Sudan University of Science

and Technology

College of Graduate Studies

Spectroscopic Analyses of Nigella Sativa to Study Effects of Temperature and Humidity

التحليلات الطيفية للحبة السوداء لدراسة تأثير درجة الحرارة والرطوبة

A thesis submitted for the Degree of Doctor of Philosophy in Physics

BY

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آية

قال الله تعالى:

﴿ وَيَرَى ٱلَّذِينَ أُوتُواْ ٱلۡعِلۡمَ ٱلَّذِيٓ أُنزِلَ إِلَيۡكَ مِن رَّبِّكَ هُوَ ٱلۡحَقَّ وَيَهۡدِيٓ إِلَىٰ صِرَٰطِ ٱلۡعَزِيزِ ٱلۡحَمِيدِ ﴾

[سبأ -6]

Dedication

To my father's soul in heaven ... Allah have mercy on him.

To my dear mother .... Allah prolong her life and assure her health and well-being.

To my wife and my life partner ...

To my brothers and sisters ...

My sons and daughters

I dedicate my research

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Praise be to Almighty Allah and thank to Allah above all else. Blessings and peace be upon our prophet Mohammed who said ((In the black seed there is a cure for every disease except death)).

I thank Almighty Allah for having accomplished what I have aspired by completing PhD in Physics.

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My wholehearted thanks to my brother Loay for the advice, effort, motivation and coordination he presented.

Abstract

The study aimed to find out the effect of humidity and temperature factors on the black seed, and to trace the effects, the FTIR method was used to track changes in the chemical structure of the Nigella-sativa by following the appearance and disappearance of the functional bonds it contains and the method of laser induced breakdown spectroscopy LIBS were also used to study the parameters of the plasma. By calculating the density of calcium ions and the degree of heat of the plasma resulting from the laser, the changes that occur in the elements of the nutrition value of the Nigella-sativa have a close relationship with the intensity of their appearance and their effect on the temperature of the resulting plasma.

Nine samples of the Nigella-sativa were prepared so that in each sample there would be 5 grams of the Nigella-sativa and soaked it to 26.2% humidity, then exposed to heat at (100 degrees Celsius) for a period of 5 minutes, then a 5 gram sample of the Nigella-sativa was soaked to a humidity of 26.2% then exposed to heat at (100 degree) for a period of 10 minutes, then sample 5 grams of Nigella-sativa and soak it at 26.2% humidity, then expose it to heat at (100 degree) for a period of 15 minutes and repeat this process for three more samples at 30% humidity in different time, and for three other samples at 41.5% in different time. When using the FTIR spectroscopy method, the result was achieved that the Nigella-sativa did not change its chemical composition, which means that it was almost unaffected by humidity and temperature.

The temperature of the plasma resulting from the Boltzmann equation was calculated, when with the calcium ion Ca I the temperature was 3354.2 K

and with the calcium ion Ca II the temperature was 2655.4 K We obtained a high percentage of calcium ions Ca I and Ca II and it was, respectively, 2.34 $X10^{18}$ cm^3 and $2.91x10^{18}cm^3$ Therefore, using the method of laser induced breakdown spectroscopy LIBS, we find that the changes occurred in the nutritional value of the Nigella-sativa, we find that it maintained the superiority of the calcium component in it, insensitive to humidity and temperature.

Through the two methods, we came to the conclusion that the Nigella-sativa is not affected by humidity and temperature up to 100 degrees Celsius, which preserves its nutritional value and is not affected by various factors. cooking, storage and transport.

ABSTRACT (Arabic)

مستخلص البحث

هدفت الدراسة الى معرفة تأثير عاملي الرطوبة ودرجة الحرارة على الحبة السوداء ولتتبع التأثيرات تم استخدام طريقة التحليل الطيفي بواسطة الاشعة تحت الحمراء FTIR لتتبع التغيرات في البنية الكيميائية للحبة السوداء (Nigella-sativa) متابعة ظهور واختفاء الروابط الوظيفية فيها، كما تم استخدام طريقة الانهيار المستحث بالليزر LIBS لدراسة معاملات البلازما وذلك بحساب كثافة ايون الكالسيوم ودرجة حراة البلازما الناتجة عن الليزر فالتغيرات التي تحدث في عناصر القيمة الغذائية للحبة السوداء لها درجة ارتباط وثيقة بكثافة ظهورها وتأثيرها على درجة حرارة البلازما الناتجة.

تم تجهيز تسع عينات من الحبة السوداء بحيث يكون في كل عينة 5 جرام من الحبة السوداء ونقعها عند نسبة رطوبة 26.2٪ ومن ثم تعريضها للحرارة عند (درجة 100 مئوية) وذلك لفترة زمنية مقدارها 5 دقائق، ثم عينة 5 جرام من الحبة السوداء ونقعها عند نسبة رطوبة 26.2 ٪ ومن ثم تعريضها للحرارة عند (درجة 100) وذلك لفترة زمنية مقدارها 10 دقائق، ثم عينة 5 جرام من الحبة السوداء ونقعها عند نسبة رطوبة 26.2 ٪ ومن ثم تعريضها للحرارة عند (درجة 100) وذلك لفترة زمنية مقدارها 15 دقيقة وتكرار هذه العملية لثلاث عينات أخرى عند الرطوبة 30 ٪ و لثلاث عينات أخرى عند 41.5 ٪ . فعند استخدام طريقة التحليل الطيفي بواسطة الاشعة تحت الحمراء FTIR تم الوصول إلى نتيجة أن الحبة السوداء لم يتغير تركيبها الكيميائي أي أنها تكاد تكون غير متأثرة بالرطوبة والحرارة.

وتم حساب درجة حرارة البلازما الناتجة من معادلة بولتزمان فعند ايون الكالسيوم Ca I كانت درجة الحرارة 3354.2 K وعند ايون الكالسيوم Ca II كانت درجة الحرارة 2655.4 K وحصلنا على نسبة عالية من ايون الكالسيوم Ca I و Ca II وكانت على التوالي $2.34X10^{18}$ cm^3 و $2.91x10^{18}cm^3$ لذلك نجد عند استخدام طريقة الانهيار المستحث بالليزر LIBS لمعرفة التغيرات التي حدثت في عناصر القيمة الغذائية للحبة السوداء نجد أنها حافظت على تفوق وجود عنصر الكالسيوم فيها غير متأثرة بالرطوبة والحرارة.

ومن خلال الطريقتين وصلنا الى نتيجة أن الحبة السوداء لم تتأثر بالرطوبة والحرارة حتى 100 درجة مئوية مما يحافظ على قيمتها الغذائية وعدم تأثرها بعوامل الطهي المختلفة والتخزين والنقل.

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CHAPTER ONE

Introduction and Basic Concept

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Introduction and Basic Concept

1.1 Introduction

Nigella sativa (N. sativa), black seed and black cumin are all the names of what is scientifically known as Nigella sativa, which is cultivated in different parts of the world and especially cultivated in the countries of the eastern Mediterranean [1]. It is an annual flowering plant, due to its aromatic nature, it is used as a spice in cooking. It is also used as a carminative and diuretic by the peoples of the East [1]. The active ingredients in N. sativa have beneficial effects against many diseases, including cancer. It is also linked to the values and customs of the regions of the Middle East. It has been proven in the noble hadith on the Prophet, prayers and peace be upon him, that he said ("The black seed is a remedy for all disease except the death "), because many generations have inherited traditional medicine in many ways to use the black seed. And since they have these multiple uses in food and medicine, we must put them under scientific study to monitor and confirm the benefits. This chapter summarizes the background (section 1.1.1), the context and purposes (section 1.1.2) and the basic concept in (1.2) Types of Spectroscopy, 1.3 Fourier Transform Infrared (FTIR) spectroscopy, (1.4) laser Induced Breakdown Spectroscopy (Libs), (1.5) Difference between FTIR and Libs spectroscopy, (1.6) Spectrophotometer, (1.7) Thesis Outline. Includes an overview of the remaining chapters of the thesis.

1.1.1 Background

The advancement of different aspects of science, the overlap of the tools of knowledge, their relevance and influence on each other and the specialization of each science have not prevented the influence of science to study the nature which is interested in the interaction of matter, whatever it is. the question. Being with the surrounding environment, through the physical factors that undoubtedly have a great influence on the properties, properties and composition of the material, even if it is limited or has a weak effect. From the definition of natural sciences, it was necessary to study some of the physical properties that affect materials such as humidity and temperature.

In the case of this study, we got the idea and its purpose through culinary practices and baking, because we are not ignoring the stories of popular medicine and the intergenerational transmission of herbal medicine practices. The black seed is designed to study the knowledge of the effect of heat and humidity on it, due to its consistency and the emphasis on its nutritional and medicinal benefits, but we have not found any 'specific study dealing with the effect of these physical factors on it. This study was from an angle that shows the effect of physical factors on black seed to give previous research a new angle, as we hope it will add a special imprint in this area.

1.1.2 Context and Purposes

Keep track of cooking methods and candy preparation, and listen to traditional medicine practitioners use the black seed and the review of previous scientific studies that have been exposed to black seed stemmed from the idea that knowledge of the effect of heat and humidity on black seed should be studied, in order to confirm its nutritional benefits and medicinal, but we did not find a specific study dealing with the effect of these physical

factors on it. This study was from an angle that shows the effect of physical factors on black seed to give previous researches a new angle, as we hope it will add a special imprint in this area.

In our knowledge of previous studies and research in this area, we find that they were divided into different sections which were discussed in the second chapter marked by previous studies and the black seeds, from which we concluded that none of these studies was exposed to these factors. and their effect on the black seeds, and therefore our focus on that part in particular, which is a study of the effect of temperature and humidity on black bean, we did not expose it to more degrees higher than what it is exposed to during the baking or candy making process.

After determining the context of the research, the idea of the purpose and objectives of the study was defined. When using the black seed in cooking and exposing it to different temperatures, when chewing, or when wetting and soaking in water.

Objectives of the study:

How do heat and humidity effect on black seed.

Do these contacts affect the functional and nutritional composition of the black seed.

Does the process of transportation from production areas to consumption in different climatic conditions affect it.

