عالية وتعطي نتائج تقارب تلك التي تم التوصل اليها بطرق تحليلية معقدة خاصة فيما يتعلق بتحديد فترة النضوج. وبهذه الطريقة تم تمييز عينات زيت حسب العمر الزمني أو تلك التي تم غشها عمداً باضافة زيوت نباتية لها بنسب مختلفة.

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List of abbreviations.

Symbol	Abbreviation Caption
PPE	Photopyroelectric
$PVDF$	Polyvinylydene difluoridride film
IR	Infrared
DMF	Dimethylformaminde
$BPPE$	Back photopyroelectric
$FPPE$	Forward photopyroelectric
H_0	Optical flux of the incident light
Q_1	Heat developed in pyroelectric sensor (PVDF)
Q_2	Heat developed in the sample
L_m	Thickness of the sample
L_p	Thickness of opaque sensor (PVDF)
β	Absorption coefficient
δ	Diffusion coefficient
μ_m	Length of sample
μ_p	Length of opaque sensor (PVDF)
$V(\omega,t)$	PPE voltage
$\upsilon_0(\omega,t)$	Factor for current modulation
ω	Periodic modulation frequency
R_f	Feed back resistor
P	Pyroelectric coefficient
S	Area of the opaque sensor

C_p	Volume specific heat of the pyroelectric sensor
C_m	Volume specific heat of the sample
α_m	Thermal diffusivity of the sample
α_p	Thermal diffusivity of the sensor
η	Density
e_m	Thermal effusivity of the sample
e_p	Thermal effusivity of the sensor
K	Thermal conductivity
Γ	Signal amplitude
ϕ	Phase
f	Modulation frequency
I	Emerging intensity
I_0	Incident intensity
a	Esctinction coefficient
x	Distance travel within the substance
DL	Diode laser
ε	Thermal emissivity
W	Radiation emittance
σ	Boltzman constant
δP	Change in emitted power
d	Foil thickness
ρ	Foil density
$FTIR$	Fourier Transform Infrared
NIR	Near Infrared

Chapter One

1.1 Introduction

There was great interest in the study of virgin olive oil in view of reports of its importance to human health. The new findings about olive oil healthy virtues have increased interest and consumption of this material. The European Union classifies virgin olive oils into three categories: extra virgin, virgin and lampante. Olive oil is the major product of Mediterranean countries. The mature olive fruit may reach an oil content of (20%) on fresh weight basis in about (6-8) months after full bloom. In the year 1980 more than 400 deaths and 20,000 casualties occurred from the disease known as Spanish toxic syndrome, caused by the consumption of adulterated oil (Jimeno 1982, 4-6). Therefore, the detection of adulteration is of importance. In addition the determination and detection of virgin olive oil adulteration are getting more topics of important in food industry (Cabras, Angioni, Garau, Melis, Pirisi, Karim, Minelli 1997, 2244). Adulteration has been known to exist for a long time and different physical and chemical methods have been used to solve this problem. For example ultraviolet (UV) spectroscopy is widely used to detect the adulteration of extra virgin oil with other vegetable oils (Papadopoulos, Triantis, Tzikiz, Nikokavoura, Dimotikali 2002, 135). So it is most important

to look for methods that are easy to discriminate against olive oil adulteration, storage conditions and above all determination of the best harvest time which gives ripe oil that contains all components, hence best properties that are accepted by consumers. In the following a brief review will be given for possible methods and introduce the method used in this work. The interested readers are referred to the general, historical and other relevant information of olive oil reported in appendix (A).

1.2 Photopyroelectric spectroscopy history

The first reference to the photopyroelectric (PPE) effect is the writings of Theophrastus in 314 BC, who noted that tourmaline becomes charged when heated (Clark 1960, 787). David Brewster gave the effect the name it has today in 1824. Both William Thomson in 1878 and Voight in 1897 helped develop a theory for the processes behind pyroelectricity which defined as the electrical potential created in certain materials when they are heated (Clark 1960, 788). As a result of a change in temperature, positive and negative charges move to opposite ends through migration, and an electrical potential is established. Pierre Curie and his brother, Jacques studied pyroelectricity in the 1880s, leading to their discovery of some of the mechanisms behind piezoelectricity (Clark 1960, 793). The discovery of the PPE effect and the possibility of using

it to measure the temperature change created a revolution in calorimetric and related spectroscopy techniques (Chirtoc M, Bicanic, Dadarlat, Chirtoc I 1985,57). The possibility of using the PPE effect in crystal for the detection of radiation was proposed by Ta 1938 and demonstrated experimentally by Cooper 1962 (Chirtoc *et al* 1985,57). Using PPE Lang and Steckel 1965 achieved a temperature measurement resolution of 10^{-6} K. The PPE spectroscopy theory described for modulated radiation was developed by Mandelis and Zver 1985 (Mandelis, Zver 1985, 4422). Coufal 1984 used thin pyroelectric polyvinylidene fluoride films (PVDF) to obtain pulsed and low modulation frequency spectra of PVDF films. However a readily made ferroelectric polymer such as PVDF has turned out to be the commonest pyroelectric sensor (Coufal 1984, 325). There are certain interests of using PPE spectroscopy in many field of science. Progress has been made in creating artificial pyroelectric materials, usually in the form of a thin film, out of gallium nitride (GaN), cesium nitrate ($CsNO_3$), polyvinyl fluorides, because it's important of many industrial applications (Springsten 1998, 10).

1.3 State of the problems

In the present work a simple, inexpensive, easy to handle method is suggested to investigate olive juice as well olive oil samples to test for content of olives

and oil adulteration. For this purpose a PVDF film combined with pulsed wide band infrared source constitute the basis of the experiment used in this study. Firstly the aim is to test the characteristics of the wide band infrared source to assign an optimum operating condition. Secondly, a system employing the PPE technique is built and used to study olive oil adulteration, also the ability of this technique to investigate storage condition for olive oil samples taken from several years ago. It is suggested for the first time to use this technique to monitor olive fruit content of olive oil during the ripening period of fruits. This is rather important for exact assigning of harvest time that belongs to greatest oil content of olive fruits leading to the biggest olive oil harvest of the year.

1.4 Introducing the method used in this study

Molecular spectroscopy may be defined as the interaction of electromagnetic radiation (EMR) with matter and the absorption and emission resulting from that, from which the internal structure of atoms or molecules can be obtained. The spectrum is divided into five regions: Radio wave frequency, Microwave, Infrared, Visible and ultra violate X-rays and γ-rays regions. The optical path for spectrometer is dependent on multiple factors, such as the light source area, the aperture present within the light path, lens transmittance and mirror

reflectance losses, the exit aperture and the detector efficiency (Frandas, Bicanic 1999, 1361).

One of the spectroscopic techniques that have received increased attention is photopyroelectric (PPE) spectroscopy and it is the main technique used in this study. The PPE spectroscopy was proposed as a new technique for thermal characterization of olive oil (Frandas, Bicanic 1999, 1361). The PPE method consists of the measurement of the sample temperature increase due to absorption of the radiation by using pyroelectric sensor (polyvinylidene difluoride film (PVDF) is (the pyroelectric sensor used in this work) placed in thermal contact with the sample (Coufal 1984, 59). Photo thermal spectroscopy using a pyroelectric thin film detector such as PVDF, GaN, $CsNO_3$. The pyroelectric material is characterized by a temperature dependent electrical polarization. Therefore, when heated, the pyroelectric sensor generates an electrical charge on its electrodes (Dadarlat, Gibkes, Bicanic, Pasca 1996, 157). The pyroelectric effect is simply a change in the polarization of a crystal (PVDF) when it undergoes a variation in its temperature (Frandas, Paris, Bissieux, Chirtoc, Antoniow, Egee 2000, 73).

Pulsed photopyroelectric spectroscopy provides information about optical, thermal and geometrical characteristics of opaque materials (Frandas et al

2000, 73). The aim of this study is the analysis of the applicability of the finite difference method to simulate the process by which pulsed photopyroelectric signal is generated by a pulsed heat source *i.e.* wide band infrared, both in time and frequency domains. The present study is extended to monitor virgin olive oil content during ripening period by using a photopyelectric cell, the main part of this cell is a thin sheet of inactive material called polyvinyledine difluoride film (PVDF) which becomes pyroelectrically active by polling the sheet with large amount of electric field. If a wide band pulse infrared radiation is allowed to fall on single drop sample (for example olive oil) placed on top of a PVDF, that caused electrical potential created in certain sample as a result of a change in temperature, positive and negative charges move to opposite ends of the sheet of PVDF. The absorbed radiation as a consequence generates a PPE signal which can be picked up by a phase sensitive detector. This method is free of the limitations imposed by special cases when the analytical methods are used to resolve heat. This approach is analyzed through the temperature variations in the photopyroelectric cell.

1.5 Main objectives

The objective of this study is to investigate olive oil properties dependant on many storage parameters and the ripening time of olives by monitoring oil

content of olives fruit by the detection of a photopyroelectric (PPE) signal of fresh olives juice. The pyroelectric effect is well known and it has good potential for use to measure the temperature change which created a revolution in calorimetric and related spectroscopic techniques which will be discussed later. It is rather important to establish a simple method to estimate the best ripening time for picking olives by monitoring fresh olive juice using wideband infrared (IR) absorption which depends mainly on its composition as ripening time passes. The method will also be used for olive oil adulteration.

1.6 Brief review of thesis chapters

The theory of wideband pulsed infrared (IR) source is given in the next chapter with a brief discussion of infrared spectroscopy, IR source and detectors, and general consideration of IR spectrum, as used in this study as a radiation source for photopyroelectric spectroscopy. Also the technique uses a pyroelectric polyvinylidene difluoride (PVDF) thin film detector in contact with different samples of fresh olives juice or olive oil which will be discussed in chapter two. In chapter three a description of the apparatus used in this study including the experimental set up, experimental procedure and problems under investigation. The experimental result presented in chapter four in which the characteristic study of IR source, oil adulteration, old virgin olive oil data, green olive fruits study, discrimination of olive oil samples from different

regions and storage condition study are presented. The discussions of the results are presented in chapter four. Finally conclusions, suggested further work given in chapter five and references are cited at the end of thesis.

Chapter Two

Theoretical background

2.1 Introduction

In this chapter the theoretical background of the main topics necessary for the subject are presented. The PVD film as the basic sensor in the experiment will be briefly reviewed. This is followed by an introduction to the branch of spectroscopy employing the PVDF as a thermal sensor for material characterization. To our knowledge it is the first time the PVDF is used in conjunction with a pulsed wide band I.R source. The theory and brief description of the newly developed I.R source is also given and by that the main items of the suggested method is covered.

2.2 Polyvinylidene difluoride film (PVDF)

2.2.1 Introduction

Polyvinylidene difluoride film (PVDF) is the pyroelectric sensor used in this work. PVDF material is available as thin sheets or film which is normally inactive and become piezoelectrically and pyroelectrically active by polling a region of the material with a large electric field (Frandas, Bicanic 1999, 1361). The studied PVDF were prepared by a casting method. PVDF powder

was dissolved in dimethylformaminde (DMF); $MnCl_2$ was also dissolved in (DMF). The solution of $MnCl_2$ was added to dissolved polymer with a suitable viscosity; the mixture was casted to glass dish and kept in a dry atmosphere at $(50\,^0C)$ for two weeks to insure removing of solvent trace (Tawansi, Oraby, Ahmed, AbdelRazek, AbdelAziz 1998, 1759). The thickness of the obtained film was of the range of (0.1-0.25) mm. The samples were classified into three groups: Pure PVDF film, 1(wt %) MnCl2-filled PVDF films, and 1(wt %) $MnCl_2$-filled and AgNO3-diffused PVDF films, the three groups will be denoted by G1, G2, G3, respectively (Tawansi, *et al* 1998, 1761).

2.2.2 Polyvinylidene difluoride film (PVDF) history

The word *polymer* is derived from the classical Greek words **poly** meaning (many), and **meres** meaning (parts). A polymer is a long chain molecule that is composed of a large number of repeating units of identical structure (Aklonis 1981, 894). Certain polymers, such as proteins, cellulose, and silk, are found in nature, while many others, including polystyrene, polyethylene, and nylon, are produced only by synthetic routes. Polymers can also be produced synthetically (Boyer 1974, 142). An important example is natural rubber, which is known as polyisoprene in its synthetic form. The birth of polymer

science may be traced back to the mid-nineteenth century. In the 1893s, Charles Goodyear developed the vulcanization process that transformed the sticky latex of natural rubber to a useful elastomer for tire use. In 1847 (Fried 1995, 141-350), Schonbein reacted cellulose with nitric acid to produce cellulose nitrate. This was used in the 1860s as the first man-made thermoplastic, celluloid. In 1907, Leo Baekeland produced Phenol-formaldehyde resin, and glyptal (unsaturated-polyester resin) was developed as a protective coating resin by General Electric in 1920 (Morawetz 1985, 239).

By the 1930s, researches at Due Pont in the United States had produced a variety of new polymers including synthetic rubber, nylon and Teflon. In 1938, Dow Company had produced several tons of polystyrene. The 1950s through 1970s witnessed the development of a number of high- performance polymers that could compete with more traditional materials, such as metals (Morawetz 1985, 246). Today, polymeric materials are used in nearly all areas of daily life and their production and fabrication are major worldwide-industries. The polymer used in this study is fluoropolymers which is called polyvinylidene difluoride films (PVDF). The studied PVDF films were prepared by a casting method (see introduction above). PVDF has been extensively studied because it is a Ferro electric polymer exists in at least three main crystalline modifications, designated as α, β, γ and in at least one

minor phase designated as δ. The different forms are distinguished by the conformation of the (C –C) bonds along the chain back bone (Benz, William, Euler 2002, 1093). The α-phase and γ-phase are obtained from solution deposition, oriented β-phase can be produced by stretching a PVDF film, the γ-phase with regularly repeating intervals is obtained by annealing near melting point, and the δ-phases obtained by polling in an electrical field (Benz *et al* 2002, 1094).

The four types of crystal modifications strongly depend on the solvent evaporation rate, temperature and polarity of the solvent. PVDF is known to undergo cross linking under ionizing radiation (Ivanov, Migunova, Mikhailov 1988, 119). The nature of the crystalline and amorphous phase is turn affected by the molecular weight and thermal history of a polymer, while molecular weight is determined by the synthetic effort involved in building macromolecules, the thermal history will be determined by cooling, heating rate as well as other factor (Bret, Ludwing, Marek, Urban 1996, 2077). Thermal treatment of polymer such as annealing, quenching, supercooling and other treatment, alter the morphology of semi-crystalline polymers of particular importance is annealing which for a semi-crystalline polymer near its melting temperature will result in melting of imperfectly formed crystals (Bret *et al* 1996, 2079).