The answer to the question of traditional medicine which recommends chewing it and moistening it with saliva, does this have any effect on its nutritional and medicinal value.

1.2 Types of Spectroscopy

Spectroscopy studies the scattering of light and other radiations caused by matter as a result of the light falling on it, which makes it possible to study its different properties due to the interaction between light and matter, which leads to an excitation electronics and directions of particle vibration or nuclear rotation. By measuring the absorption and emission of light or radiation from a material, spectroscopy can measure the wavelength and frequency of the resulting radiation and predict the properties of the material [1,4].

Physically, when electromagnetic radiation passes at a specific wavelength from a source through a substance containing certain compounds, the emitted photon has an energy equal to the difference between the atomic energy [1,8]. So, one of three states can occur:

Absorption: An atom at the lower level absorbs a photon of frequency hν and moves to a higher level.

Spontaneous emission: An atom in the upper plane can spontaneously decay towards the lower level and emit a photon of frequency hν if the transition between E_2 and E_1 is radioactive. This photon has random direction and phase.

Stimulated emission: The incident photon causes the disintegration of an atom of the higher plane, causing the emission of a “catalytic” photon whose properties correspond to those of the incident photon. The term "catalyst" emphasizes the fact that this type of radiation only occurs in the presence of the incident photon. The amplification is due to the similarities between the accident and the photons emitted [2,7].

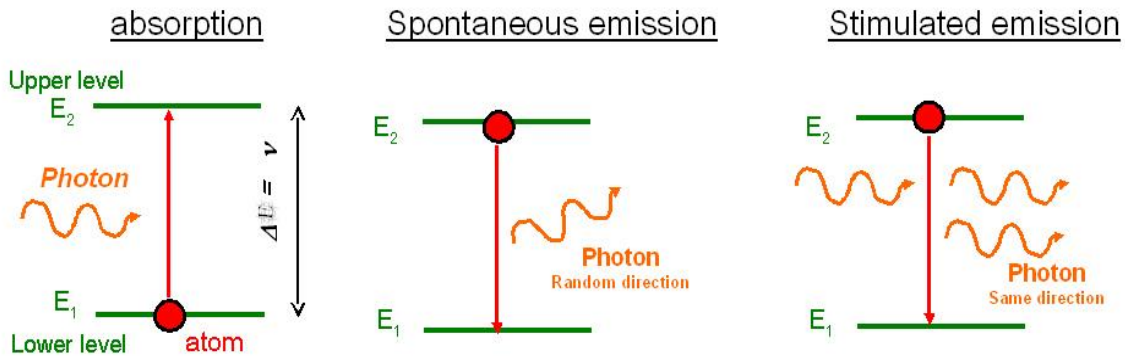

Figure (1.1) Mechanism of the interaction between an atom and a photon

Study the spectrum and thus determine the differences and changes in the different properties of a substance since the characteristic observed by a spectrophotometer varies according to the type of spectrophotometer used. For example, we find that the mass spectrometer measures the difference in mass / charge ratio, the optical spectrophotometer measures the contrast of electromagnetic radiation, and the nuclear magnetic resonance spectrometer measures the change in nuclear resonance frequencies. Based on the knowledge of these differences and changes, the different properties of the material studied can be measured and observed [3].

There are many spectroscopic techniques to determine the physical and electronic composition of different particles at the molecular or atomic level, where the principle of operation depends on the exchange of energy between a photon and a sample [3,9]. The types of spectral technologies can be classified by region of the electromagnetic spectrum or by energy.

Among the techniques based on its working principle in the process of energy absorption are X-ray absorption spectroscopy, Raman spectroscopy, rotational electron resonance spectroscopy, infrared (IR), resonance nuclear

magnetic (NMR), mass spectroscopy (MS) and ultrasound. Violet and visible spectroscopy (UV / Vis). An example of a technology based on energy emission is spectroscopy of visible atomic emissions in the UV / visible range. As is the case with emission-based photoluminescence technology where the transition from a higher energy state to a lower energy state is accompanied by irradiance such as fluorescence spectroscopy. In the technique of chemiluminescence, which occurs when the source of energy absorbed is a chemical reaction, this phenomenon is called chemiluminescence. An example is chemical illumination spectroscopy [4].

1.3 Fourier Transform Infrared (FTIR) spectroscopy

IR (which wavelength covers from 0.75 to 14 μm in the electromagnetic spectrum) spectroscopy studies the interaction between matter and infrared. Infrared spectroscopy evolved to an "infrared Fourier transform," which found that all infrared spectroscopy devices operate on the principle that when infrared radiation passes through a sample, some of the radiation is absorbed and absorbed radiation that has passed the sample, is recorded. We know that different molecules with different combinations produce different spectra, so the spectra can be used to identify and differentiate molecules [5,11].

FTIR is the preferred method for infrared spectroscopy for a number of reasons, including the fact that it does not destroy the sample, is also fast compared to older techniques, and is considered to be more sensitive and accurate. FT-IR allows collecting all spectral data in one go Instead of sequentially irradiating the sample with varying single wavelengths (disperse). [6,12].

1.3-1: How does FTIR work

When the covalent bonds of a molecule absorb radiation of a certain wavelength (λ), a change occurs in the vibrational energy of the molecular bond, noting that the relationship which adds the wavelength of the number wave is as follows:

$$\nu = 1 / \lambda \qquad (1,1)$$

The type of oscillation generated (expansion or bending) depends on the energy of the infrared radiation, and as different bonds and functional groups absorb different frequencies, the transmittance pattern varies with different particles so this absorption is measured as a function of length wave (in the form of wave numbers, usually (4000 to 600 cm-1). A continuous source generates infrared light over a wide range of infrared wavelengths. The infrared light then passes through the interferometer and is directed at the sample. The result is an infrared spectrum that acts as a separate "molecular fingerprint" that can be used to identify organic and inorganic samples, and the size of the peaks in the spectrum is a direct indication of how much material is present. Using modern software algorithms which are automatically drawn on a graph by one of the programs included in spectroscopy devices, as the spectrum is drawn on a graph with a wave number (ν cm $^{-1}$) recorded on the X axis and the transmittance is recorded on the Y axis. And using the graph that was made while creating it, organic chemists analyze the plot and find distinct peaks that can be attributed to the components of the compound and therefore the infrared is an excellent tool for quantitative analysis.

Trace the path of the rays as follows:

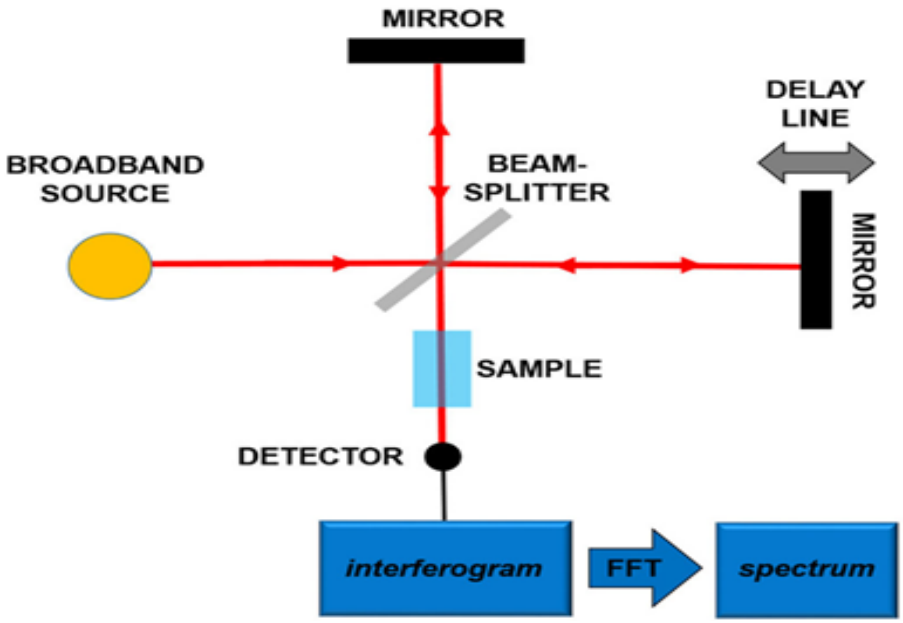

Figure (1-2): Fourier Transform Infrared spectroscopy (FTIR) principle

The Fourier transform is a mathematical function that separates waves and returns the frequency of the wave as a function of time according to the following equation:

The Fourier transform:

$$A(r) = \sum X(k)\, exp(-2\pi \frac{irk}{N}) \qquad (1.2)$$

Where:

A(r) and X(k) are the frequency domain and time domain points, respectively for a spectrum of N points.

This equation is calculated by a computer program that captures the signal from the spectroscope and converts the interference model into an infrared spectrum model that we recognize and use [7].

1.3-2: Use FTIR spectroscopy.

The infrared spectrometer covers the range of expansion vibrations in the fingerprint area / single bond area (40-1400 cm^{-1}) and also the range of bending vibrations in the area of the functional group (1400-4000 cm^{-1}) and thus facilitates the observation of molecular vibrations due to the absorption of infrared radiation.

Table (1-1) The coverage range of the infrared spectrum.

Region	Wavelength (μm)	Wavenumber (cm^{-1})
Near infrared	0.75--2.5	14000-4000
Mid infrared	2.5--25	4000-400
Far infrared	25--100	400-40

1.3-3: Analyze an FTIR spectrum

Each organic compound contains a set of functional groups which are structural units within them and are in specific arrangements of atoms and bonds. Infrared radiation is a powerful tool for identifying functional groups due to the similar absorption frequencies of these groups in different molecules. The FTIR spectrum arises from interference patterns which are "decoded" into recognizable spectra. The patterns in the spectra help identify the sample because the particles show specific infrared fingerprints, and the Fourier transform produces spectra that analysts can use to identify the substance. Scientists have established infrared absorption frequencies characteristic of organic functional groups. They are represented by the type of absorption vibrations (cm^{-1}) and the intensity. See the appendix [7,8].

1.4 Laser Induced Breakdown Spectroscopy (libs)

Laser Induced Breakdown Spectroscopy (LIBS) is a stable, simple, reliable and versatile form of atomic emission spectroscopy and is a chemical analysis technique for determining the presence or mass fraction of an element present in a sample based on a measurement of the intensity of light emitted by a flame, spark, arc or plasma [8, 17]. It has a great capacity for the rapid detection of elements in any substance (solid, liquid or gas) and quantitative analysis by LIBS is possible using conventional titration methods or non-titration methods. The main physical process that is at the heart of LIBS technology is the formation of a high temperature plasma, resulting from a high power laser pulse and a small pulse to the generation of a high temperature plasma. When a short pulse laser beam is focused on the surface of the sample, a small volume of the sample mass is excised (i.e. removed by thermal and non-thermal mechanisms) - in a process known as laser ablation. This excised mass interacts with a later part of the laser pulse to form a high-energy plasma containing free electronics and excited atoms and ions, causing the plasma to emit light with discrete spectral peaks. The light emitted by the plasma is collected and connected to the ICCD detector / spectrometer for LIBS spectroscopy. Unique spectral peaks are assigned to each component of the periodic table. By identifying different peaks of the samples analysed, their chemical composition can be quickly determined. Thus, information on the intensity of the LIBS peak can be used to determine the concentration of tracer and base elements in the sample. The LIBS analytical system (Figure 1.3) consists of a few components: (1) a short-pulse, Q-switch semiconductor laser operating at 1064 nm (or one of the dual

frequency harmonics) used to create the fine plasma on the target, (2) a combination of optics to focus the laser light on the target and to collect the light emitted as the plasma cools, (3) the matched fibre optic system and the spectrometer / detector to obtain the plasma light emission and spectral resolution of the optical spectrum, and (4) a computer to control the system and process data and analyzed by specific software[8, 9].

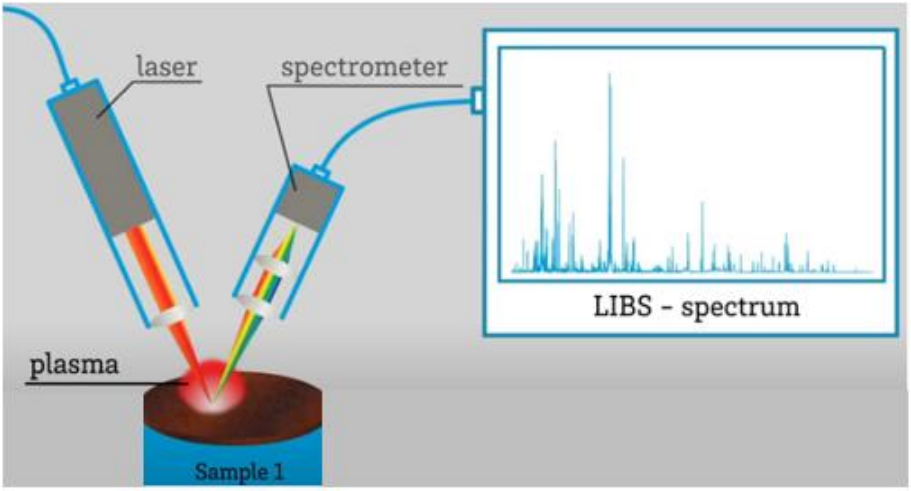

Figure (1-3): schematic diagram of simple libs system

1.4-1 Laser Induced Breakdown Spectroscopy LIBS technique

Strong points:

LIBS analysis is fast and does not primarily require sample preparation. The LIBS technique has many advantages, gives immediate results and covers a wide range of elements. It is considered a non-destructive material detection tool because the samples it contains do not require any prior preparation and can be used for both rapid and remote analysis. Titration or without titration can be used to identify unknown elements in the sample under study. There are also small portable units. LIBS is very sensitive to light elements, LIBS

spectra contain detailed synthetic information about the material, making it the ideal technique for association and source studies.

However, there are limitations in the area of analytical techniques and LIBS has three main limitations. First, there are large differences in firing intensity, largely because the laser does not interact with the sample in exactly the same way for every laser pulse. This is often overcome by averaging multiple spectra of the same material. Second, primary analysis using univariate or multivariate titrations does not lead to precision. Finally, as with any spectroscopic technique, the spectra produced by a single LIBS instrument are unique to that instrument, and the same sample analyzed on a similar instrument will be slightly different [9,10].

LIBS is used in many possible applications, such as element detection in nuclear reactors. Detection of elements on the high seas. Space mission; Detection of elements on other planets. Environmental monitoring (soil and particle pollution). Analysis of materials (metals, plastics). Forensic medicine and biomedical studies (dental and bone analyzes). Military and security needs (explosive particles, chemical and biological warfare agents such as anthrax). Restoration / restoration of art (pigments, precious metals / debris) [10].

1.4-2: Analyze LIBS technique spectrum

The principle of operation of the LIBS is based on a laser - usually a neodymium-impregnated aluminum yttrium garnet laser (ND: YAG) - which passes through a lens to focus the laser beam with a diameter of about 50 μm and obtain a focused pulsed laser - in the energy range of 5 to 6 mJ / pulse It pulses 50 times per second (50 Hz) on a sample in a very short time. The

duration of the pulse is 1 to 2 nanoseconds (one billionth of a second) resulting in density high enough to create a plasma around the target area.

Plasma expands when bombarded by a laser and excites electrons in the atoms that make up the plasma. When electrons relax and atoms return to a stable state, they emit photons characteristic of the element and electronic transitions. A monochromatic spectrophotometer, prism or grating is used to scatter light. The CCD array combines radiation emitted over a specified wavelength range, typically 170 to 1100 nm.

The on-board spectrophotometer analyzes the light emitted by measuring the wavelength and intensity (amount) of light at specific wavelengths - the optical spectrum [10]. Each element of the periodic table is assigned unique LIBS spectral peaks. The on-board software compares the spectral lines at known wavelengths to identify the elements present, and uses the intensity of these lines, with an on-board calibration, to determine the focus of the element.

By identifying different peaks of the analyzed samples, their chemical composition can be determined quickly. Often times, information about the intensity of the LIBS peak can be used to determine the concentration of trace and key elements in the sample [10,22].

1.5 Difference between FTIR and Libs spectroscopy

laser Induced Breakdown Spectroscopy (Libs): Profile and depth analysis of successive coating layers the Libs technique identifies the constituent elements of the material studied, then determines their presence by measuring the density of the plasma.

Fourier Transform Infrared (FTIR) spectroscopy: A technique that identifies the functional groups contained in an unknown sample by measuring the intensity of absorption by the bond or the type of vibration that occurs there [11,16].

1.6 Spectrophotometer

Principle of Spectrophotometer

The spectrophotometer an apparatus used for recording and measuring spectra by measure light intensity as a function of wavelength. It does this by diffracting the light beam into a spectrum of wavelengths, detecting the intensities with a charge-coupled device, and displaying the results as a graph on the detector and then on the display device, a prism (or) grating is used to split the incident beam into different wavelengths. By suitable mechanisms, waves of specific wavelengths can be manipulated to fall on the test solution. The range of the wavelengths of the incident light can be as low as 1 to 2 nm [12].

Instrumentation of Spectrophotometer:

The essential components of spectrophotometer instrumentation include, a table and radiant energy source materials that can be excited to high energy states by a high voltage electric discharge (or) by electrical heating serve as excellent radiant energy sources. A monochromatic, to break the polychromatic radiation into component wavelength (or) bands of wavelengths. A monochromatic resolves polychromatic radiation into its individual wavelengths and isolates these wavelengths into very narrow bands [12,25].

Prisms:

A prism disperses polychromatic light from the source into its constituent wavelengths by virtue of its ability to reflect different wavelengths to a different extent. Two types of Prisms are usually employed in instruments. Namely, 600 cornu quartz prism and 300 Littro Prism.

Grating:

Gratings are often used in the monochromators of spectrophotometers operating ultraviolet, visible and infrared regions.

Transport vessels (cuvettes), to hold the sample

Samples to be studied in the ultraviolet (or) visible region are usually glasses (or) solutions and are put in cells known as “CUVETTES”. Cuvettes meant for the visible region are made up of either ordinary glass (or) sometimes Quartz.

A Photosensitive detector and an associated readout system most detectors depend on the photoelectric effect. The current is then proportional to the light intensity and therefore a measure of it. Radiation detectors generate electronic signals which are proportional to the transmitter light. These signals need to be translated into a form that is easy to interpret. This is accomplished by using amplifiers, Ammeters, Potentiometers and Potentiometric recorders [13,20].

Applications:

Some of the major applications of spectrophotometers include the following:

Detection of concentration of substances.

Detection of impurities.

Structure elucidation of organic compounds.

Monitoring dissolved oxygen content in freshwater and marine ecosystems.

Characterization of proteins.

Detection of functional groups.

Respiratory gas analysis in hospitals.

Molecular weight determination of compounds.

The visible and UV spectrophotometer may be used to identify classes of compounds in both the pure state and in biological preparations [14].

1.7 Thesis Outline

The research was divided into chapters where we discussed in the first chapter the introduction and basics, in which we provided some background on the black seed and its uses. We have also mentioned the objectives, goals, reasons and limitations of the research. In this chapter we have presented the types of spectral studies and their bases and we have focused on the two methods in which we have carried out the research, namely the Fourier transform method and the Laser Induced Breakdown Spectroscopy (LIBS) method. As for the second chapter, which is punctuated by previous studies, we follow the studies that have been carried out on the black seed in various pharmaceutical and nutritional fields.

In the third chapter marked by Materials and Methods, we presented there the materials used and the methods used to conduct the practical side of the research and in the fourth chapter the Results that we achieved, discussed and concluded with the conclusion.

CHAPTER TWO

Nigella sativa and Literature Review

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2.1 Introduction to black seeds

The scientific term Nigella sativa has other synonyms like Nigella damascena, Nigella ciliaris, Nigella arvensis and Nigella hispanica. Nigella sativa is also known by colloquial names such as Black Cumin (English), Habbet as-Suda (Arabic) [4,19]. The literature has also revealed that black cumin is native to the Mediterranean region, but is currently cultivated in different parts of the world. Recently, many medicinal values have been adopted for black cumin seeds and their oil [4] Black cumin (Nigella sativa) is an annual flowering plant belonging to the buttercup family.