2.2.3 Description of PVDF

Polyvinylidene difluoride film (PVDF), is simple semi-crystalline material which is called also photo sensitive material. PVDF is the most important fluoropolymers which is obtained by the emulsion free-radical polymerization. It has a chemical structure of some important fluoropolymers (Bret *et al* 1996, 2081) as shown below:

$$PVDF \longrightarrow [----- CH_2 ----- \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}} -----].$$
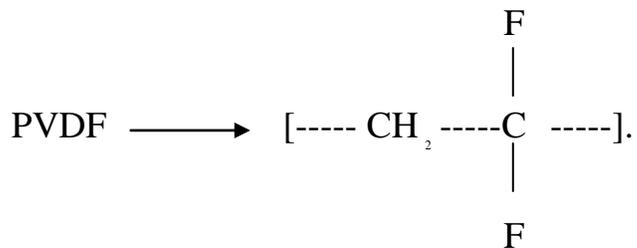
The direct use of radiation is complicated by dehdrofluorination side reaction, which become appreciable at increased absorption doses, this is why using additives contributing to the effectiveness of the cross linking seems reasonable unsaturated compounds are usually taken as sensitizing additives, (Samuels 1974, 95). The fact that permeability of semi-crystalline polymer depends on the relative amount of amorphous and crystalline phases is well documented, the nature of the crystalline and amorphous phase in turn affected by the molecular weight and thermal history of a polymer, while molecular weight is determined by the synthetic effort involved in building

macromolecules, the thermal history will be determined by cooling, heating rate as well as other factor (Ludwing, Marek, Urban 1996, 2086), (Turi 1981, 387). PVDF is an inexpensive and readily available in thickness down to (25µm) sandwiched between two aluminum foils and it is easily handled as seen in Fig: 2.1. It can be attached to curved as well as flat surface (Zott, Heusinger 1978, 1025).
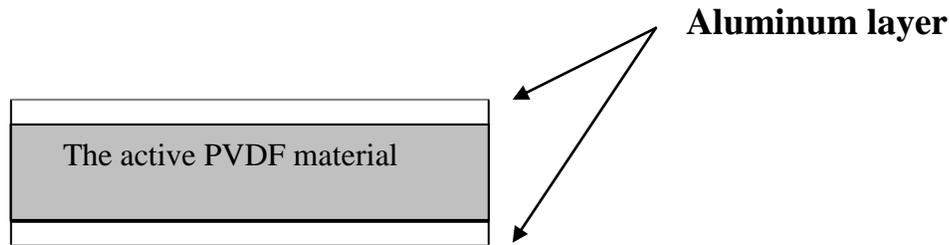
Fig: 2.1. Schematic illustration showing the PVDF.

2.3 Photopyroelectric spectroscopy

The photopyroelectric (PPE) method is associated with the electrical potential created in certain materials when they are heated due to the absorption of radiation. A result of change in temperature, positive and negative charges move to opposite sides (Wang, Mandelis, Garcia 1999, 229), this is achieved when a pyroelectric sensor is in thermal contact with a sample, since very small change in temperature resulting from absorption radiation produced pyroelectric charges (Mandelis 1984, 338). It is a requirement that the

incident radiation must be modulated to detect temperature variation resulting in the sample (Wang, Mandelis, Au-Leong 2001, 103), since continues radiation is not desirable because this will increase sample temperature until evaporation and due to the intrinsic property of pyroelectric sensor respond only to discreet temperature variations (Frandas *et al* 2000, 69). There is different configuration of the PPE method (Mandelis, Zver 1985, 4421). The most important configuration is the back configuration (BPPE) and the front configuration (FPPE). The PPE technique in back detection (BPPE) configuration with a partially transparent sample (m), (absorption coefficient β) and opaque sensor (p) is shown in Fig. 2.2

(m)   **(p)**

$H_0(\lambda,\omega)$ $H_0 e^{-\beta L_m}$ Q_1

Q_2 $Q_2 e^{-\sigma x}$
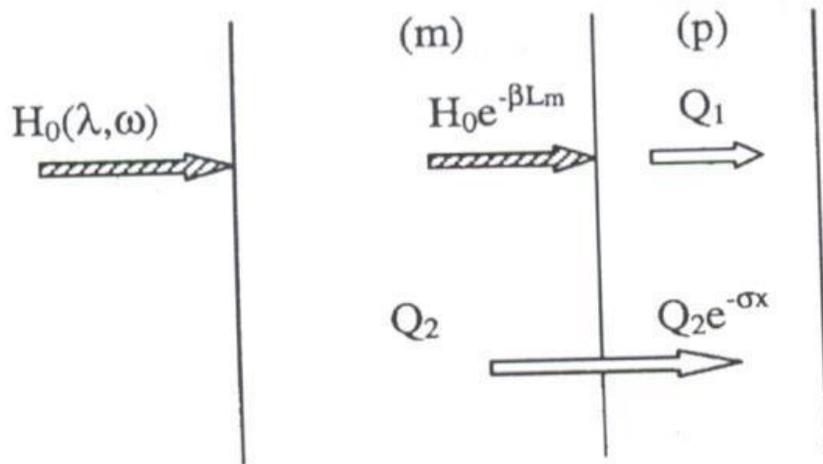
Fig.2.2. Schematic illustrating the back-detection BPPE (After Frandas *et al* 2000, 70)

Where:

P: is the pyroelerctric sensor.

m: is the sample.

Q_1: is the heat developed in pyroelectric sensor (P).

Q_2: is the heat developed in the sample.

H_0: is the optical flux of the incident light.

The heat source Q_1 generates the pyroelectric effect by absorption of the radiation transmitted through the sample of thickness (L_m). Heat source Q_2 is due to optical absorption in the sample (Frandas *et al* 2000, 72). It contains information on optical transmission from the surface into the sample depth and on optical absorption at the very same depth. This heat is then transmitted via thermal wave to the pyroelectric sensor (Chirtoc, Bentefour, Gloriex, Thoen 2001, 109). In other words, by adjusting the experimental parameter, it is possible to perform spectroscopy either in transmission or absorption mode, or to measure the samples parameters (Frandas, Paris, Egee 2000, 69). If the interest is only in the thermo physical properties, the sample must be made opaque or use of the front detection (FPPE) as seen in Fig.2.3.
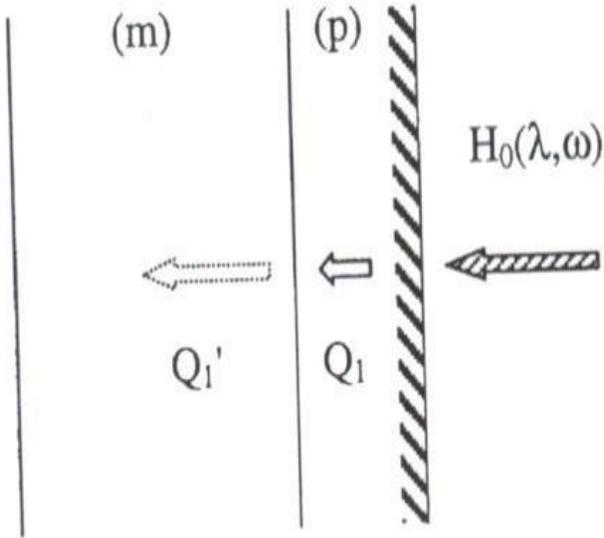
Fig.2.3. Schematic illustrating the front detection FPPE (After Frandas *et al* 2000, 70).

Contrary to the BPPE, in the FPPE approach, it is the sensor that faces the impinging radiation. The thermal wave propagating across the sensor Q_1 reaches eventually the rear face and leaks into the sample Q'_1. Thus the incident radiation heats the sensor first, the sample absorbs this heat depending on its characteristics, and i.e. it acts as a heat sink (Frandas *et al* 2000, 70).

For a periodic modulation ω ($\omega = 2\pi f$ where f is the modulation frequency) and for a monochromatic radiation (wave length λ= constant), the PPE voltage response $V(\omega,t)$ (Chirtoc, Mihailescu 1989, 606) is given by:

$$V(\omega,t) = v_0(\omega,t)\Gamma(\omega)\exp(i\omega t) \qquad\qquad 2.1$$

Where:

$V(\omega,t)$: is the PPE voltage.

$v_0(\omega,t)$: is the factor for current modulation.

$\Gamma(\omega)$: is the signal amplitude.

If the signal is processed by an inverting current preamplifier having a feed –

back resistor R_f, the factor V_0 for current modulation operation has the

form (Chirtoc *et al* 1989, 607)

$$V_0 = \frac{P H_0 S R_f}{2 L_p C_p}$$
2.2

Where:

P: is the pyroelectric coefficient.

H_o: is the optical flux of the incident light.

S: is the area of the opaque sensor.

L_p: is the thickness of opaque sensor.

C_p: is the volume specific heat of the pyroelectronic sensor.

R_f: is the feed back resistor.

Heat diffusion in the sensor or in the sample is governed by the diffusion coefficient (σ) for the sensor material length (µ) given by:

$$\mu = \sqrt{\frac{2\alpha}{\omega}}$$

Where:

K: is the thermal conductivity.

α: is the thermal diffusivity which is equal to:

$$\alpha = \frac{K}{C}$$

$C = \eta\, c$ is the volume specific heat.

η is the density, and (c) is the specific heat.

A quantity that characterizes the heat transfer between two media is the thermal effusivity: $e = (CK)^{\frac{1}{2}}$. For given (α) and (e), C and K are computed from,

$$C = k\alpha^{-\frac{1}{2}} \qquad\qquad\qquad 2.4$$

$$K = e\alpha^{\frac{1}{2}} \qquad\qquad\qquad 2.5$$

For the BPPE configuration as represented in Fig. 2.2, the sample and the sensor are both thermally thick *i.e.* $L_m/\mu_m > 1$, $L_p/\mu_p > 1$, and the sample is opaque (Frandas *et al* 2000, 72).

Where:

L_m : is the thickness of the sample.

μ_m : is the length of the sample.

L_p : is the thickness of the material sensor *i.e.* PVDF.

μ_p : is the length of the sensor.

The signal amplitude $|\Gamma|$ and the phase Φ are reduced (Chirtoc *et al* 1989, 608) as follows:

$$|\Gamma| = 2\exp\left[-\left(\frac{\omega}{2\alpha_m}\right)^{\frac{1}{2}} L_m\right]\left[1+\left(\frac{e_m}{e_p}\right)\right]^{-1} \qquad 2.6$$

Where:

α_m **:** is the thermal diffusivity of the sample.

e_m **:** is the thermal effusivity of the sample.

e_p : is the thermal effusivity of the sensor.

Where: $\qquad \alpha_m = \pi \left(L_m \middle/ slope \right)^2$ $\qquad\qquad\qquad\qquad$ 2.7

Contrary for FPPE configuration shown in Fig. 2.3, If the sample is thermally thick $(L_m/\mu_m > 1)$ and the sensor thermally thin $(L_p/\mu_p > 1)$, the signal amplitude depends on the samples reciprocal effusivity (e_m):

$$|\Gamma| = \frac{\sqrt{w}}{e_m} C_p L_p \qquad\qquad\qquad\qquad 2.8$$

Whereas if the sample and the sensor are thermally thin, the signal amplitude depends on the samples volume specific heat (Chirtoc *et al* 1989, 608):

$$|\Gamma| = \frac{1}{1 + \left(C_m L_m \middle/ C_p L_p \right)} \qquad\qquad\qquad\qquad 2.9$$

Where:

C_m: Volume specific heat of the sample.

C_p: Volume specific heat of the pyroelectric sensor (PVDF).

The photopyroelectric (PPE) method is proposed as a new technique for thermal characterization of olive oil (Frandas, Bicanic 1999, 1361). The (PPE) method was shown capable of providing temperature-dependent value of thermo physical parameters (thermal diffusivity, thermal effusivity,thermal conductivity and volume specific heat for oils (Frandas *et al* 1999, 1361).

The PPE method consist of the measurement of the sample temperature increase due to absorption of the radiation by using pyroelectric sensor (polyvinylidene difluoride film (PVDF) is the pyroelectric sensor used in this work), placed in thermal contact with the sample (Coufal 1984, 59). The pyroelectric material is characterized by a temperature dependent electrical polarization. Therefore, when heated, the pyroelectric sensor generates an electrical charge on its electrodes (Vanasse 1981, 65). The information on the thermal parameter of the sample is contained in rather complicated expression for the amplitude (Γ) and the phase (ϕ) of the measured PPE signals. The mathematical expression simplify consideration if certain experimental condition are met; various configurations and detection schemes to obtain values of thermo physical parameters and their temperature dependence have been proposed (Dadarlat, Gibkes, Bicanic, Pasca 1996, 157), as seen in Figure (2.4) below.
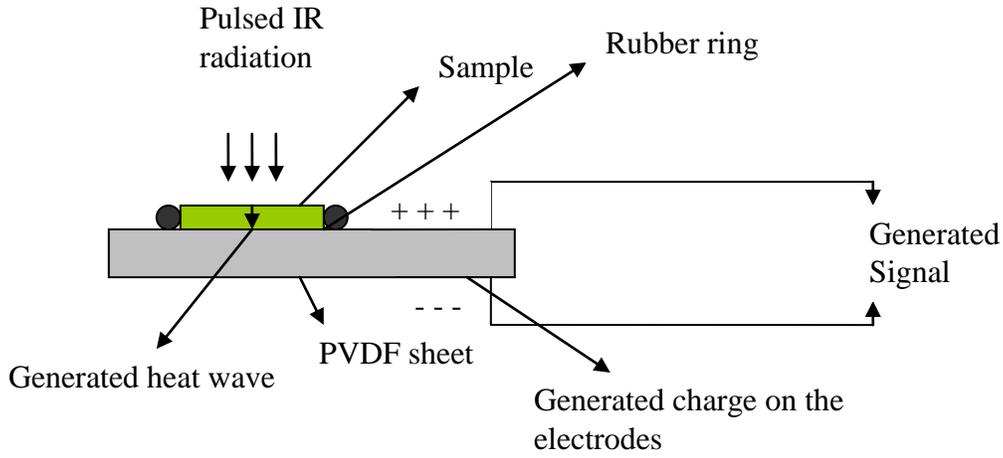
Fig.2.4. PPE signal generated as a result of radiation absorption in sample.