The active ingredients in N. sativa have beneficial effects against many diseases, including cancer. For example, this is effective in reducing the risk of developing atherosclerosis by lowering low-density lipoprotein cholesterol in the blood and elevation of high-density lipoprotein cholesterol in the blood [5]. The seeds have been reported in previous studies, studied the fatty acid and amino acid combinations of N. sativa. Imported from the Middle East, it reported that the seeds showed a combination of 21% protein, 35-5% fat, 5-5% moisture and 3-7% ash, and the rest were total carbohydrates [6,16,17]. Compounds with antimicrobial activities are found in N. sativa volatile oil. Seed by Egyptian workers. Literature data on the chemical composition of N. sativa. The seeds are very limited. The purpose of this investigation was to determine the approximate composition and some of the

exact components of N. sativa. Seeds. There is not much research on the effect of physical factors on black seed and its components in this area.

Figure (2-1): Black seed is in its cluster

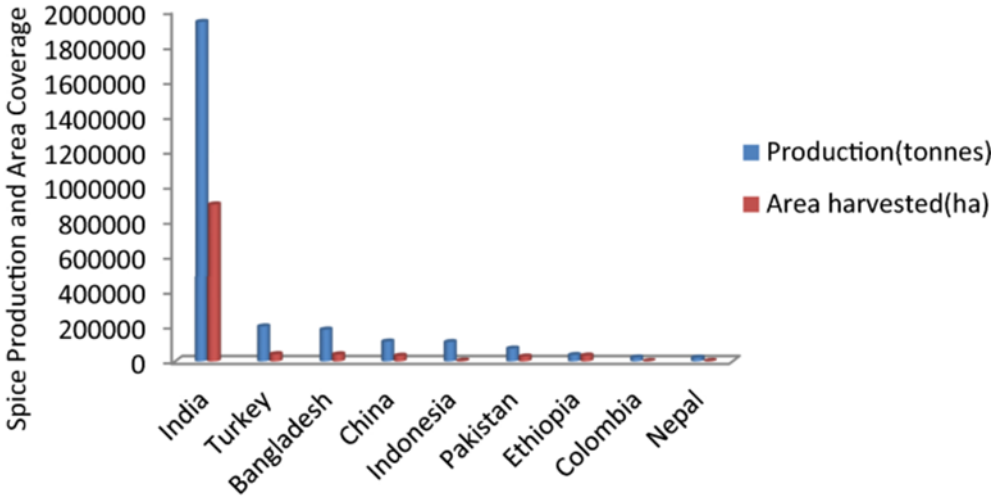

Figure (2-2): Top Spice producers countries – sours: FAO STAT(2019)

In this chapter, previous studies that have been conducted on black seed in medical and chemical aspects have been listed. The studies that have been carried out on the black seed in its use in traditional medicine have been listed

in paragraph 2.2, and the studies that have been carried out on it in its chemical composition, paragraph 2.3 has also been the subject of a monitoring.

In paragraph 2.4 previous studies were listed in the area of the use of black seed as a nutritional value. In the last paragraph, the effect of nutritional values was examined by temperature and humidity.

2.2 Nigella sativa, medicine and folk medicine:

Tracing the history of black seed research, we find that researchers' interests have focused on two aspects, the first aspect being the chemical and structural components of black seed and the second side the uses of black seed. in folk medicine by tracing the history of its use in ancient civilizations and previous nations. Most of the research and studies have been specifically included in this section. Most of them concern the use of black seed in the treatment of different diseases, some depend on its effect on diseases of the skin, hair, heart [7]. For example, it is effective in the diminishing the risk of atherosclerosis by decreasing the serum low density lipoprotein cholesterol level and increasing the serum high density lipoprotein cholesterol levels [8].it exerts therapeutic and protective effect in diabetes by decreasing morphological changes and preserving pancreatic beta-cell integrity [9].and by beneficially changing the hepatic enzyme activities [9,10].it is effective against hypertension [9,22]. it has a potent antihistaminic effect on airways of asthmatic patients [10,17]. its components are promising agents to complement schistosomiasis specific treatment [11,13]. its oil protects kidney tissue against oxygen free radicals, preventing renal dysfunction and morphological abnormalities [11,9]. Nigella sativa is used in the treatment of

many diseases in many countries globally. Its beneficial effects on health, especially against diseases such as cancer, diabetes and cardiovascular disease have been highlighted [11,22]. Antioxidant Properties of Nigella sativa Analysis of the antioxidant content of N. sativa has indicated that N. sativa has a higher content of volatile-oil antioxidants than non-volatile oil antioxidants [12,22].

2.3 Chemical composition of Nigella sativa

Through my reading of the researches conducted in this part, we can divide it into two major parts, one of which relates to the chemical makeup of black seed, which includes the formulas, chemical compounds, and acids that make up the black seed. In this part, the researchers, refer to crude fiber, protein, fat, ash and total carbohydrates in good agreement with the values reported by Papian [12,22]. Metal comparison The content of seeds with literary values indicates that the main differences are in the quantities Calcium and potassium. These were reported at 0.582%. And 1.06%, respectively, by Babayan [13]. the study by Babayan also we can conclude that the seeds are rich in protein and fat Potassium content. Formulations of fatty acids and steroids from seed oil, the current study also confirmed that eicosadienoic acid It is found in N. sativa seed oil. Arachidic acid, it also turned out to be a trace component. In N. sativa L. seed oil, / 3-sitosterol was Predominant sterols (69.4%); campesterol and stigmasterol They were 11 to 9% and 18.6%, respectively. It's like The composition of sterols in cream seed oil, which Belongs to the Annuacae family it’s 11.2% campesterol, 19.0% stigmasterol and 69.2% 3-sitosterol. However, the composition of sterols from oils, it is closely related to the plant family Phenolic compounds and

their effects may vary depending on Type and focus [13]. These compounds can be considered a major factor in the use of the seeds as a local medicine and as a flavoring agent in many foods [13,23].

Thymoquinone the Basic Active Substance of Nigella sativa. Nigella sativa use in various forms, as a powder, oil or extract in traditional treatment [14,22]. Thymoquinone, which is one of the most important bioactive components of N. sativa and is responsible for its many biological effects, it was reported that thymoquinone exists as a volatile oil in a proportion of 18.4%–24.0% [14]. Other analyses have indicated that the concentration of thymoquinone is 52.6 mg/100g and 20.13 mg/100 g [14,18].

2.4 Nutritional composition of Nigella sativa

By following the research's published in this section, we can conclude that the researchers A rough analysis of the seeds of black cumin (Nigella sativa L.) showed an average composition of 20.3%: protein, 45.4% fat, 7.1% moisture, 7.4% ash and the rest as total carbohydrates. Sodium, iron, zinc and copper are found at lower levels. Lead and molybdenum were also detected in traces. Linoleic acid (57%) followed by oleic acid (21. 8%).The main unsaturated fatty acid was, while palmitic acid (13.1%) was the main saturated. Glutamic acid (23.95%), aspartic acid (9.32%) and arginine (8.90%) were the major amino acids present while tryptophan and methionine were the secondary amino acids. These results indicate the high nutritional potential of black cumin seeds, in particular as a source of proteins (20.3 ± 0.63%) and fats (45.4 ± 0.53%), in particular unsaturated fatty acids (84%) which can be used as a nutritional supplement [24,26].

2.5 Fixed and Volatile Oils of Nigella sativa

Through previous studies, fatty acids have been identified in black seed oil extract, which accounts for about 99.5% of total fatty acids, because four saturated fatty acids (17.0%) and four polyunsaturated fats (82.5%) were found. Linoleic acid (55.6%), oleic acid (23.4%) and palmitic acid (12.5%) The main volatile compounds were transanthole (38.3%), p-cymene (14.8%), limonene (4.3%) and Carbone (4.0).%). The acid composition determined by this survey is similar to literary values [25,26].

Aqueous distillation of the seed extract of N. sativa gave a yellowish volatile oil. Determination of Essential Oils- Indicators by Gas Chromatography / Mass Spectrometry, fixed oil of Nigella sativa and its derivatives [25,26]. Hypoglycemic and analgesic studies on Nigella sativa. Volatile black seed oil against the multiple immunostimulating effects of ethanol extract. The oil consists of six phenylpropanoid compounds (46.1%), nine monoterpenoid hydrocarbons (26.9%), four monoterpenoid ketones 6.0%), eight non-perpenoid hydrocarbons (4.0%), three monoterpenoid alcohols (2.7%), two sesquiterpenoid hydrocarbons (1.0%). The oil is therefore characterized by a large amount of phenylpropanoid [25].

Fixed oil extracted (total fatty acid composition) and the volatile oil of Nigella sativa seed cultivated in Iran was determined by GC and GC / MS. Eight fatty acids (99.5%) and thirty-two compounds (86.7%) were identified in Fixed and volatile oils, respectively. The main fatty acid in the fixed oil was linoleic acid [25,26].

Fixed oil extracted (total fatty acid composition) and the volatile oil of Nigella sativa seed cultivated in Iran was determined by GC and GC / MS.

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2.6 Physical factors and their effects on food

The advancement of aspects of different sciences, the overlap of knowledge tools, their correlation and effects on each other and the specialization of each science have not prevented the effect of science from studying nature, which is interested in the interaction of matter, however it may be with its surrounding environment, by physical factors which undoubtedly have a great influence on the characteristics and properties and the composition of the material, even if it is limited or has a weak effect. From the definition of natural science, it was necessary to study some of the physical properties that affect materials such as humidity and temperature.

In the case of this study, we got the idea and the purpose from it through the culinary practices and the preparation of the sweets, because we do not neglect the accounts of folk medicine and the transmission of herbal medicine practices between generations.

The Nigella sativa was determined to study the knowledge of the effect of heat and humidity on it, due to its consistency and the emphasis on its nutritional and medical benefits, but we did not find specific study dealing with the effect of these physical factors on her, so this study was a continuation of previous research, which we hope will add a special imprint in this area.

CHAPTER THREE

Materials and Methods

CHAPTER THREE

Materials and Methods

3.1 Introduction

This chapter describes the experimental part including the samples preparation, equipment and devices, experimental setup, and the procedure for spectroscopic analyses using FTIR spectroscopy of Black Seed to study the temperature and humidity effect, and also the analysis study of plasma parameters of Calcium Ion in Black seed by laser induced breakdown spectroscopy (LIBS).

3.2 The experimental part for spectroscopic analyses of Nigella sativa to study the temperature and humidity effect

3.2.1 Instruments

A group of tools was selected to help get good results for the research,

Humidity and temperature measurement

as the device (BENETECH GM 1363B - humidity and temperature meter) was chosen to measure temperature and humidity simultaneously, as shown in the picture.

Figure (3-1) Humidity and Temperature Meter.

FTIR method analyzer device:

The device used the FT-NIR spectrometer for research use only (Spectrum Two N) Part Number (L160000A). From PerkinElmer company, with specifications value Dimensions 450 × 300 × 210 mm (W × D × H), Weight Approximately 13 kg, Power input 100–230 V, 50/60 Hz, Max 65 VA, Laser Class 1, Detector $LiTaO_3$, operating temperature range 5 °C to 45 °C, Storage temperature range −20 °C to 60 °C, Maximum relative humidity 80% (non-condensing) with CaF_2 windows, optical system collect data over a total range of 8,300 to 350 cm^{-1}. The instrument is connected to a PC, via a wireless network using the optional wireless router. a computer supported by

the identification and spectroscopy application to follow the spectra of black seeds [26].

Figure (3-2) FTIR Spectrometer (Spectrum Two N).

Libs method analyzer device

LIBS instrumentation

An optical system was formed so that the external lights do not affect the plasma and obtain a light overlay. The setup of the LIBS experiment shown in Figure consisted below:

Figure (3-3) Optical System for Libs.

3.3 The experimental part for analysis by FTIR spectroscopy

3.3.1 Samples Preparation

Samples were purchased from N. sativa seeds. From the local markets, the 2019 crop. Different humidity values were specified. By soaking in water of different humidity and temperatures with a device (BENETECH GM 1363B - humidity and Temperature Meter) the digestion and milling and emulsifying process was carried out, and samples were prepared by Fourier spectroscopy method and grinding of the black seed after being exposed to the temperature and humidity required to reduce the size of the particles to less than 5 mm, which is the diameter. Otherwise, the larger particles will scatter the infrared beam and cause a fundamental gradient of the spectrum [27].

Nine samples of the Nigella-sativa were prepared so that in each sample there would be 5 grams of the Nigella-sativa and soaked it to 26.2% humidity, then exposed to heat at (100 degrees Celsius) for a period of 5 minutes, then a 5 gram sample of the Nigella-sativa was soaked to a humidity of 26.2% then exposed to heat at (100 degree) for a period of 10 minutes, then sample 5 grams of Nigella-sativa and soak it at 26.2% humidity, then expose it to heat at (100 degree) for a period of 15 minutes and repeat this process for three more samples at 30% humidity in different time, and for three other samples at 41.5% in different time.

Then they were crushed and squeezed to get their food juice in the form of an emulsifier, then the material was transferred to an oven at a temperature of 100 degrees to see the effect of the temperature at different times of 5, 10 and 15 degrees. Celsius. The sample was crushed and ground to a fine powder

until it crystallized and was invisible and became somewhat "mushy" and adhered to the mortar (the mixture was close to the consistency of toothpaste). The mixture was then transferred to the moor panels and the panels were pressed together to adjust the thickness of the sample between the infrared transmission windows. Then it was inserted into the infrared beam path and the spectrum was turned on. Results were recorded after 5, 10 and 15 minutes with different humidity values (26.2%, 30%, 41.5%).

3.3.2 The Experimental Setup

At first, visible and ultraviolet rays were used to determine the expected values of sample components according to previous studies using the LAMBDA 365 UV / Vis spectrometer. Wavelength: 572 nm; Measurement Mode: Absorbance; Cell 10 mm from PerkinElmer.

From the results obtained from the above device, the device used the FT-NIR spectrometer for research use only (Spectrum Two N) Part Number (L160000A). The instrument is connected to a PC, via a wireless network using the optional wireless router. [22].

FTIR spectroscopy is a major step forward over the traditional dispersive infrared approach for a number of reasons, including the fact that the entire FTIR spectrum is collected in a fraction of a second and the spectra are summed to signal light. FTIR-spectroscopy (FTIR) is a methodical analogue that measures the size of the molecular structure of the molecule. FTIR spectroscopy is a case in point that can be used as an infrared and modular energy module. Infrared light is absorbed at certain frequencies associated with the vibration-binding energies of the functional groups in the molecule. A characteristic pattern of the bands, the molecule vibration spectrum, is

formed. The location and intensity of these spectral bands give the impression of a molecular structure, making FTIR spectroscopy a highly adaptable and useful technique [23].

The Fourier Spectrometer simultaneously collects spectral high-resolution data over a wide spectral range. This provides a major advantage over a spectrophotometer, which measures intensity over a narrow range of wavelengths simultaneously [25].

The samples were prepared with the known scientific image in such cases by taking three samples and exposing them to different humidity and temperature and taking the measurement results every five minutes up to 15 minutes according to table (3.1).

Table (3.1) Sample results at different humidity, temperatures and times

sample	humidity	temperature	sample name	time	search best hit description	search best hit
S1	26.2%	100°C	S1.1	5min	methyl linoleate natural	F62290
			S1.2	10 min	methyl linoleate natural	F62290
			S1.3	15min	methyl linoleate natural	F62290
S2	30%	100°C	S2.1	5min	methyl linoleate natural	F62290
			S2.2	10 min	methyl linoleate natural	F62290

			S2.3	15min	methyl linoleate natural	F62290
S3	41.5%	100°C	S3.1	5min	methyl linoleate natural	F62290
			S3.2	10 min	methyl linoleate natural	F62290
			S3.3	15min	methyl linoleate natural	F62290

3.3.3 The Experimental Procedure

A pressurized pellet technique was used for sample preparation in which a small amount of the ground black seed sample was closely mixed. Grind and grind into a fine powder until crystallized It can no longer be seen and becomes somewhat "doughy" and adheres to mortar (mixture approximates the consistency of a toothpaste).

This finely ground mixture was then pressed under very high pressure into a vacuum mold or small press to form small pellets (about 1-2 mm in thickness and 10 mm in diameter). This results in granules that are transparent to the infrared radiation and operate in this manner [25].

The mixture is then transferred to the mull plates & the plates are squeezed together to adjust the thickness of the sample between IR transmitting windows. This is then mounted in a path of IR beam and the spectrum is run. Then the mixture was inserted between the two screws and the upper screw A was joined until the powder was pressed onto a thin disc, after pressing the sample screws A & A1 were removed and a steel cylinder with granules

inside was placed in the path of the infrared beam and the granule. Then I repeated the above steps to other samples of different time to show what happen in the sample [25,11].

3.4 The experimental part for analysis study of plasma parameters of Calcium ion in Nigella sativa by laser induced breakdown spectroscopy (LIBS)

3.4.1 Samples preparations:

Samples were purchased from seeds of N. sativa. From the local market, the 2019 harvest. The black seed is a small pill that contains fatty compounds surrounded by scales when exposed to direct plasma impulses that lead to burning it and not benefiting from the nutrients it contains [26].

Nine samples of the Nigella-sativa were prepared so that in each sample there would be 5 grams of the Nigella-sativa and soaked it to 26.2% humidity, then exposed to heat at (100 degrees Celsius) for a period of 5 minutes, then a 5 gram sample of the Nigella-sativa was soaked to a humidity of 26.2% then exposed to heat at (100 degree) for a period of 10 minutes, then sample 5 grams of Nigella-sativa and soak it at 26.2% humidity, then expose it to heat at (100 degree) for a period of 15 minutes and repeat this process for three more samples at 30% humidity in different time, and for three other samples at 41.5% in different time.

Then they were crushed and squeezed to get their food juice in the form of an emulsifier, then the material was transferred to an oven at a temperature of 100 degrees to see the effect of the temperature at different times of 5, 10 and 15 degrees. Celsius. The sample was crushed and ground to a fine powder until it crystallized and was invisible and became somewhat "mushy" and

adhered to the mortar (the mixture was close to the consistency of toothpaste). The mixture was then transferred to the moor panels and the panels were pressed together to adjust the thickness of the sample between the infrared transmission windows. Then it was inserted into the infrared beam path and the spectrum was turned on. Results were recorded after 5, 10 and 15 minutes with different humidity values (26.2%, 30%, 41.5%).

We used of a device (BENETECH GM 1363B - hygrometer and temperature) to measure humidity and temperature. after that

it was crushed and squeezed to get its nutritional juice as an emulsifier, then was squeezed and squeezed with constant pressure of 400 kg / cm so that the oily substance and nutritional value does not come out, and also density of the material affects the LIBS signal. then was converted into a circular disc containing black and white dots. After that, the material was transferred to a furnace at a temperature of 100 degrees to see the effect of the temperature at different times 5, 10 and 15 degrees Celsius.

This process was repeated to prepare samples at different temperature of corresponding humidity and time.

3.4.2 The Experimental Setup

LIBS instrumentation:

An optical system was formed so that the external lights do not affect the plasma and obtain a light overlay. The setup of the LIBS experiment shown in Figure 3.4 consisted of:

Laser:

neodymium-doped yttrium aluminum garnet (Nd:YAG) Laser with a wavelength of 1064 nm has pulse energy 120 mJ a pulse width of 10 nanoseconds and a frequency of 10 Hz was used.

Focusing, Collection and Spectrometer system:

A LIBS 2000+ peripheral optical spectrometer equipped with a CCD detector, a bundle of optical fibers, a lens, a translation stage and a computer was used. The laser light is focused by a compact lens with a focal length of 10 cm and is located 5 cm from the surface of the sample [6]. The experiments were performed under normal air pressure and room temperature. Light is collected from the fine plasma by an optical fiber, which is positioned at an angle of 45 degrees to the laser beam. The other end of the optical fiber is connected to a LIBS 2000 + 0.1 nm spectrometer. Then the spectral signal is stored on a computer and analyzed with the ThorLabs.