Here two configurations have been used; the standard (back) configurations with thermally thick sample and sensor, and the inverse (front) configuration with thermally thin sensor and thermally thick sample. For the first configuration the modulated light is absorbed by the opaque sample. For a thermally thick sample and sensor the amplitude (Γ) and phase (ϕ) of the signal are given by the simplified expression (Marinell 1992, 54).

$$\Gamma = \frac{const}{e_m + e_p} \exp\left(-\sqrt{\frac{\pi f}{\alpha_m}}\right) L_m \qquad\qquad 2.10$$

$$\phi = -\sqrt{\frac{\pi f}{\alpha_m}} L_m \qquad\qquad 2.11$$

Where e_m : is the thermal effusivity of the material (sample).

e_p : is the thermal effusivity of the pyroelectric sensor.

α_m : is the thermal diffusivity of the sample.

L_m **:** is the thickness of the sample.

f : is the modulation frequency.

In the inverse (front) configuration the modulated light is absorbed directly by the sensors electrode, the sample acting as heat sink. When the sensor is thermally thin and the sample is thermally thick the amplitude is given by (Dadarlat, Gibkes, Dicunicand 1996, 162):

$$\Gamma = \frac{const}{e_m} \qquad\qquad 2.12$$

While the phase is constants that appear in equation (2.10) and (2.12) depends on the light irradiance, the pyroelectric coefficient of the sensor and the equivalent electrical impendence of the measuring system.

For sensors of (300μm) thick signal crystal of LiTaO3 was used in the back configuration and a (9μm) thick polyvinylidene difluoride(PVDF) foil in the front configuration, the sample thickness were (585μm) and (2mm) for the two configuration(Dadarlat et al 1996,158). For this study only one drop of the sample were used.

2.4.1 Infrared spectroscopy

The quality of an infrared (IR) spectrum strongly depends on the method of sample preparation and the optical interface between the sample and the infrared instrument-usually defined by a sampling accessory (Feinstein 1990, 412). It must be appreciated that the physical state and how the sample is treated will influence the appearance of the spectrum. Furthermore, different sampling accessories that use different principles of optical measurement produce variations in the appearance of the final spectrum for the same sample (Feinstein 1990, 412). The intensity of an infrared (IR) absorption band is proportional to the square of the transition moment (or infrared active dipole moment). The absolute intensity of an infrared band also depends upon the direction of the transition moment (dipole electric field vector) and the field direction vector (electric field vector) of the incident infrared radiation (Harrick 1995, 63).

The increase in the use of infrared spectroscopy, both as a structural diagnostic tool and for analytical purposes, during the past 40 years mostly due to instrumental developments (Lovell 1991, 186). When infrared radiation passes through a sample of any substance the intensity is reduced by the same factor for each equal increase in distance traveled. Thus, if the

reduction in intensity is due only to absorption rather than to scattering and absorption then:

$$I = I_o e^{-ax}$$
2.13

Where x: is the distance traveled from a reference surface within the substance, I_o: is the intensity at the reference surface and a: is called the absorption coefficient (Lovell 1991, 187).

2.4.2 IR Sources

Different types of sources are used in IR spectroscopy namely lasers and the usual conventional sources. For example, solid laser sources are heated rods, usually of ceramic material. The temperature of operation is about $(1200^0 C)$ (Colthup 1990, 99). The choice of this temperature represents a compromise between total radiative output, the proportion of energy at longer wavelengths and the life time of the source (Salthouse, Ware 1972, 37). The output approximates to the spectrum of a black body with its maximum in the near infrared region. The relative energy is in the interval (400-600) cm^{-1}, close to the long-wavelength limit of some instruments, is some two orders of magnitude lower than at the emission maximum, and many instruments now scan down to (250-200) cm^{-1} (Salthouse et al 1972, 38).The spectrometer energy throughput is held approximately constant in dispersive instruments by

increasing the monochromatic slit width in scanning from short to long wavelengths (Harrick 1995, 67). In the present work a newly developed wideband source is used, a brief description of the source is given in the next section.

Infrared tunable diodes laser are a powerful tool for high resolution absorption spectroscopy and trace gas detection (Weidmann, Courtois 2000, 361). A diode laser (DL) spectrometer requires the use of a high power source with a narrow line width and low intensity noise (Herzberge 1972, 152).

Infrared laser spectroscopy generally requires infrared laser sources with outstanding spectral properties, i.e., narrow line width, wide wavelength tunability and smooth beam profile (Wiley 1987, 122). Suitable coherent light sources for mid-infrared spectroscopy are molecular gas lasers, semiconductor lasers, and recently all-solid-state pumped nonlinear conversion devices (Agarwal 1995, 219-272).

2.4.3 Wideband Infrared (IR) source

The source of light used in this study is a wideband infrared (IR) source which based on electrical heating of foil of a thin metal alloy up to red heat ($900^{o}C$), and cooled by its own radiation. The source with an active area of

27 mm^2, spectral range (0.7-13) μm, with resistance (1.7-4.2)Ω, and the out

put power is about (20-50)mw as seen in Figure (2.5) below.
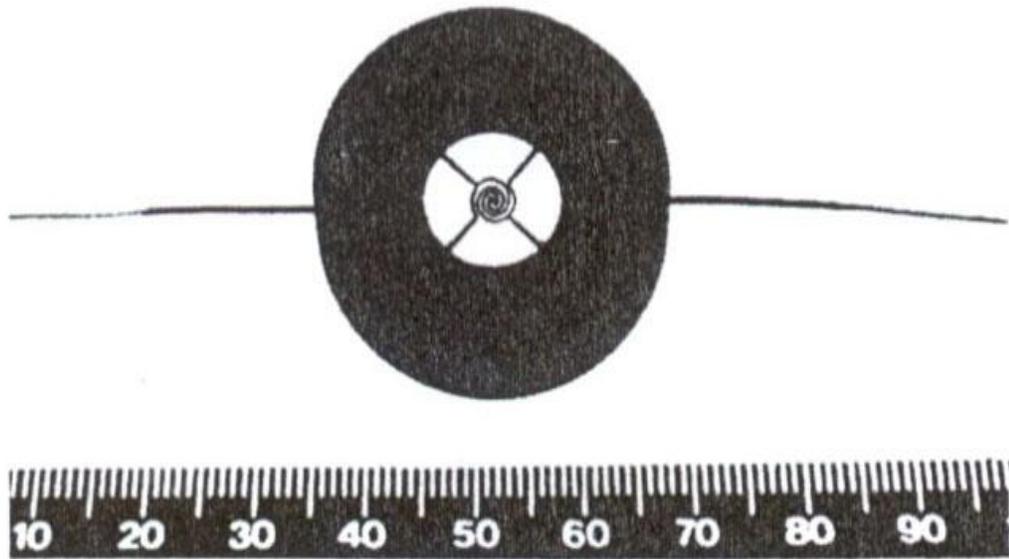
Fig.2.5. View of assembled bispiral infrared source (After Laine et al 1997,

   318).

It is based on separated indium metal foil geometry (Laine, Jourani,

Carpenter, Sedgbeer 1997, 315). The basic concept of the pulsed thin metal

foil thermal source is that of pulsed electrical heating followed by rapid

radiative self-cooling as seen in Figure (2.6) below.
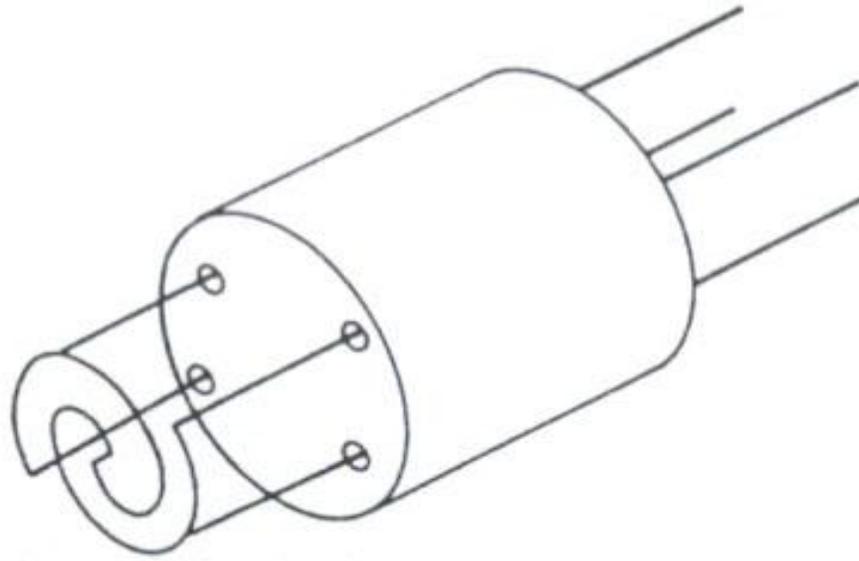
Fig.2.6. Sketch of miniature pulsed 1.7 mm diameter bispiral infrared source

(After Laine _et al_ 1997, 319).

If the radiating area and emissivity of the foil is sufficiently large and the foil is thin enough, the maximum frequency of operation may be calculated in a first approximation by equating the energy radiated to the stored thermal energy, over a period of one thermal cycle (Lain _et al_ 1997, 320).

For a black body radiator with an ideal thermal emissivity, $\varepsilon=1$, the radiant emittance (W cm^{-2}), at 1000K is 5.67 Wcm^{-2} and at 1200K, 11.78Wcm^{-2}. The rapid rise in radiant emittance with absolute temperature T occurs through Stefan-Boltzmann law: $W=\sigma T^4$, where $\sigma=5.67\times10^{-8}\,Jm^{-2}K^{-4}s^{-1}$.For an imperfect radiator, $W=\varepsilon\sigma T^4$. The change of radiation emittance δW with a small change of temperature δT is then given by differentiation. The change

in emitted power δP from double sides of source is:

$$\delta P = 8 S \varepsilon \sigma T^3 \delta T \qquad\qquad 2.14$$

Where S is the area of a single side of the foil. The power change δP per cycle required to raise the foils temperature by an amount. δT, is given by:

$$\delta P = {c_p \, \rho \, d \, S \, \delta T} \Big/ {pulse\ duration} \qquad\qquad 2.15$$

Where:

c_p : is the volume specific heat of the material.

ρ : is the metal foil density.

d : is the foils thickness.

From equations (2.14 and 2.15), the frequency of source thermal pulse is given by:

$$f = {8 \, \varepsilon \, \sigma \, T^3} \Big/ {c_p \, \rho \, d} \qquad\qquad 2.16$$

Eq.2.16 indicates that no dependence between frequency and area of the foil. Assuming some typical values, take a $25 \mu m$ thick foil of iron for which $\rho = 7.22 \times 10^3 \, Kg \ m^{-3}$, $c_p = 440 J \ K^{-1} Kg^{-1}$, $T = 1300 K$, and $\varepsilon = 0.8$, then $f = 10 Hz.$

This is rather appreciated value and it is enough for most small signal detection (Laine *et al* 1997, 321).

(Laine *et al* 1997, 323), managed to manufacture subminiature bispiral infrared sources with diameters as small as $1.7\,mm$ using $20\,\mu m$ thick foils as seen in Fig.2.6.

Infrared camera of the bispiral is given in the Figure (2.7) below:
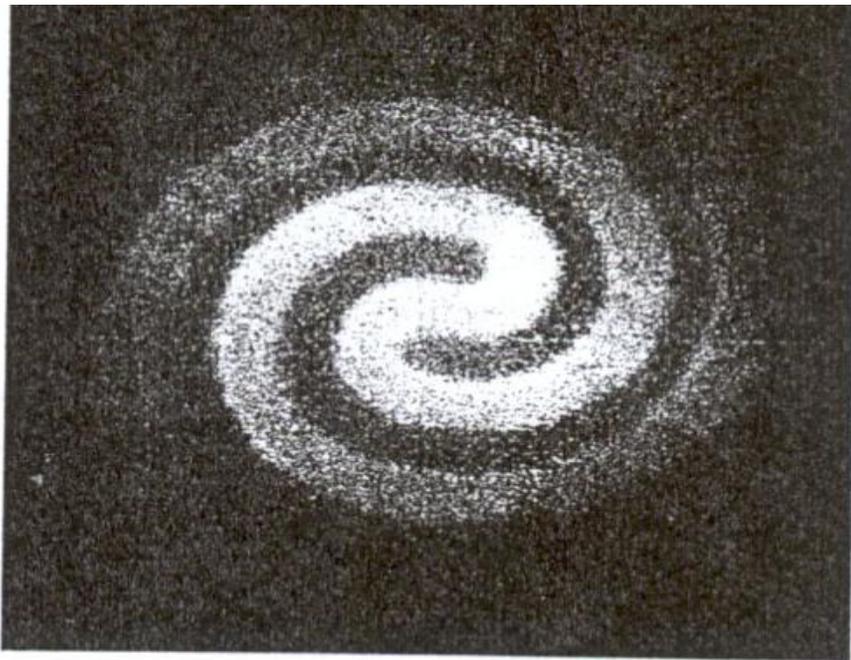
Fig.2.7. Infrared camera image $(4 - 6\,\mu m)$ of hot 1.7mm bispiral (After Laine *et al* 1997, 318).

2.4.4 IR detectors

A suitable detector for the above source must have important properties such as sensitivity and good speed of response. High sensitivity is essential because the energy of the source is in the microwatt range, and the speed of response must be such as to cope with the nature of the pulsed IR source, typically about 15Hz, or with the much higher modulation frequencies involved in Fourier transform instruments (Nye 1985, 49).One thermal source that has detection ability to wide range of wavelengths is the thermocouple. A more sensitive but of less mechanical strength is the Golay cell (Nye 1985, 51). Pyroelectric detectors are somewhat less sensitive than thermocouples but have a considerably faster response and this makes them particularly suitable for use in FTIR spectrometers (Bower, Maddams 1992, 15).

The number of investigations on collected samples necessary to study the absorption of polarized infrared radiation and many types of equipment incorporate a polarizer or polarizer's to permit such studies (Bower *et al* 1992, 24-29).

At present the wire grid polarizer is the most important type of IR polarizer in use, which consists of a group of parallel, equally spaced strips of metal on a substrate transparent to the infrared source radiation. A high degree of polarization is produced in infrared radiation if the separation of the strips is

less than about a quarter of a wavelength which passes through the grid, and the electric vector of the transmitted beam is perpendicular to the strips (Salthouse *et al* 1972, 57). Since spectrometers of any type have different transmission factors for two principal polarization directions at right angles, the polarization direction of the polarizer should be set at (45) degree to these direction if it, rather than the sample, is to be rotated when making polarization measurements on the oriented samples. The polarizer is sometimes placed in the common beam of a double-beam instrument, but for the most accurate work it should be placed next to the sample, with a compensating absorber in the reference beam if necessary (Srchatrapimuk, Cooper 1978, 134)

2.4.5 General consideration of infrared spectrum

Infrared is a form of electromagnetic radiation extending between the visible ultraviolet (approximately 700nm) and the microwave region (approximately 200μm), (Hollas 1996, 83). In this thesis, it will be described as pulsed wideband light source radiation, although light is normally used to describe visible radiation. Most infrared (IR) interactions with matter are recorded as absorptions of energy, either as a direct or indirect measurement. Emission measurements may be performed; measurements may be made by light transmission through the sample or by reflection directly from the sample

surface or from an interface (Hollas 1996, 127). Infrared (IR) spectroscopy is one of the analytical techniques available for the measurement of absorption or emission of radiation as a consequence of vibrations within a molecule between the component atoms.