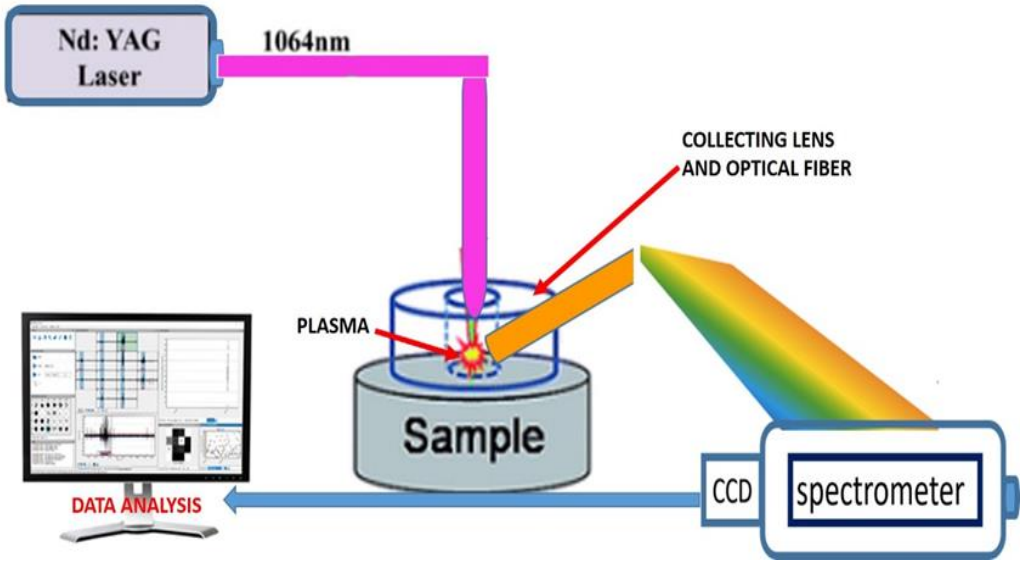

Figure 3.4 Experimental Setup of LIBS.

3.4.3 The Experimental Procedure

After the samples were prepared using pressurized pellet technology and exposing them to the required humidity and temperature (sample preparation

method above), the sample was transferred to the system after placing a name on each sample that was exposed to the laser beam from the plasma generator and it is one 5 cm away from it and the time of each pulse was 10 nanoseconds. At a frequency of 10 Hz, the pulse energy was 120 mJ, the detector was gated in synchronization with the laser pulse. then the data was collected and transferred to the computer through a USB connection using an application from ThorLabs OSA. Then the steps mentioned above were repeated for other samples of different times to show what is happening in the sample [26].

CHAPTER FOUR

Result and Discussion

CHAPTER FOUR

Results and Discussion

4.1 Introduction

In this chapter, the results of practical and related aspects of the results of spectroscopic analyzes using FTIR spectroscopy of black seed were recorded to study the effect of temperature and humidity, as well as the results of the study of Analysis of calcium ionic plasma parameters in black seed by means of laser-induced breakdown spectroscopy (LIBS). These results were discussed and compared to previous studies by each method, so that we followed the FTIR results to discover the changes that occur in the bonds and the chemical composition structure of the black seed, and then we followed the results. laser-induced breakdown spectroscopy (LIBS) to find out the density of calcium ions in black seed.

4.2 The results of spectroscopic analyses of Nigella sativa to study the temperature and humidity effect using FTIR spectroscopy.

Tables (4-1 to 4-6) show the results of different values of the effect of temperature and humidity on samples using FTIR spectroscopy. Figures (4-1 to 4-24) list the results of the search for the compounds included in the composition of the samples after the influence of temperature and humidity on them.

Results of black seed samples after the influence of different values of temperature and humidity:

Table (4-1) The analyzed data of sample S1, at 26.2% and 100º C

sample	humidity	temperature	sample name	time	search best hit description	Search Best Hit
S1	26.2%	100 °C	S1.1	5min	methyl linoleate natural	F62290
			S1.2	10 min	methyl linoleate natural	F62290
			S1.3	15min	methyl linoleate natural	F62290

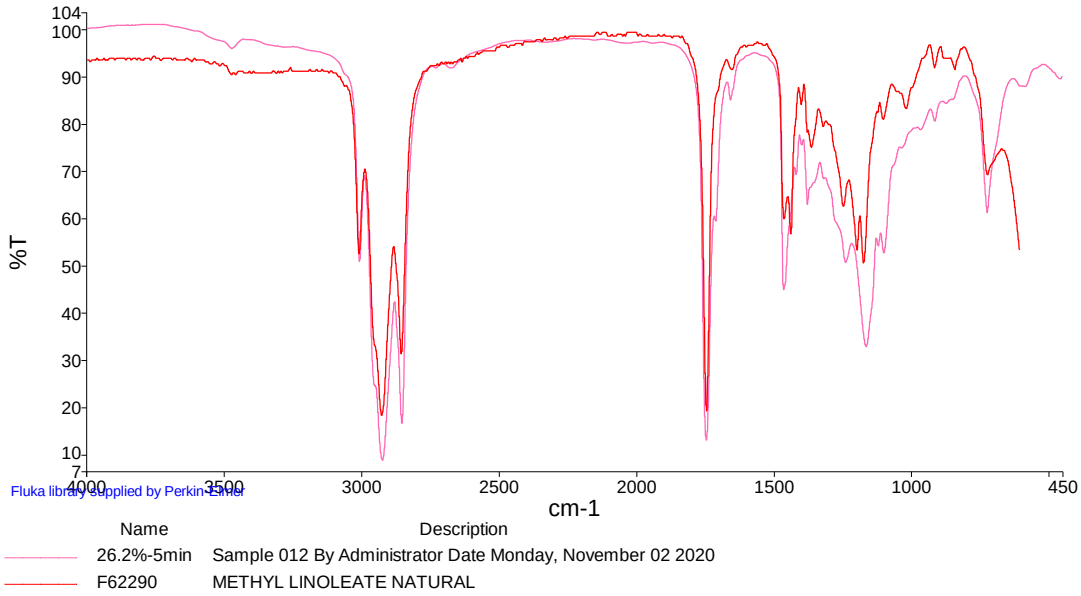

Figure (4-1) FTIR spectrum of sample (S1) at 26.2% -5min compare with Fluka library.

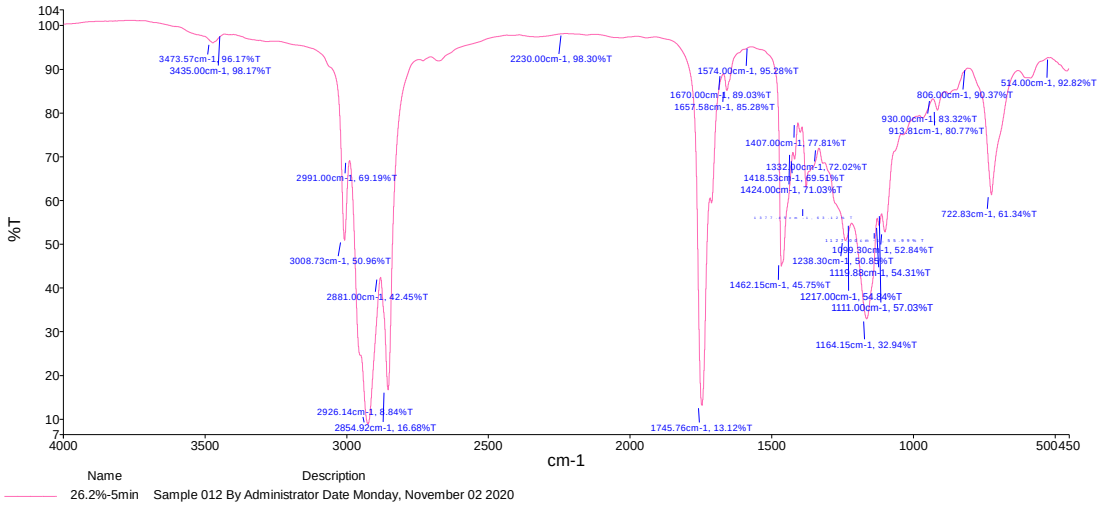

Figure (4-2) FTIR spectrum of sample (S1) at 26.2% -5min with peaks by Fluka library.

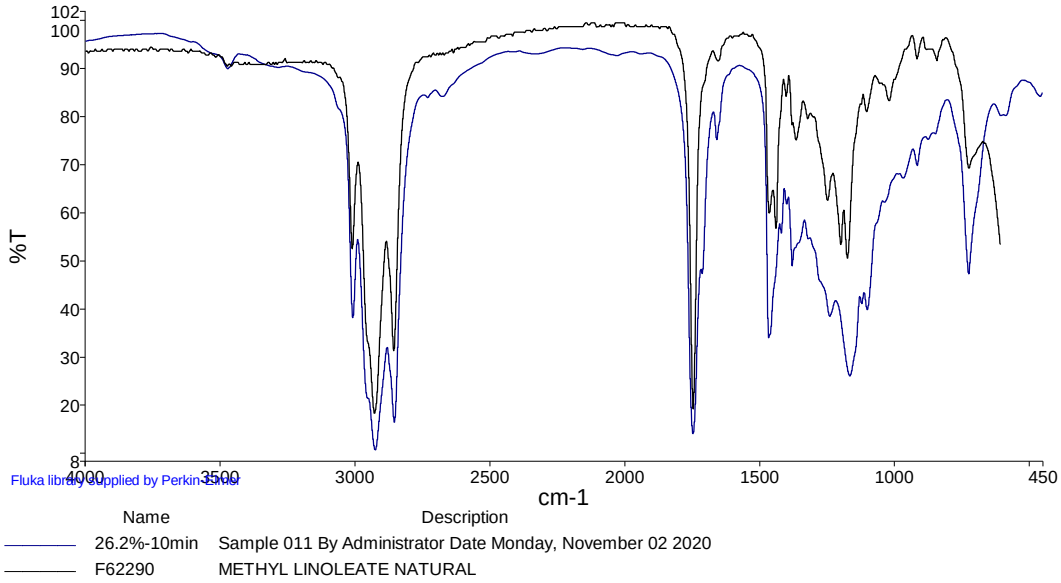

Figure (4-3) FTIR spectrum of sample (S1) at 26.2% -10 min compare with Fluka library.

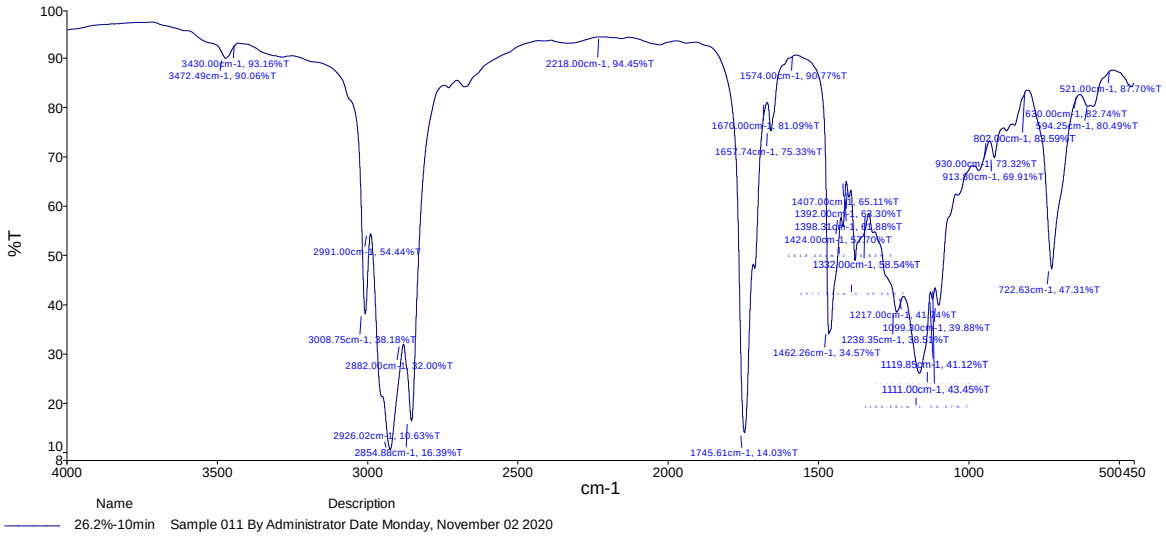

Figure (4-4) FTIR spectrum of sample (S1) at 26.2% -10 min with peaks by Fluka library.

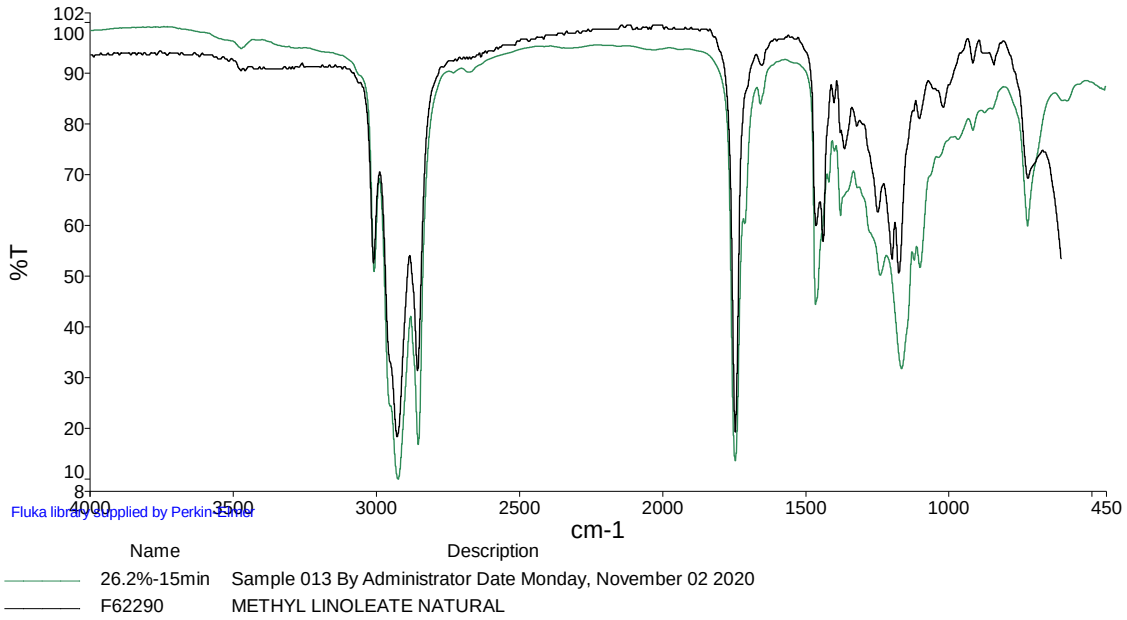

Figure (4-5) FTIR spectrum of sample (S1) at 26.2% -15 min compare with Fluka library.

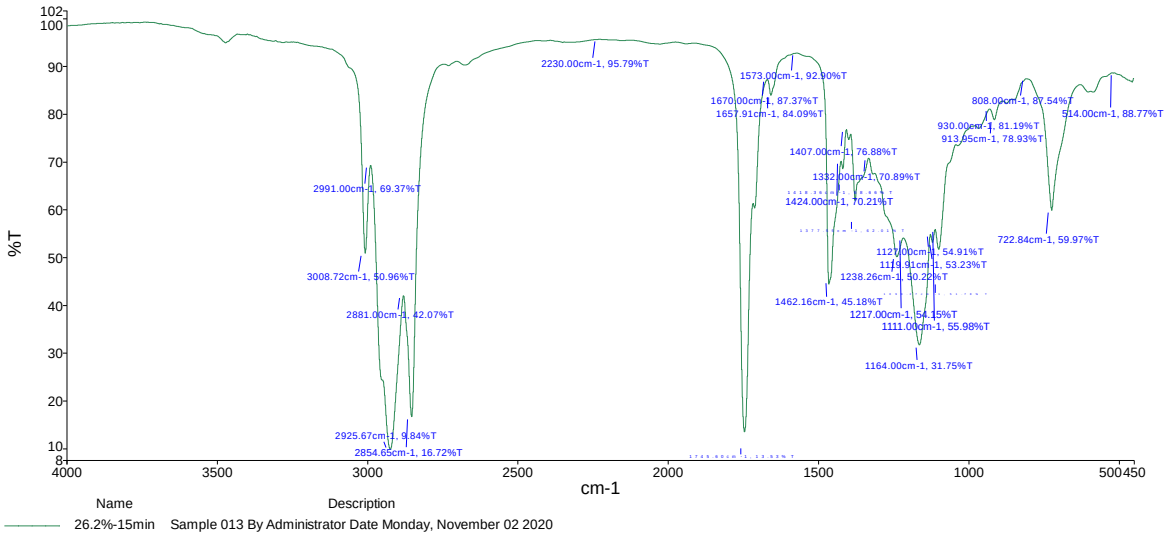

Figure (4-6) FTIR spectrum of sample (S1) at 26.2% -15 min with peaks by Fluka library.

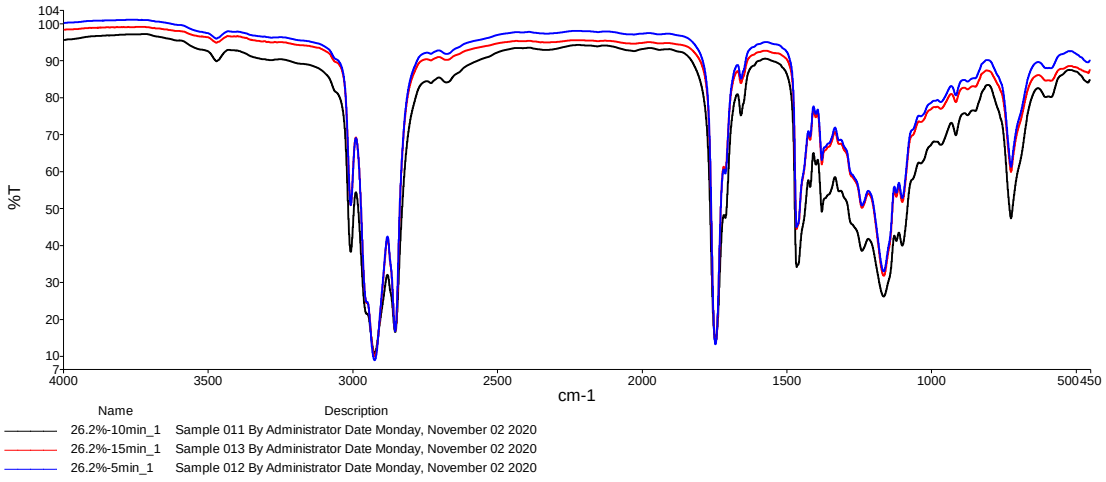

Figure (4-7) FTIR spectrum of sampled (S1) compare in different time.