The infrared spectroscopy can be applied to measurements in at least three spectral regions: the near infrared, the mid-infrared, and the far infrared, today the mid-infrared spectral region defined by the energy range 4000-400 cm^{-1} (2.5-25µm:2500-25000nm in units of wavelength). This range tends to be arbitrarily defined, but the upper spectral limit does define the extent of all the fundamental molecular vibrations (Burns, Ciurczak 1992, 158).

The region below 400 cm^{-1} is referred to as the far infrared, the spectral region above 4000 cm^{-1} (2500nm) and extending out to the visible region of the electromagnetic spectrum (approximately 700 nm) is known as the near infrared (NIR) (Burns *et al* 1992, 159). The instrumentation for this region has been differentiated from instrumentation covering the fundamental region (mid-and far-IR), and so NIR as a technique has been treated separately from traditional IR spectroscopy (Burns *et al* 1992, 160). The NIR spectral region is composed of absorption related to vibration overtones and combination absorptions. The absorptive associated with these is less, by one or more orders of magnitude, than the fundamental vibrational absorptions. It is

accepted that NIR is easily handled for sample than traditional IR spectroscopy (Hollas 1996, 128).

Chapter Three

Experimental

3.1 Introduction

In this chapter a description of the apparatus used in this study including the experimental set up *i.e.* the experimental arrangement used for characteristic study of the IR source and the complete photopyroelectric detection system used to monitor olive oil quality and olives fruit oil content during the ripening period. Also description is given for the experimental procedure, problems under investigation and finally authentication of the system used in this study. This is rather important for determining the optimum harvest time that belongs to greatest oil content of olive fruits leading to the biggest olive oil yield of the year.

3.2 Photopyroelectric cell

Fig. 3.1 shows the photopyroelectric sample cell design which was used for the present study. It consists of a square piece of biaxial PVDF foil 1cm $\times$ 1cm size $25\,\mu$m thickness, metallised on both sides with aluminum foil to provide the reflecting surface and facilitate electrode connections. This is important since only the heat propagating from the sample is detected and not that generated

through direct interaction between radiation and detector. The foil was glued to perspex glass substrate for support. The liquid sample was placed on the top of the foil using dropper. The cell was enclosed in an aluminum box to minimize the ambient electromagnetic interference, prevent the evaporation of the liquid during measurements and reduce air turbulence. The aluminum box had a (1cm $\times$ 1cm) size opening to let the infrared radiation in. Two electrodes were connected to the top and bottom of the foil with silver paint.
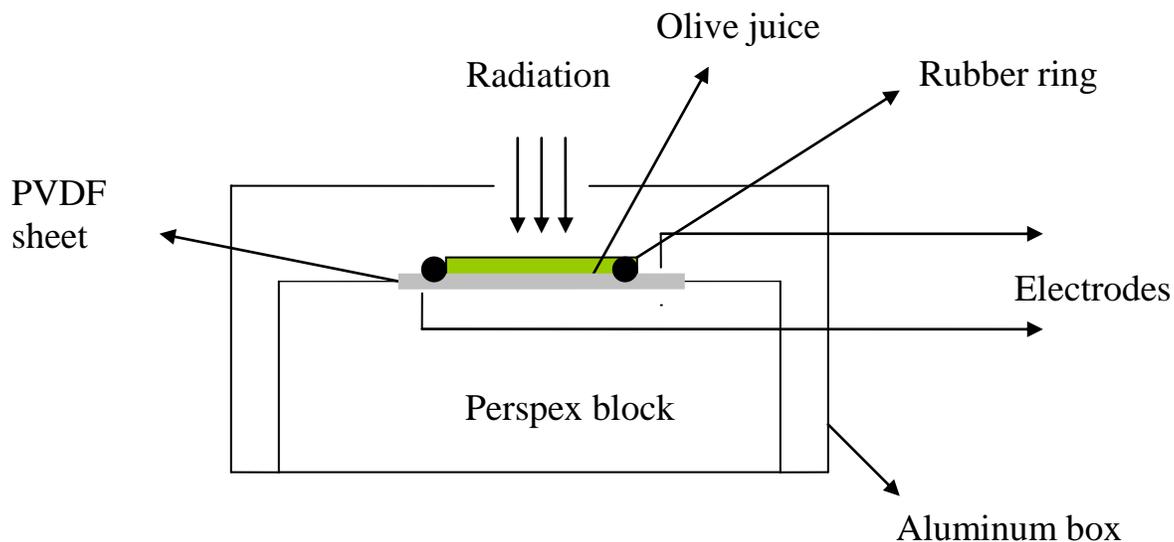
Fig: 3.1. Photopyroelectric cell used in this study.

3.3 Equipment

The equipment list used in this study include: Phase sensitive detector, power function generator, pyroelectric detector, wideband infrared source, Ammeter, sheet of polyvinyledine fluoride metallised film, aluminum box, silver paint, connecting leads, battery(9v), fixed table, dropper, plastic cylinder, block of perspex glass, circular rubber, silicon, optical bench, oscilloscope.

In this study IR absorption of olive oil or fresh olives juice was indirectly measured as a PPE signal using radiation from a miniature pulsed wideband IR source. It has a fecuralloy radiation filament of 2mm diameter encapsulated in a can 8 mm diameter and~10mm long and emitting at 0.7-13 μm. The source is driven by an AC signal from a power function generator, a current of 0.2 Amps is needed to drive the source. Radiation is allowed to fall on single drop sample placed on top of the PVDF. The absorbed radiation as a consequence generates a PPE signal which can be picked up by a phase sensitive detector.

3.4 Experimental set up

3.4.1 Wideband infrared source characteristics study

It was usefull to first understand the characteristics of the IR source used in this study. For this purpose the apparatus were arranged as shown in Fig. 3.2.

Study was then carried out for the following aims. The relation between the source power versus the varying distance of detector from the IR source, and that resulting from varying pulsation frequencies were studied. The IR source power is dependant on the current, so it was necessary to find the optimum operating current value stuitable for experimental coditions. Results are presented in section 4.2.

```
┌──────────────┐           ┌──────────────────────┐          ┌──────────────────────┐
│              │ ········▶ │                      │          │  Phase-sensitive     │
│  I.R source  │           │ Pyroelectric detector│ ───────▶ │  Detector            │
│              │           │                      │          │                      │
└──────────────┘           └──────────────────────┘          └──────────────────────┘
       ▲                        │        │                              │
       │                        │        │                              │
       │                        ┤├                                      ▼
┌──────────────┐              +  │  -                        ┌──────────────────────┐
│  Power       │                                             │                      │
│  Function    │                 Battery                     │    Oscilloscope      │
│  Generator   │                                             │                      │
└──────────────┘                                             └──────────────────────┘
```
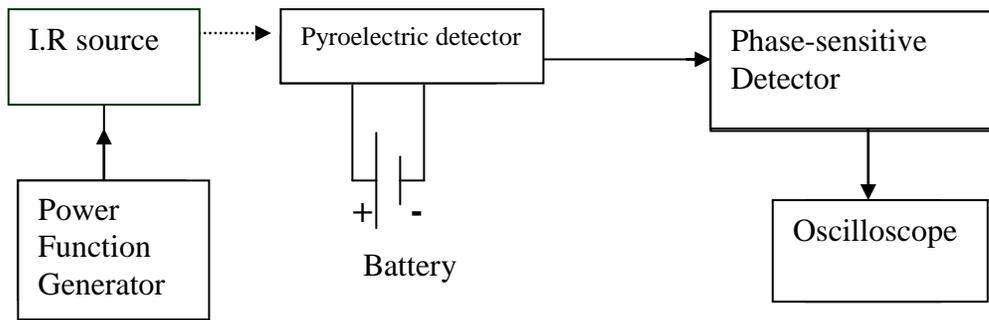
Fig: *3.2.* Experimental arrangement used for characteristic study of the IR

source.

3.4.2 PVDF experimental arrangements

In this study the absorption of IR radiation by a single drop of olive oil placed on the tope of a polyvinylidene film was measured as a PPE signal, the absorbed radiation generates a PPE signal which can be picked up by a phase sensitive detector as seen in Fig. 3.3. For olives oil content monitor the fresh

fruits were picked at the intended time of investigation and one single drop from an olive was gently squeezed directly on a PVD film in a region bounded by a rubber ring enough to hold only one drop of the fresh natural olive juice. The resulting absorption of the IR radiation by the drop of juice generates a heat wave that is sensed by the PVD film and transformed into a voltage i.e. PPE signal that can be detected using phase sensitive detector. The system was found easy to operate.
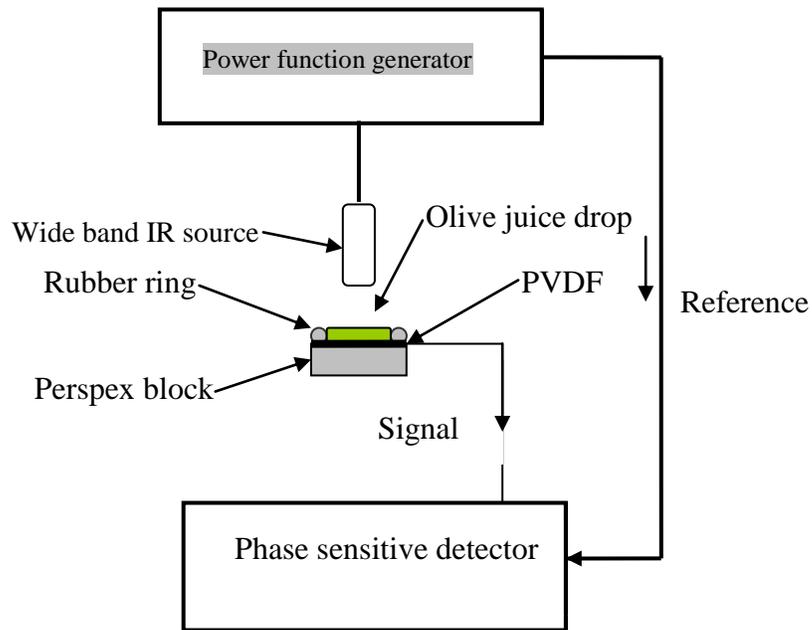
Fig: 3.3. Complete photopyroelectric detection system used to monitor olives ripening time and olive oil adulteration.

3.5 Problems under investigation

In this work the technique will be used to study the characteristic of wide band infrared source by using system shown in Fig. 3.2, in order to maintain the relation between varying distances, frequency and current versus the output photopyroelectric signal. Using the system shown in Fig. 3.3, this technique will be used to study olive oil adulteration with less expensive sunflower and soy-beans oils, also to study the best storing conditions to olive oil and the effect of air in the package container during storing period. This technique will be used for the first time to monitor the progress of olive fruit oil content during the ripening period of fruits. This is rather important for exact assigning of harvest time that belongs to greatest oil content of olive fruits leading to the biggest olive oil harvest of the year and above all the best olive oil product with the most favorable properties.

3.6 Description of experiment

The experimental set-up is shown in Fig. 3.2, and Fig. 3.3. It makes use of a new technique first to study the characteristics of the wide band infrared source by using the equipment that shown in Fig. 3.2, the system used to study the characteristics of the infrared wideband source is composed of a pyroelectric detector, function generator, and phase-sensitive detector. The

relation between the signal (arbitrary unit) resulting from varying the distance at fixed frequency and current, and that resulting from varying frequency at fixed distance and current were studied. The source power at fixed distance and frequency was investigated as the current is varied to find the optimum operating condition of the source. Then the optimum experimental conditions are set and kept unchanged for the rest of experiment.

In order to study the absorption output signal resulting from mixing pure olive oil with corn oil, soy-beans and sunflower oils at different concentrations another arrangement of the system was used Fig. 3.3. By this arrangement deliberate olive oil adulteration was studied. Also the ability of the system to distinguish pure olive oil from different regions for same production year was investigated. Distinguishing pure olive oil from different production years for the same region and also the ability of the system to find the best storage condition for virgin olive oil was carried out.

For olives oil content monitor the fresh fruits were picked at the intended time of investigation and rubbed by fingers so their flesh transformed into a soft juicy form. One single drop from an olive was gently squeezed directly on a PVD film (see Fig.3.2) in a region bounded by a rubber ring enough to hold only one drop of the fresh natural olive juice. The resulting absorption of the

IR radiation by the drop of juice generates a heat wave that is sensed by the PVD film and transformed into a voltage i.e. PPE signal that can be detected using phase sensitive detector. The system was found easy to operate.

3.7 Authentication of the system

After the complete system was arranged as shown in Fig. 3.3. It can be tested using a single drop of olive oil placed on the PVD film (see Fig. 3.3). The resulting absorption of the IR radiation by the sample generated a heat wave that is sensed by PVD film and detected by using phase sensitive detector. The signal to noise ratio calculated was found to exceed 200 in most cases.

3.8 Cleaning the cell

Cleaning the photopyroelectric cell was found to be important in this work, since olive oil samples used in this study produced oily films which possessed a low vapor pressure. Cleaning the cell was achieved by inserting a piece of cotton wool soaked with a cleaning agent such as acetone. To be sure that the cell was completely clean the system was connected and there was no signal detected with the phase sensitive detector.

3.9 Conclusion

In this project a simple yet inexpensive and easy to perform method that allows good monitor of the olive oil content during the ripening period, also the best optimum operation condition of the wideband infrared source are presented. Preliminary results of the photopyroelectric spectroscopy monitor of olives content using wide band pulsed IR source have shown a very encouraging results comparable to other complicated systems, The value of signal to noise ratio found to exceed 200 in most cases.

Chapter Four

Results and discussions

4.1 Introduction

In this work, results taken along two paths: Firstly the characteristic of the wideband infrared source was studied, and secondly photopyroelectric wideband study of olives oil contents, adulteration and storage conditions were studied. Relevant to the characteristic of wideband IR source, the study was done to measure radiation from the source at different distances, frequencies, and output currents versus the output signal in arbitrary unit that will be absorbed by using a phase sensitive detector. For the photopyroelectric monitor the study involved: adulteration of virgin olive oil with different oils like soy-beans and sunflower oils, the spectrum resulting from olive oil at different years from the same region, and the absorption output signal of virgin olive oil at different regions but from the same production year. The technique was also used to study the output signal resulting from different samples of olive oil stored at different conditions, i.e. in room light, in the dark and in containers glass, plastic, in full or partially filled containers. The main purpose of this study is to use the photopyroelectric spectroscopy to monitor olive fruit oil content during ripening period.

4.2 Characteristic study of IR source

The system used to study the characteristics of the infrared wideband source is formed of a pyroelectric detector, function generator, and phase-sensitive detector as seen in Fig.3.2. The relation between the signal representing the source power taken by varying the distance of detector from the source while keeping the driving frequency and current constant, and that resulting from varying frequency at fixed distance and current were studied. This was carried keeping in mind to look for the optimum operating condition of the source. Then the right source are set and left unchanged for the rest of experiment.

4.2.1 Change of source radiation versus distances

After arranging the system as shown in Fig.3.2, in order to study the relation between the out put signal of wideband IR source at different distances of the pyroelectric detector from (2-40)cm, while driving the source using a function generator at fixed frequency of 12 Hz, fixed current at 200mA. The aim of this procedure is to find the effect of varying distances at the resulting power from the source.

From the results obtained it is concluded that when the detector distance is increased the signal (i.e. source power) found to be decreased. Since as detector is moved far from the source the radiation becomes divergent hence

radiation detection is weak according to the inverse square law where $I \alpha \frac{1}{r^2}$,

in addition absorption of radiation by air in the assigned region increased and

this refers to the relation $I = I_o e^{-ax}$ as mentioned in section (2.4.1), (see Fig: 4.1).
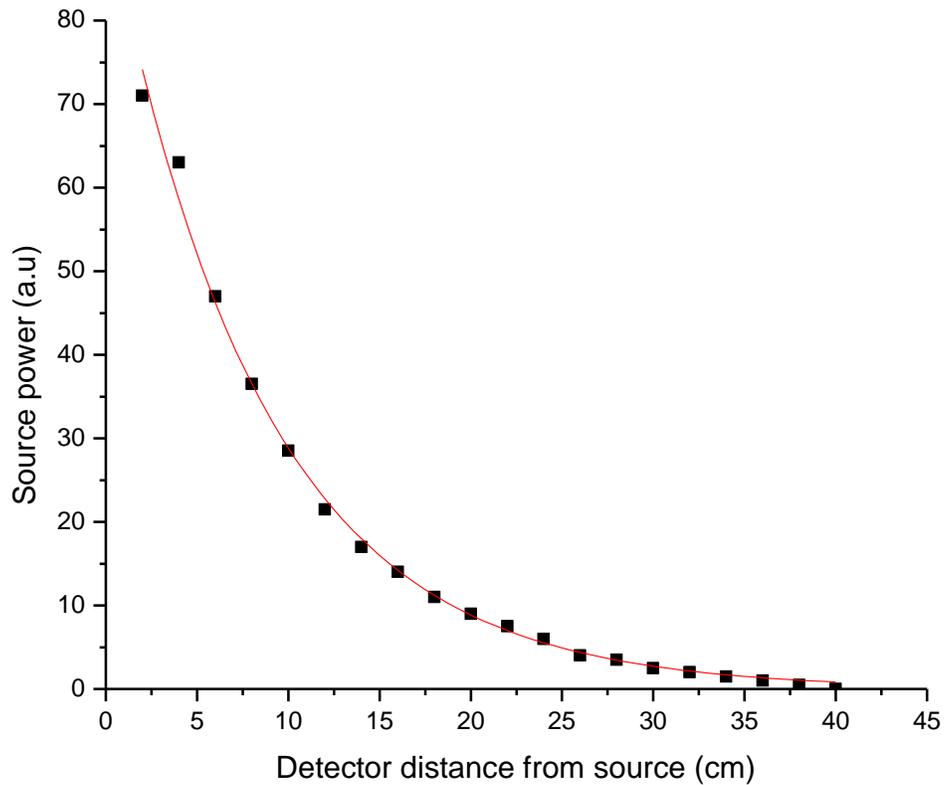
Fig:4.1.Graph of IR source power versus detector distance from souirce

4.2.2 Source power versus driving frequency

By using the same system as before the effect of varying source driving

frequency from (10-115) Hz on the output signal of the source power at fixed

current of (200) mA and distance at (2cm) was studied.

From the results obtained its concluded that when the driving frequency of the infrared source is increased the source power decreased until a frequency of ~ 75Hz is reached, the power level stabilized at low constant value. Driving the source at high frequencies resulted in the radiation of the infrared source looks like a continuous light rather than pulsed. This affected the source behavior as it lost the self cooling property. Hence it is important to mention that higher frequencies are not preferred and this in fact contradicts the main objective behind using this type of source (see Fig.4.2).
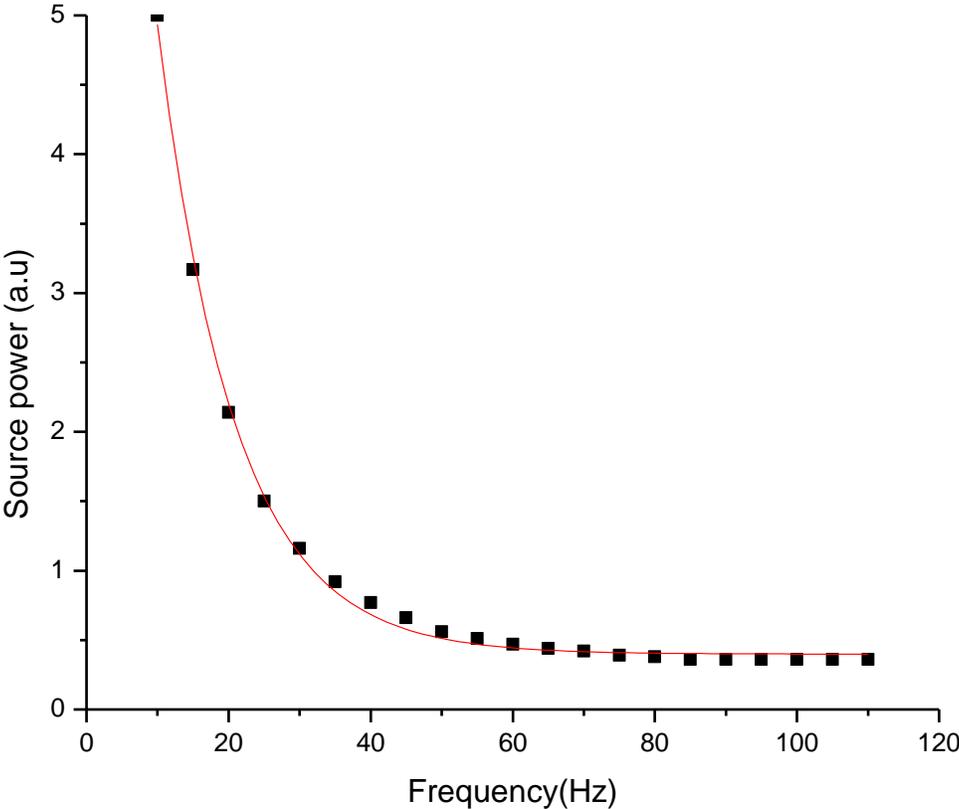
Fig:4.2. Graph of IR source power versus driving current frequency.

4.2.3 IR Source power versus current

Investigation of the relation between IR source power dependence on currents at a fixed distance (2cm) and frequency of (12) Hz, was carried out. The aim of this study is to understand the effect of varying current on the output power of IR source to assign the best operating current for the source.

From the result obtained it is concluded that when the supplied source current increased the source power found to increase. There is a limit to maximum current that can be supplied to the source and in this study it is (200mA), (see Fig.4.3) higher current values may result in source burnout. The range of output power of this source is from (20 ~ 50)mW and it is very sensitive to high current, since the source based on electrical heating of thin metal foil and cooling is by its own radiation. It must be remembered that choice of the optimum current is vital for both life span of the source and its operation.
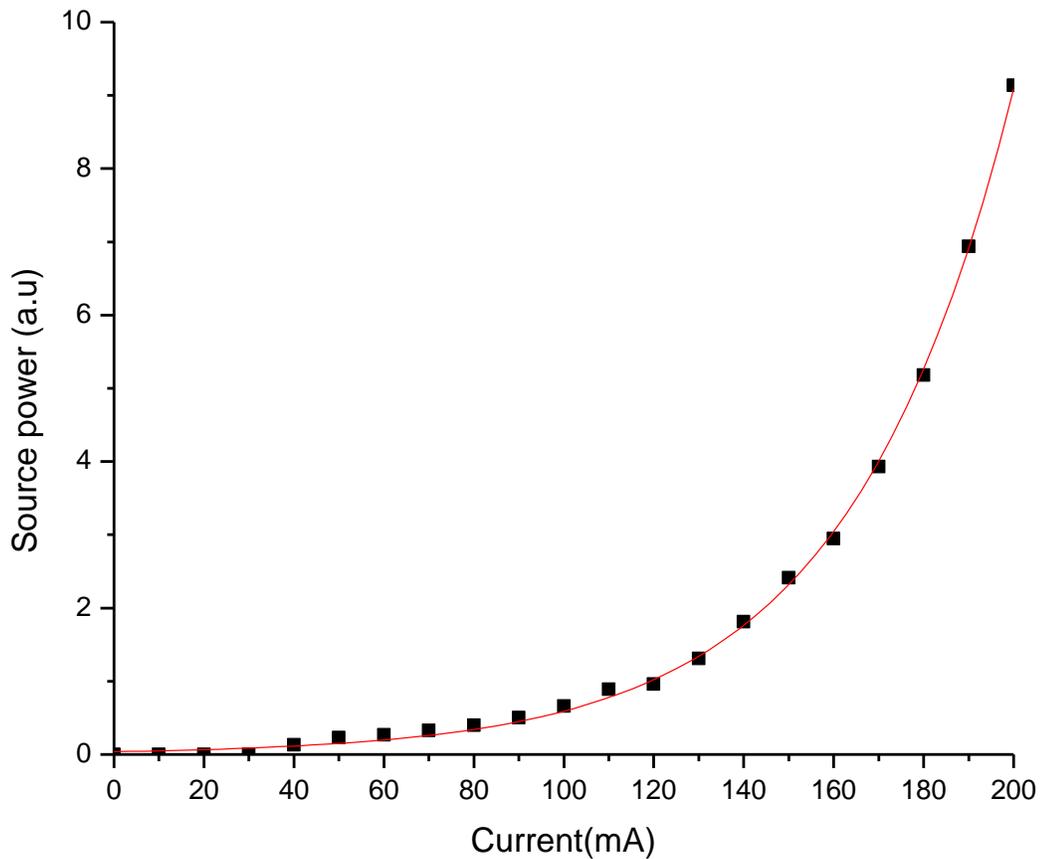
Fig:4.3. Graph of IR source power versus different current.

4.3 Tested samples

4.3.1 Storage conditions

Samples collected for long time ago from different geographical regions and stored under different storage conditions in filled or half filled plastic or glass containers in room light or in the dark. The type of cultivar of each sample was not easy to determine since some olive fields contain more than one type and samples were gathered from the same fields for the corresponding harvest

seasons as a collective sample. The idea is to test the method ability to distinguish between samples of different properties resulting from geographical region or storage conditions.

4.3.2 Adulterated samples preparation

For the investigation of detection of adulteration of the olive oil with vegetable oils i.e. (corn, sunflower, soy-beans oils), mixtures of the sample extra virgin olive oil with each one of the vegetable oils were prepared. For each vegetable oil, eleven mixtures were prepared with percentages 0%, 10%, 20%, 30%, until 100% of the respective oil in the genuine olive oil sample. Altogether 33 admixtures were prepared. One single drop of each mixture was tested by using the empirical system shown in Fig.3.3. These admixtures were tested immediately after their preparation.

4.3.3 Olives oil content samples

Olive (*Olea eurpea*) cultivated in Jerusalem from two different regions were harvested at different stages of ripeness. Olives are picked for investigation at the day of measurement and taken directly to the laboratory for study. Two olive fields assigned in the vicinity of Jerusalem area from which samples were investigated. The cultivars are known locally as Romi and Improved Nabali. The first cultivar was one of the oldest planted in the region while the second is

believed to be a developed version of the first. The two cultivars fields are ~ five km apart, i.e. in the same geographical region. This assures that samples reach the laboratory and investigated directly after being picked up. Investigation started in September where olives look green and hard and carried out through the season toward the end of January of next year. At the beginning of October olives fruit still look green and by the end of the 2nd week some of the olives became spotted (mostly green with purple spots). Olives turn to fully purple before they change to black at the beginning of the 2nd week of November. It is important to note that not all olives on the tree have the same color at one time but the majority does. For example by the end of 3rd week of October about 1/3 of olives are nearly purple and about 50% have this color by end of October. By the end of the first week of November 70% were black. At the end of the 2nd week of November it is noticed that 95% of olives are black. It is worth mentioning that this cycle might not repeat it self at exact times of the year every year, since olives ripening depend on the climate at particular time of the year and mainly on the temperature. Following the changes of olives color there expected a corresponding change in the nature of olives juice and its color as well. The juice color was white – greenish at the beginning of October, white bright - reddish at the beginning of November and

ends to be a thick dark purple slurry at the end of November. Olives are picked at the day of measurement and taken directly to the laboratory for testing.

4.4 Experimental olive oil data

The results of section(4.2), yield that the optimum operating conditions for performed our tests are (2cm distance, 10Hz frequency and 200mA current), such conditions were used in all our tests described in the following sections.

4.4.1 Oil adulteration data

As mentioned in the introduction (1.1) olive oil adulteration can be very dangerous to human life but it is very important to find easily methods to detect adulteration. In this study a new technique will be used to distinguish pure virgin olive oils from adulterated olive oils, by using the experimental system shown in Fig.3.3.

Olive oil adulteration investigation was carried out by deliberately adultering olive oil samples from the harvest year 2004 with seed oils. The following vegetable oils were used: Sunflower, Soy-beans and corn oils. Adulteration of the sample was increased in steps of 10%. One single drop of adulterated samples was used for each test.

The results proved the ability of the system to distinguish the adulteration percentage as well as the type of seed oil used as an adulterant.

In this work it's shown that the absorption PPE signals of virgin olive oils as well as vegetable oils (corn, sunflower, soy-beans oils) gave significant differences in absorption signals. Results have confirmed that the adulterated samples absorb less as adulteration percentage increase as seen in Fig.4.4. Which can be used to discriminate virgin olive oil from vegetable oils and the possibly for the determination of the adulteration of virgin olive oils with cheaper vegetable oils, discrimination analysis using 33 mixtures was able to classify the samples as pure virgin olive oil and adulterated olive oils based on their PPE signals obtained by using the simple system shown in Fig. 3.3.
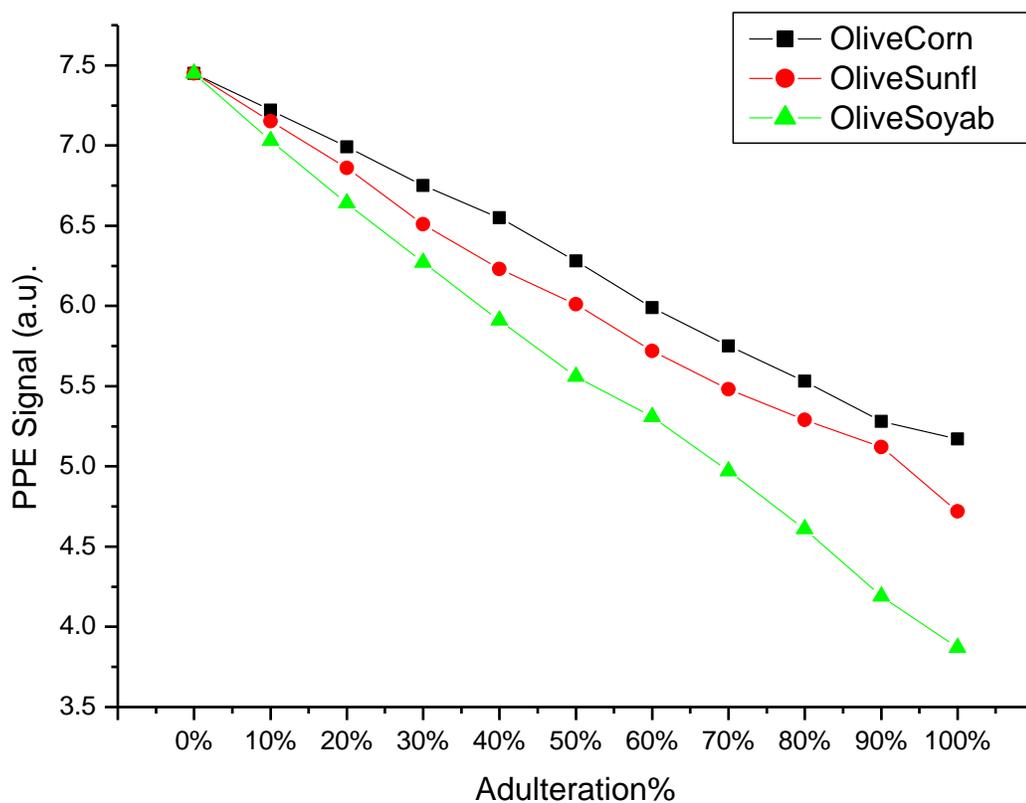
Fig:4.4. IR absorption signal of adultered olive oil samples.

4.4.2 Olive oil storage conditions results

4.4.2.1 Introduction

The standardization and packaging of olive oil, as every edible product, is important because it contributes to the preservation of oil quality at its highest possible level until its consumption. All parameters involved from production to consumption, i.e. Oxygen, light, plastic, and glass. In this section, some parameters relative to the storage condition of olive oil are presented, followed

by a description of the type of packaging and their influence on olive oil quality.

4.4.2.2 PPE study of olive oil samples stored in room light and darkness:

This part of study will investigate the ability of the system to distinguish between olive oil samples from different production years (94-97), and the same region, some stored in the dark and some in the room light in fully filled plastic containers. The aim of this study is to determine the effect of room light and dark on stored samples of olive oil. The system found to be easy to detect the difference between these samples can be distinguished.

The effect of room light on samples was investigated by comparing their PPE signals with those stored in the dark as shown in Fig. 4.5.
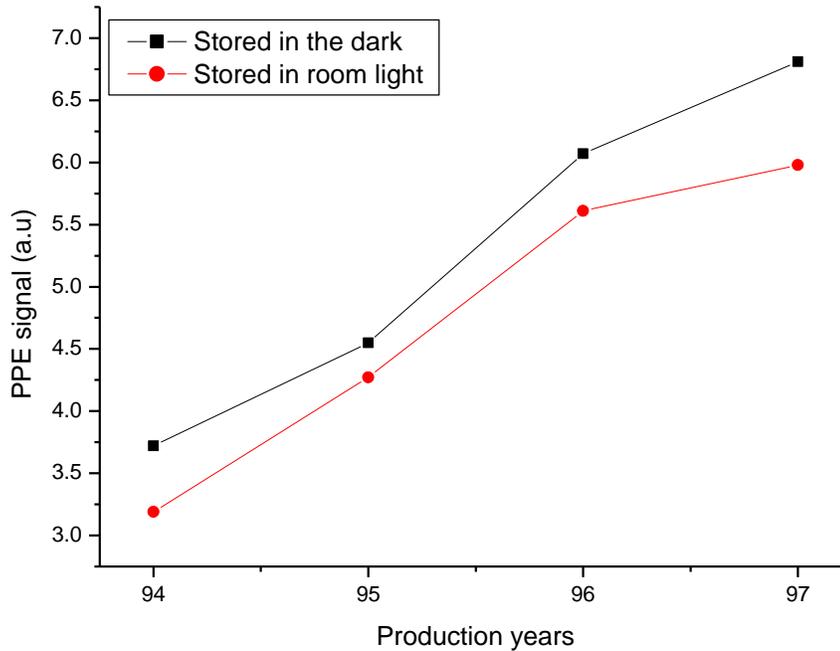
Fig.4.5.Photopyroelectric signal of olive oil samples from different production years and the same region, stored in the dark and light in fully filled plastic containers.

From the results obtained its concluded that PPE signals were different for samples stored in room light and those stored in the dark this mean that samples stored in room light will absorb less radiation from those stored in dark place, since the heat generate in the sample depends on the absorption coefficient (β) according to equation $Q_2 = H_0 e^{-\beta L_m}$, and the heat developed in the sensor (PVDF) depends on the diffusion coefficient (σ) according to equation $Q_1 = Q_2 e^{-\sigma x}$ as describe in section (2.3). Higher signals confirm storing in a dark place is important because exposure to light will start a reaction that will change oil properties may be due to chemical structure change. During storage, olive oil oxidized and undergoes a slow, continuous,

and irreversible deterioration until it becomes inedible since light will activate the oxidation process. Thus from these results virgin olive oil must be stored in a dark place and protected even from room light.

4.4.2.3 Effect of storage container

The signal resulting from different olive oil samples produced from the same regions that are stored in glass and plastic bottles was studied. The results are shown in Fig. 4.6.
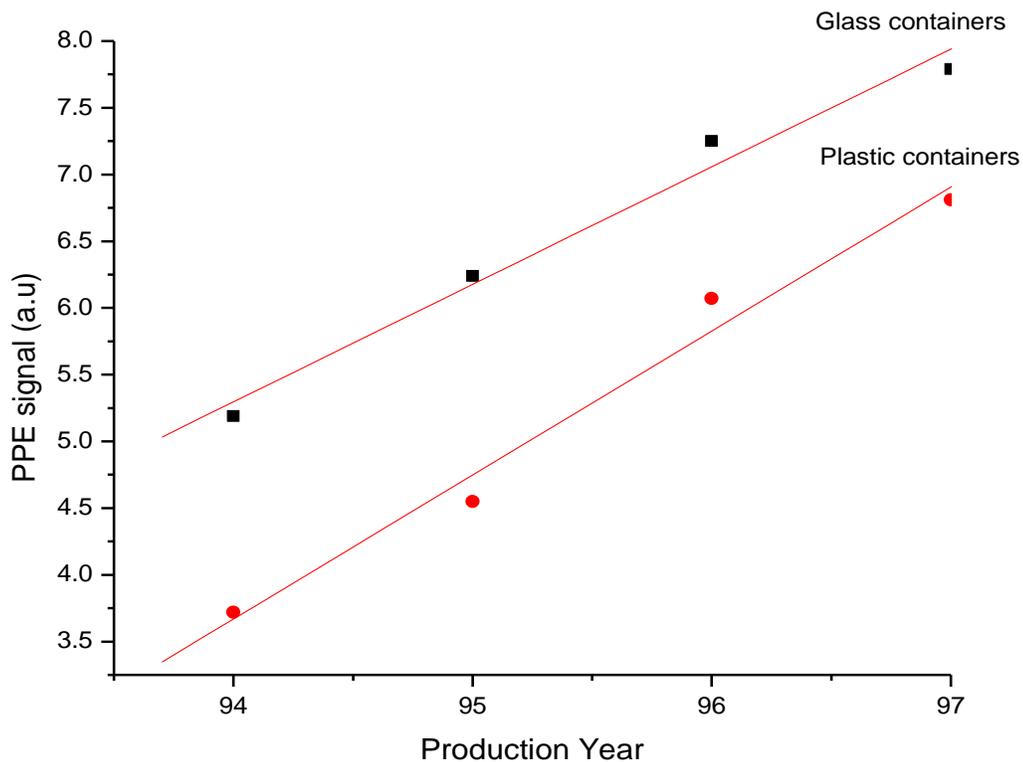
Fig:4.6. Photopyroelectric signal of olive oil samples from production years 1994-1997, of the same region stored in glass and plastic containers fully filled and kept in dark room.

Results showed that glass is superior to plastic as a storage container. The standardization and packaging of olive oil as well as every edible product, is very important because it contributes to the preservation of oil quality at its higher possible level until its consumption. The glass container still remains one of the best types of packaging for edible oils because of advantages such as protection from Oxygen (zero transition of Oxygen), humidity, microorganisms (Kiritsakis, Kanavouras 2002, 628-638). Another major advantage there is no interaction between glass containers and oil which protected olive oil from any change on its components and preserved the quality of olive oil during time, and glass is easily cleaned and this helps to remove microbes adhering to the container walls. Plastic bottles are used extensively for packing and bottling of vegetable oil, but they are not always suitable for this purpose, because the interactions that occur between the olive oil and the plastic material which affected the quality and safety of olive oil. Plastic containers have the advantage of low price, low weight, easy in use and handling. But they have disadvantages that affect the quality of oil, such as permeability to Oxygen (transition of Oxygen through the wall), Carbon dioxide, light and humidity. Another major disadvantage is the dissolution of low molecular weight substances (monomers) *i.e.* Polyethylene (PE) and Polyvinylchloride (PVC) from plastic to oil (Tsimis, Karaasidest 2002, 151), which affects the organic

properties of the oil when packed in plastic bottles and this will minimize the absorption PPE signal.

From the results shown in Fig. 4.6, the absorption PPE signals for oil samples stored in glass containers are different from absorption signals of samples stored in plastic containers. The higher the signal the stronger the indication of good unpolluted samples.

4.4.2.4 The effect of left air layer above stored olive oil sample

The ability of the system to distinguish virgin olive oil samples from production year 1994 through 1997, stored in filled and half filled containers in room light from the same region (Hebron) are shown in Fig.4.7.
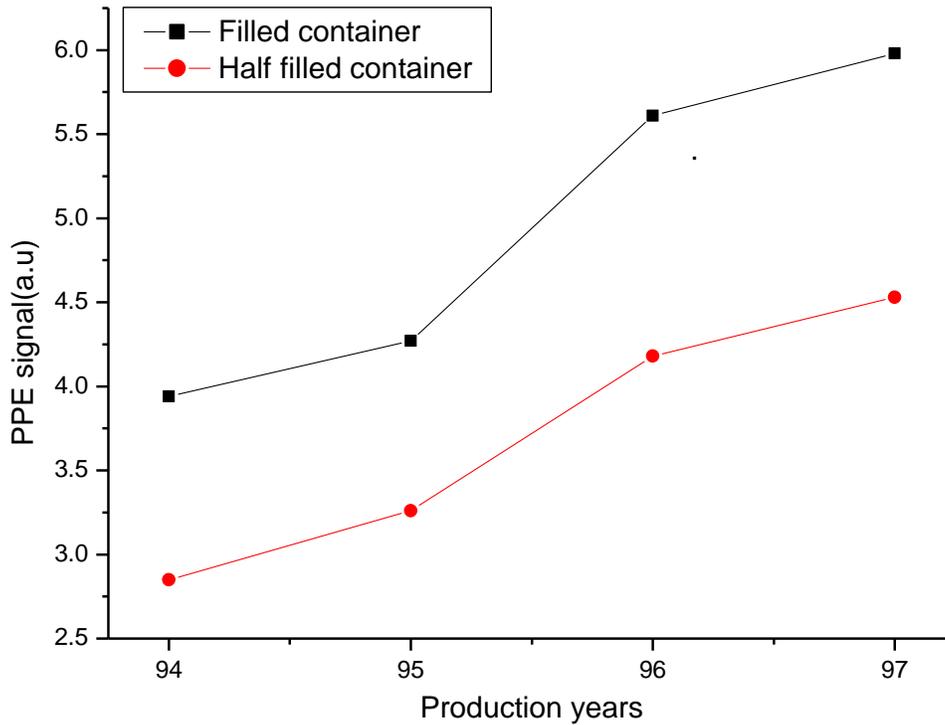
Fig:4.7.Photopyroelectric signal of olive oil samples from production years 1994 through 1997, stored in half filled containers in room light.

From the results obtained it is concluded that the resulting signals are different from samples stored in filled to those that were stored in half filled containers, as shown in Fig. 4.7. The resulting PPE signals for filled is larger than half filled since the air exist in the half filled samples will minimize the absorption signal and Oxygen inside air may cause olive oil to become rancid and this will change the original taste of virgin olive oils since there is a chemical interaction between Oxygen inside air and olive oils (Turkan, Michael 2001, 1392). In addition full containers kept oil properties in better conditions than those which left a layer of air on top. It seems that interaction with air left in the container

has its effect on oil properties leading to deterioration (see in Fig. 4.7) since there is a strong chemical interaction between Trisytric Acid, Oleic Acid ($CH_3(CH_2)_7CH = CH(CH_2)_7COOH$) (monounsaturated fatty acid) and Oxygen (O_2) which transform the monounsaturated fatty acid to momosaturated fats that will change oil properties and minimize the absorption signal. It is better to transfer the olive oil to a smaller container and fill till to half neck and seal the lid tightly to prevent air penetration.

4.4.2.5 Olive oil samples from different regions data

The ability of the system to distinguish pure olive oil from different regions for same production year was investigated. By doing this experiment it is concluded that the resulting signals are different from one region to another, since virgin olive oil depends on many factors related to olive cultivation and to the harvesting time, methods of storage and extraction, kind of soil, irrigation of olive trees and so on. Results are illustrated in Fig. 4.8.
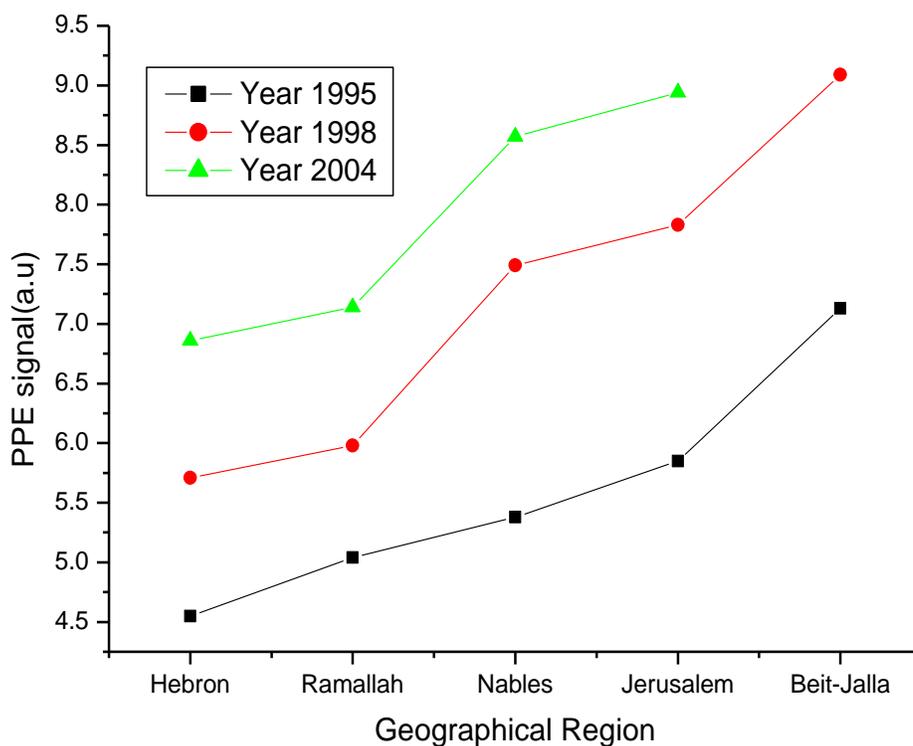
Fig:4.8.Photopyroelectric signal of olive samples from different regions
for the production years 1995, 1998 and 2004.

As seen in Figure above it is concluded that the absorption signal are not the same, this mean that every region has its special quality of olive oil which is different from one region to another. Since the absorption PPE signal depends on the heat developed in the sample (Q_2) and the heat diffusion in the sensor (Q_1) as described in section (2.3) so olive oil from Hebron absorbs less radiation (Q_2) than those from other regions and this will minimize the absorption signal.

4.4.2.6 Olive oil at different year's data

It is an advantage to distinguish between samples of different production years and hence shelf life of oil samples. PPE studies have shown that it is possible to distinguish samples according to age (see Fig. 4.9).

From the results obtained it is concluded that the resulting signal are not the same, but it differ from one year to another, and the signals are increasing with increasing years i.e. recently produced samples, since olive oil loose some of its components during time that can result in a considerable decrease in the oil quality due to losses of potentially acceptable organoleptic characteristics which will affected and decrease the absorption signal, as illustrated in Fig.4.9.
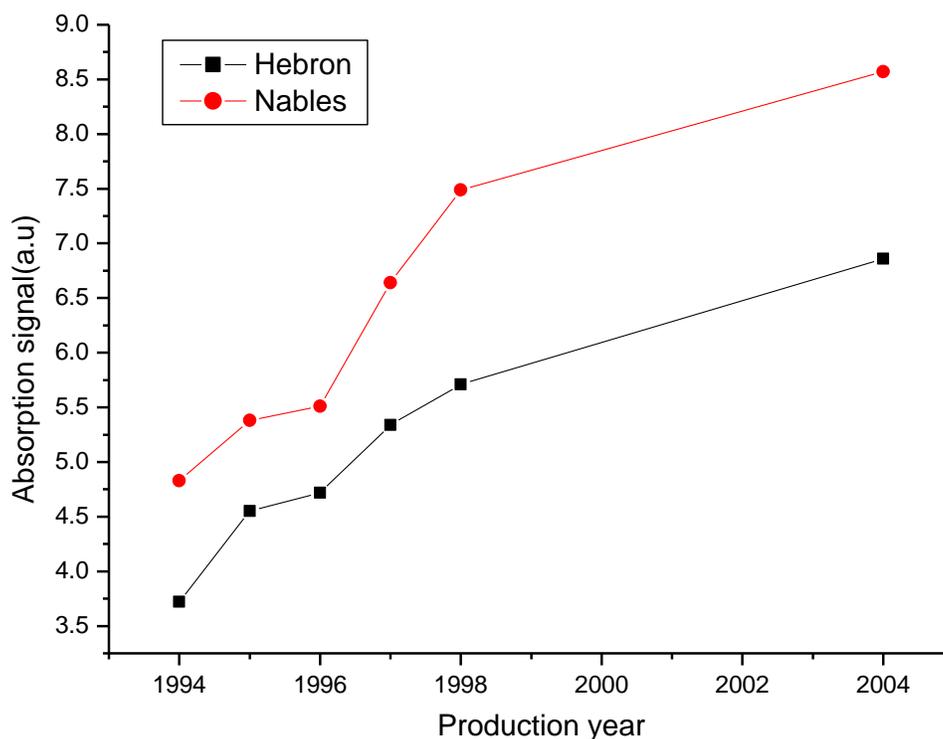
Fig:4.9. Photopyroelectric signal of olive oil from different
production years from the regions of Hebron and Nablus.

4.5 Green olives fruit study

The technique was used for the first time to monitor the constituents of fresh

olives juice as the ripening time passes in its most critical period September

through December, as seen in Fig. 4.10.
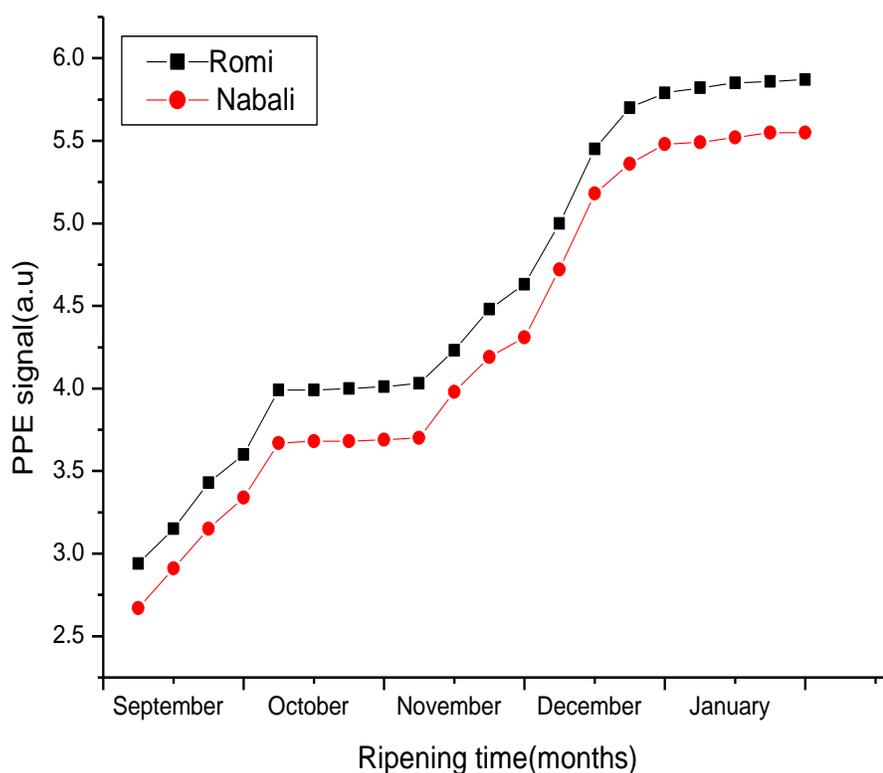
Fig:4.10. Photopyroelectric IR absorption signals of fresh olive juice versus ripening time during the period Septemper through January.

The main objective of this study is to investigate olive oil properties dependant on many parameters and the ripening time of olives by monitoring oil content of olive fruit by the detection of a photopyroelectric (PPE) signal. The pyroelectric effect is well known and it has good potential for use to measure the temperature change which created a revolution in calorimetric and related spectroscopic techniques (Baeten, Meurens, Morales, Aparicio 1996, 2228). It is rather important to establish a simple method to estimate the best ripening time for picking olives by monitoring fresh olive juice wideband IR absorption which depend mainly on its composition as ripening time pass.

Fig.4.10. shows the result for the two cultivars Romi and improved Nabali. Results show that there is an increase in the level of the signal as ripening time approached its peak, and then it came to a stable period from the first week of October to first week of November. A heavy rain for two days in that period after which a surge in the level of signal was noted. This increased until the beginning of December after which stabilization in the level of signal continued until the beginning of February where investigation stopped. The broadband stabilization indicates that IR absorption is the same, i.e. the fresh drop of olive juice maintained the same composition over the specified period. It is important to note that all specified natural ripening signs do exist right through the season apart from the beginning of October where all olives were green. Even at the end of the season green olives can be found at the trees and their absorption signal was the same as that of the black olives. Their color depends on their position on the tree and the amount of lighting they receive. Previous studies on olive oil using laser optoacoustics had shown that olive oil has an absorption spectrum in the range (9 –11 µm) (Maali 1998, 84), which coincides with part of the spectrum of the IR source used in this study. Keeping in mind those cultivars might not be the same in addition to other environmental differences our results agrees with the complicated analytical compositional study results of Nergis *et. al.* (2000) for oil accumulation in

olive fruit of the cultivar called Domat. It is worth mentioning that the harvest time should not exceed the end of November even though there is an increase in the signal, but the change in the nature of juice leads to bad olive oil that does not appealed to the consumer as we heard from experienced farmers. It can be concluded that the best harvest date is the period from mid of November to the end of this month noting that the approximate date depends on the climate of the season. Any further delay is not necessary as indicated by the bad looking of the fresh juice which changes to purple rather than the homogenous white-greenish color.

Chapter Five

Conclusions and further work

5.1 Conclusions

In this work, PVDF film is used in conjunction with wideband IR source. It is proved that this technique can be used to study of olive oils quality and olive fruit oil content during the ripening period by using PPE technique. It is used to distinguish virgin olive oils from other seed oils, since in the previous years there was a great attention to olive oil throughout the world for its superior quality and importance to human health compared to other seed oils.

Results in this work taken along two ways: Firstly the characteristics of wideband IR source and secondly PPE study of olive oils contents, adulteration and stored conditions.

Relevant to the characteristic of IR source, the study was done to measure radiation from the source at different distances, frequency and output currents versus the output power of the source as measured by a pyro-detector. From the results obtained to this part, it is concluded that the output signal is inversely proportional to the square distance as mentioned in section (4.2.1), since the radiation become divergent hence radiation detection is weak, in

addition absorption of radiation by air in the assigned region increased. Moreover the radiation of IR source will look like continuous light rather than pulsed at high frequencies nearly up to 50Hz which will affect the source behavior, since higher frequencies are not preferred and this contradicts the main objective behind using this type of source, continuous light will evaporate small liquid sample that will be measured.

In this work it is important to mention that when the supplied source current increased the source power was found to be increased. There is a limit to the current that can be supplied to the source which is 200mA, since higher current values may result in source burnout.

For PPE monitor the study involved adulteration of virgin olive oils with different vegetable oils, this work have shown that the resulting output signals resulting from virgin olive oils is different than other signals resulting from other vegetable oils (corn, sunflower and soy-beans oils), by using this technique it gave significant differences in the output signals which can be used to discriminate virgin olive oils from vegetable oils, and possibly for the determination of the adulteration of olive oils with cheaper oils. Also it is concluded that adulterated samples absorbs less radiation as adulteration percentage increase. Moreover, this technique was used to study the condition

for stored olive oils. From this it is concluded that samples stored in dark room are in better condition than those stored in light room, PPE signals were different since storing in a dark place is important because exposure to light changed the chemical structure of olive oil as mentioned in section (4.4.2.2). During storage, olive oil oxidized and undergoes a slow, continuous, and irreversible deterioration until it becomes inedible. Thus from these results virgin olive oil must be stored in a dark place and protected even from room light. It is concluded that glass is superior to plastic as a storage container. The standardization and packaging of olive oil as well as every edible product, is very important because it contributes to the preservation of oil quality at its higher possible level until its consumption. The glass container still remains one of the best types of packaging for edible oils because of advantages such as protection from Oxygen, humidity, microorganisms. Another major advantage is there is no interaction between glass containers and oil, and glass is easily cleaned and this helps to remove microbes adhering to the container walls. Plastic bottles are used extensively for packing and bottling of vegetable oil, but they are not always suitable for this purpose because of the interactions that occur between the olive oil and the plastic material which affects the quality and safety of olive oil due to the formation of section (4.4.2.3). Plastic containers have the advantage of low price, low weight, easy in use and

handling. But they have disadvantages that may affect the quality of oil, such as permeability to light, Oxygen, Carbon dioxide and humidity. It is also concluded that storing olive oil in full filled container is better than in partially filled, since in case of full containers oil properties saved from deterioration as a result their isolation from air. For partially filled containers the air exists above the oil interacts with it resulting in loss of valuable properties, so it's useful to keep olive oils away from air in order to save its contents and taste unchanged.

Olives ripening can be distinguished as indicated by the natural change of olives color. Clearly olives loose their green color by loosing chlorophyll content during ripening period. The objective of this study is to investigate olive oil accumulation in olives during the ripening time by monitoring oil content of olive fruit by the detection of a photopyroelectric (PPE) signal. The pyroelectric effect is well known and it has good potential for use to measure the temperature change which created a revolution in calorimetric and related spectroscopic techniques. It is rather important to establish a simple method to estimate the best ripening time for picking olives by monitoring fresh olive juice wideband IR absorption which depend mainly on its composition as ripening time pass. The system is simple, inexpensive and sensitive with signal to noise ratios exceeding 200 in most applications.

5.2 Further work

The system built in this study was essentially important since it is not complicated, inexpensive, easily handled compared to other complex systems. The method was also used for olive oil adulteration and properties study which proved simple technique. The technique can be used in monitoring other fresh liquid samples to distinguish one sample from another. It is suggested to use this technique to distinguish the DNA of different type of plants and animals. Also one can assign the best condition for storing liquid samples and assign the best harvesting time for other fruits and vegetables.

Appendix

<p align="center">**Appendix A**</p>

General, historical information of olive oil and olive tree.

Introduction:

It was reported (Boardman 1976, 187) that olive tree spreaded from Iran to Syria and Palestine from which it is then spread to the rest of the Mediterranean basin 6,000 years ago. It is among the oldest known cultivated trees in the world - being grown before the written language was invented. It was being grown on Crete by 3,000 BC and may have been the source of the wealth of the Minoan kingdom. The Phoenicians spread the olive to the Mediterranean shores of Africa and Southern Europe (Boardman 1976, 196). Olives have been found in Egyptian tombs from 2000 years BC. The olive culture was spread to the early Greeks then Romans. As the Romans extended their domain they brought the olive trees with them (Zohary 1993, 293).

1400 years ago the Prophet of Islam, Muhammad (peace be upon him), advised his followers to apply olive oil to their bodies and to eat as well, and he himself used oil on his head. The use of oil is found in many religions and cultures. It has been used during special ceremonies and also as a general health measure (Zohary 1993, 297). During baptism in the Christian church, holy oil, which is

often olive oil, may be used for anointment. At the Chrismmass olive oil blessed by the bishop, "chrism", is used in the ceremony. Like the grape, the Christian missionaries brought the olive tree with them to California for food but also for ceremonial use. Olive oil was used to anoint the early kings of the Greeks and Jews and the Greeks anointed winning athletes. Olive oil has also been used to anoint the dead in many cultures (Zohary 1993, 307).

In our area Palestine especially on the Mount of Olive in Jerusalem there is a lot of old olive trees which called *Roman olive trees* can be seen. It is reputed to be over 2000 years old (Boardman 1976, 189). The exact specimens of the olive trees on the Mount of Olives are not known. The olive tree has been manipulated by man for so many thousands of years that it is unclear which varieties came from which other varieties. Varieties in one country have been found to be identical to differently named varieties in another (Forbes 1996, 475). Olive trees still exist in the Middle East which represents the original stock from which all other olives are descended. In the past several hundred years ago the olive trees has spread to North and South America, Japan, New Zealand and Australia (Bonnet 1950, 205).

The only vegetable oil that can be consumed as it is freshly pressed from the fruit is olive oil which is a natural juice that preserves the taste, aroma,

vitamins and properties of the olive fruit (Willett 1990, 341-379). In the last thirty years there was great interest in the use of olive oil in our life to protect our self from many diseases such as, heart disease which is proportion to the concentration of cholesterol in the blood (Christopoulou, Lazaraki, Komaitis, Kaselimis 2004, 466), (Yaqoob 2002, 114). Olive oil has a useful effect on controlling cholesterol levels, due to its fatty acid composition (Beltr, Uceda, Jimnez, Aguilera 2003, 504). Fatty acids are substances found in fats and oils (Wendroff, Wee 1997, 154). Fatty acids can be: Cholesterol, when it does not exceed certain levels, is active for the structure of cell walls (Harwood, Yaqoob 2002, 685). The greatest exponent of monounsaturated fat is olive oil, and it is a prime component of the Mediterranean diet (Keys, Menott, Karvonem 1986, 903). The useful health effects of olive oil are proportion to its high content of monounsaturated fatty acid, and its high content of antioxidative substances (Ozaktas, Cigizoglu, Karaosmanoglu 1997, 175), (Nergiz, Enges 2000, 57). Olive oil is very well acceptable by the stomach. In fact, olive oil's protective function has a good effect on ulcers and gastritis (Nestle 2000, 1201). It activates the secretion of bile and pancreatic hormones much more naturally than drugs. Consequently, it lowers the incidence of gallstone formation, people who consume 25 milliliters (mL) - about 2 tablespoons - of virgin olive oil daily for 1 week showed less oxidation of cholesterol and higher levels of

antioxidant compounds, particularly phenols, in the blood (Nestle 2000, 1195).

But while all types of olive oil are sources of monounsaturated fat, extra virgin

olive oil, from the first pressing of the olives, contains higher levels of

antioxidants, particularly Vitamin E and phenols, because it is less processed

(Caponoi, Gomis, Pasqualone 2001, 231). Olive oil is clearly one of the good

oils, one of the healing fats (Keys et al 1986, 906). Most people do quite well

with it since it does not upset the critical omega-6 to omega-3 oil and most of

the fatty acids in olive oil are actually omega-9 oil which is monounsaturated,

fatty acid classified into three categories, omega-9 which refers to the fatty acid

in olive oils, omega-6, omega-3 which refers to the fatty acid in other fruit oils

(Willett 1990, 354). Spanish researchers suggest that including olive oil in your

diet may also offer benefits in terms of colon cancer prevention (Serrano,

Yago, Manas, Calpena, Mataix, Martinezvictroria 1997, 630).   Their study

results showed that rats fed diet supplemented with olive oil had a lower risk of

colon cancer than those fed safflower oil-supplemented diets. In fact, the rats

that received olive oil had colon cancer rates almost as low as those fish oil

(Lipworth, Martinez, Angell, Hsieh, Trichopoulos 1997, 186).

Types of Olive Oil

Olive oil is produced only from green olives. Nearly the entire production of green olives in Italy is converted into olive oil. Flavor, color, and consistency vary, due to different olive varieties, location, and weather (Keys et al 1986, 907). Virgin olive oil classified into three categories. According to the European Union these three categories are: extra virgin, virgin and lampante, depending on their different sensory and chemical characteristics (Diego, Garcia, Ramon. 2004, 484), (Garcia, Gonzalez, Aparicio 2004, 486). All of these type are pure olive oil, where the word pure refers to the fact that no other vegetables oil are mixed in. Brief description of each type is given below:

1. Extra virgin olive oil

Any olive oil that is less than 1% acidity which has a free acidity, expressed as oleic acid, of not more than 1 gram per 100 grams , produced by the first pressing of the olive fruit through the way of extraction process (Diego *et al* 2004, 486). Most olive oils today are extra virgin in name only, meeting only the minimum requirement. Extra virgin is a chemical requirement that does not indicate quality and taste (Garcia et al 2004, 487).

2. Virgin olive oil

It is produced from olives that are slightly riper than those used for extra-virgin oil exactly the same manner. This oil has a slightly higher level of acidity (2%), virgin olive oil which has a free acidity, expressed as oleic acid, of not more than 2 grams per 100 grams (Diego *et al* 2004, 487).

3. Lampante olive oil

It is solvent-extracted from olive pulp, skins and pits; then refined (Keys et al 1986, 913). It is lighter in color and blander than virgin olive oil. It is more general-purpose olive oil. This oil is slightly higher level of acidity from extra virgin and virgin olive oils, which has a free acidity, expressed as oleic acid, of not more than 3.3 grams per 100 grams (Diego *et al* 2004, 487).

Extraction of olive oil

There was great interest in the study of virgin olive oil in view of reports of its importance to human health. The new findings about olive oil healthy virtues have increased interest and consumption of this material. Virgin olive oil depends on many factors related to olive tree cultivation and to the harvesting, storage (Lopez, Martinezbordiu, Delome, Carbrera, Sanchez 1996, 52) and olive processing steps of particular importance for olive oil quality are the olive

cultivar, the pedoclimatic conditions of cultivation, as well as the pruning fertilization and irrigation of olive trees (Li-chan 1994, 4), (Mataix 1993, 583). The good quality of olives at the moment of picking is decisive, but not the only factor ensuring a good quality of the olive oil (Luciano, Simona, Daria 2002, 587), (Aparicio, Ferreiro, Alonso 1994, 895). Generally, olives are picked from the tree by hands or by mechanical device. In some cases, olives are picked after falling on the ground or in good situation collection by nets placed under the trees crown. Upon collection, olives may be polluted with vegetable impurities, such as leaves and mineral impurities like soil, dust and stone fragment (Menzi, Panfili, Esti, Pezziferrato 1998, 117). Therefore set of precautions must be taken to avoid negative influences on quality of virgin olive oil and on the mechanical steady of the equipment used for olive oil extraction, mainly by removing the previous contaminants crushed leaves increase the oil green color and gives the organoleptic sensation of green leaves, that may not appeal to consumers (Luciano *et al* 2002, 590). The extraction of virgin olive oil by mechanical means is possible because some technological operations help to separate the oil droplets from the cell of olives flesh (Mendoza, Casado, Gomez, Roman 1996, 165), (Bianchi, Catalano 1996, 139). Olive crushing, using the granite mills tons or the metallic crushers, is a procedure of major importance because it gives rise to the breaking of

vegetable cells containing oil, when an olive oil mill is supported with a pressure system olive crushing is generally carried out by a granite mill stones (Morales, Aparicio, Rios 1994, 458). The resulting oil paste is subsequently pressed by a hydraulic press. In this way good extraction yields are obtained (Luciano *et al.,* 2002, 591).

Olive oil is a major product of Mediterranean countries. The mature olive fruit may reach an oil content of (20%) on fresh weight basis in about (6-8) months after full bloom. In the course of ripening the color of the olives changes from green to purple. The characteristics of the olives differ between the olives at different stages of ripening (Huisman, Schols, Voragen 1996, 123). Reported results have shown that addition of exogenous enzymatic preparations to the olive paste could increase the oil yield (4 - 7 %), depending on the degree of ripening. It is concluded that the degree of ripening is vital for both oil quality and oil yield (Sayago, Morales, Aparicio 2004, 482).

In the last thirty years there has been a growing interest in the use of olive oil in cooking because of the greater knowledge of Mediterranean food and the a wariness of the healthy virtues of a Mediterranean diet, and particularly olive oil. In spite of this the consumption of olive oil is negligible outside the Mediterranean region, where most of the worlds olive oil is produced and

consumed, and which provides nearly all exports and receives a majority of the imports (Grigg 2001, 163). This seems to be due to the very demanding climatic requirements of the olive tree and the fact that virtually all olive trees are grown in a Mediterranean-type climate. Although the olive trees was taken to areas with a similar climate during the European expansion after 1492. In spite of the role of Mediterranean population settling in the continent. The very high cost of olive oil compared with other oil seeds has made its penetration of non Mediterranean markets very difficult (Grigg 2001, 127).

Appendix B

Experimental data of IR source characterstics study.

Distances(cm)	Source power (a.u)
2	71.0
4	63.0
6	47.0
8	36.5
10	28.5
12	21.5
14	17.0
16	14.0
18	11.0
20	9.0
22	7.5
24	6.0
26	4.0
28	3.5
30	2.5
32	2.0
34	1.5
36	1.0
38	0.5
40	0.0

Table B₁: Source power as measured at different distance from the source.

Frequency(HZ)	Source power (a.u)
10	5.00
15	3.17
20	2.14
25	1.5
30	1.16
35	0.92
40	0.77
45	0.66
50	0.56
55	0.51
60	0.47
65	0.44
70	0.42
75	0.39
80	0.38
85	0.36
90	0.36
95	0.36
100	0.36
105	0.36
110	0.36

Table B$_2$: Source power dependence on the driving frequency.

Current (mA)	Source power (a.u)
0	0
10	0
20	0
30	0
40	0.13
50	0.23
60	0.27
70	0.33
80	0.40
90	0.50
100	0.66
110	0.89
120	0.96
130	1.31
140	1.81
150	2.41
160	2.95
170	3.93

180	5.18
190	6.94
200	9.14

Table B₃: Source dependent on the driving current.

Appendix C

Experimental data of olive oil and fresh olives juice study.

Adulteration Percentage (Seeds+Olive) Oil	PPE Signal (a.u) (Olive+Corn) Oil	PPE Signal (a.u) (Olive+Sunflower) Oil	PPE Signal (a.u) (Olive+Soyabeam) Oil
0%	7.45	7.45	7.45
10%	7.22	7.15	7.03
20%	6.99	6.86	6.64
30%	6.75	6.51	6.27
40%	6.55	6.23	5.91
50%	6.28	6.01	5.56
60%	5.99	5.72	5.31
70%	5.75	5.48	4.97
80%	5.53	5.29	4.61
90%	5.28	5.12	4.19
100%	5.17	4.72	3.87

Table C₁: PPE signal of different olive samples adulterer with seeds oils.

Year	Condition	PPE Signal(a.u)	Year	Condition	PPE Signal(a.u)
94	Stored in:	3.72	94		3.19
95	Plastic	4.55	95	Stored in:	4.27
96	Full filled	6.07	96	Plastic	5.61
97	Dark place	6.81	97	Full filled Light place	5.98

Table C₂ : PPE signal of olive oil samples at different storage conditions.

Year	Condition	Signals(a.u)	Year	Condition	Signals(a.u)
94	Stored in:	5.19	94	Stored in:	3.72
95	Glass full	6.24	95	Plastic full	4.55
96	Filled	7.25	96	Filled	6.07
97	Dark place	7.79	97	Dark place	6.81

Table C₃ : PPE signals of olive sample stored in different containers.

Year	Condition	PPE Signal(a.u)	Year	Condition	PPE Signal(a.u)

94	Full filled, Room light Plastic bottle	3.19	94	Half filled Room light Plastic bottle	2.85
95		4.27	95		3.26
96		5.61	96		4.18
97		5.98	97		4.53

Table C₄ : PPE signals of olive oil sample at different storage condition.

Regions	Year (1995)	Year (1998)	Year (2004)
Hebron	4.55	5.71	6.86
Ramallah	5.04	5.98	7.14
Nablus	5.38	7.49	8.57
Jerusalem	5.85	7.83	8.94
Biet-Jalla	7.31	9.09	

Table C₅ : PPE signals of olive samples from different production

years and geographical reigns.

Production year	Hebron	Nabuls
94	3.72	4.83
95	4.55	5.38
96	4.72	5.51
97	5.34	6.64
98	5.71	7.49

Table C₆ : PPE signals for different regions and years.

Ripening	PPE	PPE

time (months)	Signal (a.u). Romi	Signal (a.u). Nabali
1/9/2004	2.94	2.67
8/9/2004	3.15	2.91
15/9/2004	3.43	3.15
22/9/2004	3.60	3.34
29/9/2004	3.99	3.67
6/10/2004	3.99	3.68
13/10/2004	4.00	3.68
20/10/2004	4.01	3.69
27/10/2004	4.03	3.70
3/11/2004	4.23	3.98
10/11/2004	4.48	4.19
17/11/2004	4.63	4.31
24/11/2004	5.00	4.72
1/12/2004	5.45	5.18
8/12/2004	5.70	5.36
15/12/2004	5.79	5.48
22/12/2004	5.82	5.49
29/12/2004	5.85	5.53
2/1/2005	5.86	5.55
15/1/2005	5.87	5.55

Table C₇: Olives content of oil monitor during the ripening period.

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