Table (4-2) List of Searched Library References of sample S1, at 26% and different time.

	search reference spectrum description	search score in 5min	search score in 10 min	search score in 15 min
1	cis-androsterone	0.629926	0.608116	0.628518
2	(+)-camphor-10-sulfonyl chloride	0.685122	0.641309	0.689136
3	bis(2-ethylhexyl) sebacate	0.749377	0.675344	0.748268
4	dimethyl azelate 90-95%	0.794502	0.744857	0.792787
5	ethyl linoleate	0.826481	0.787519	0.825535
6	ethyl myristate	0.83096	0.738249	0.828048
7	ethyl palmitate	0.869538	0.775036	0.866414
8	butyl stearate	0.877618	0.783842	0.875753
9	methyl elaidate gc reference	0.901784	0.833905	0.900066
10	methyl linoleate natural	0.937858	0.906069	0.93753

Table (4-3) The analyzed data of sample S2, at 30% and 100 º C

sample	humidity	temperature	sample name	time	search best hit description	search best Hit
S2	30%	100 °C	S2.1	5min	methyl linoleate natural	F62290
			S2.2	10 min	methyl linoleate natural	F62290
			S2.3	15min	methyl linoleate natural	F62290

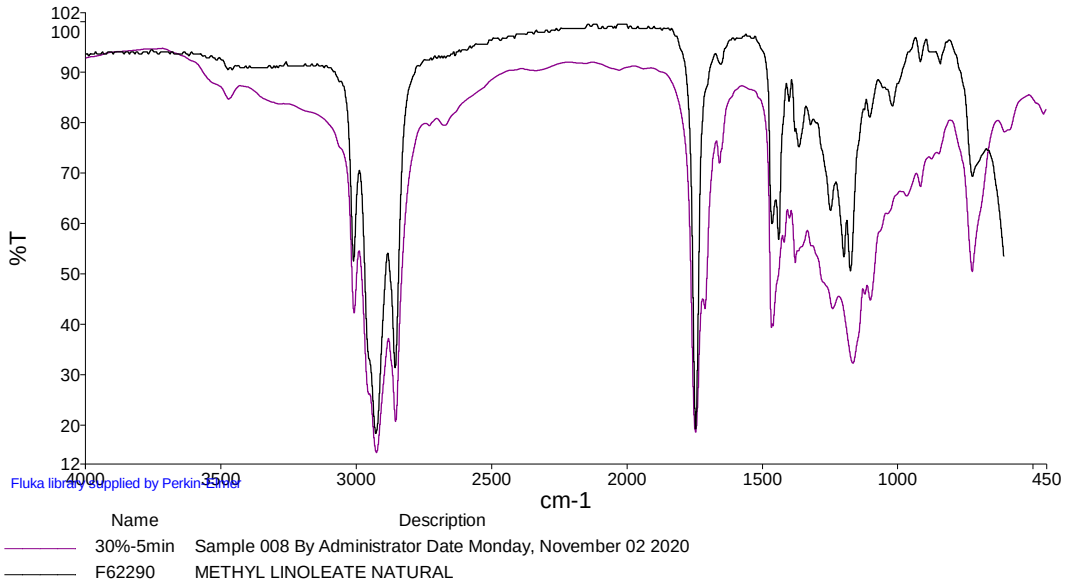

Figure (4-8) FTIR spectrum of sample (S2) at 30% -5min compare with Fluka library.

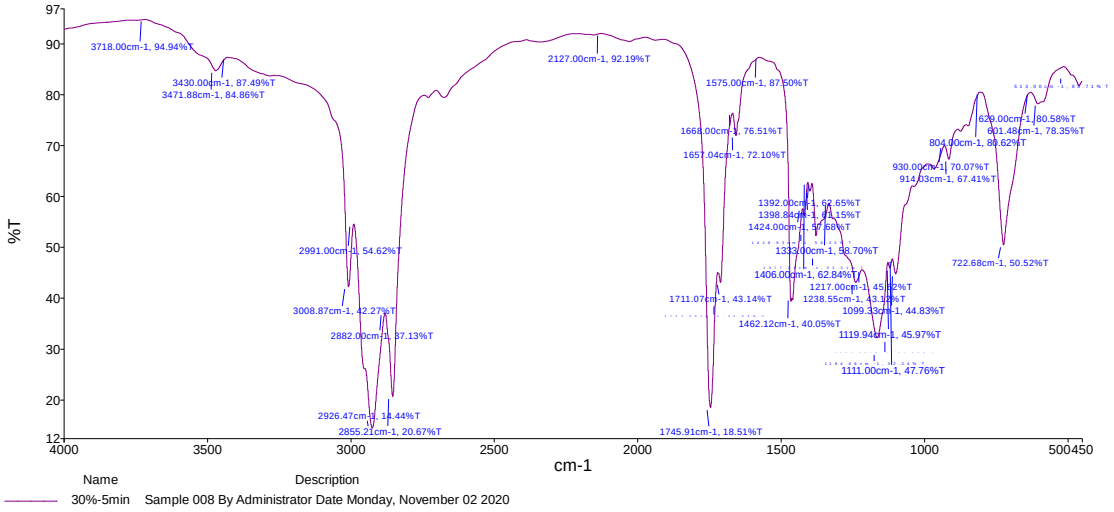

Figure (4-9) FTIR spectrum of sample (S2) at 30% -5 min compare with peaks by Fluka library.

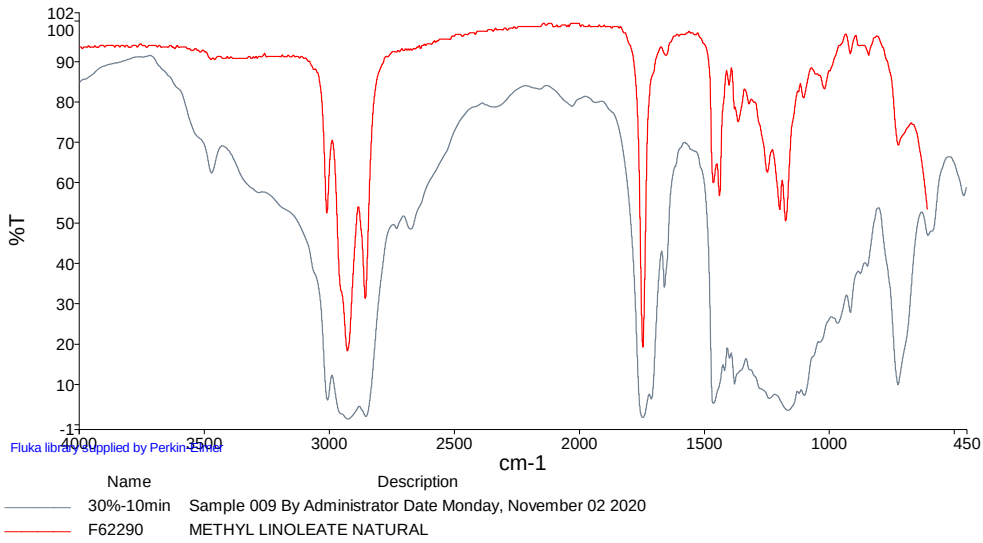

Figure (4-10) FTIR spectrum of sample (S2) at 30% -10 min compare with Fluka library.

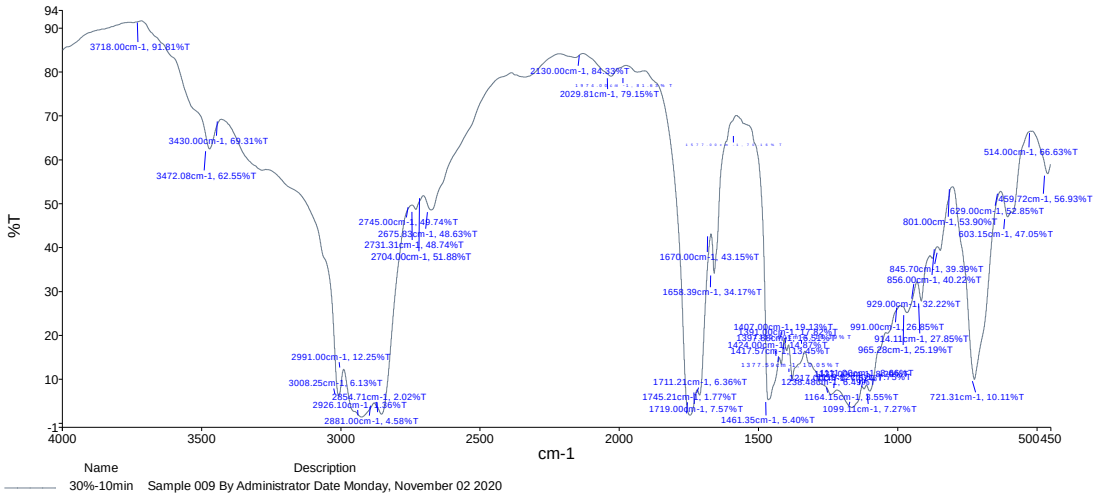

Figure (4-11) FTIR spectrum of sample (S2) at 30% -10 min compare with peaks by Fluka library.

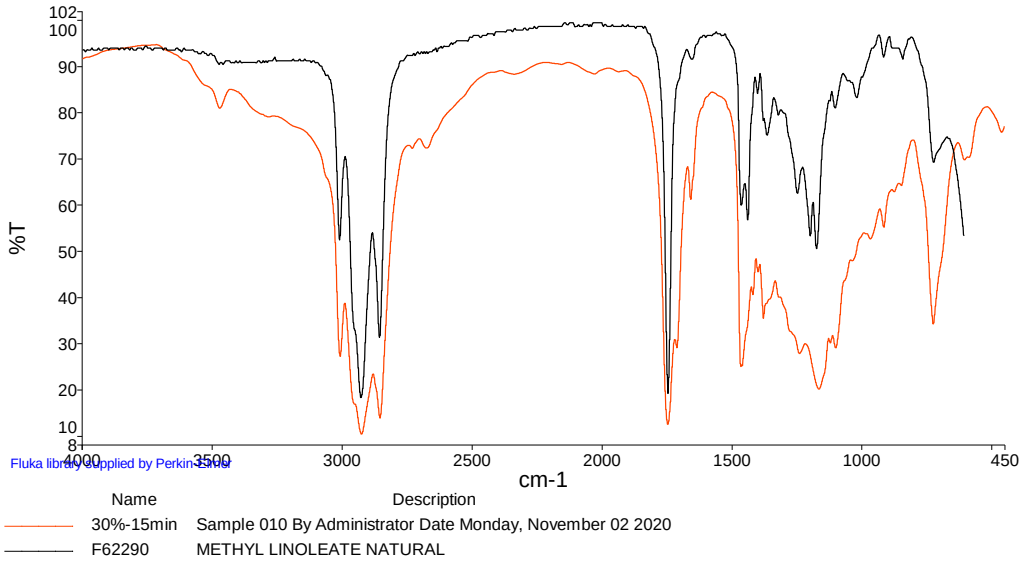

Figure (4-12) FTIR spectrum of sample (S2) at 30% -15 min compare with Fluka library.

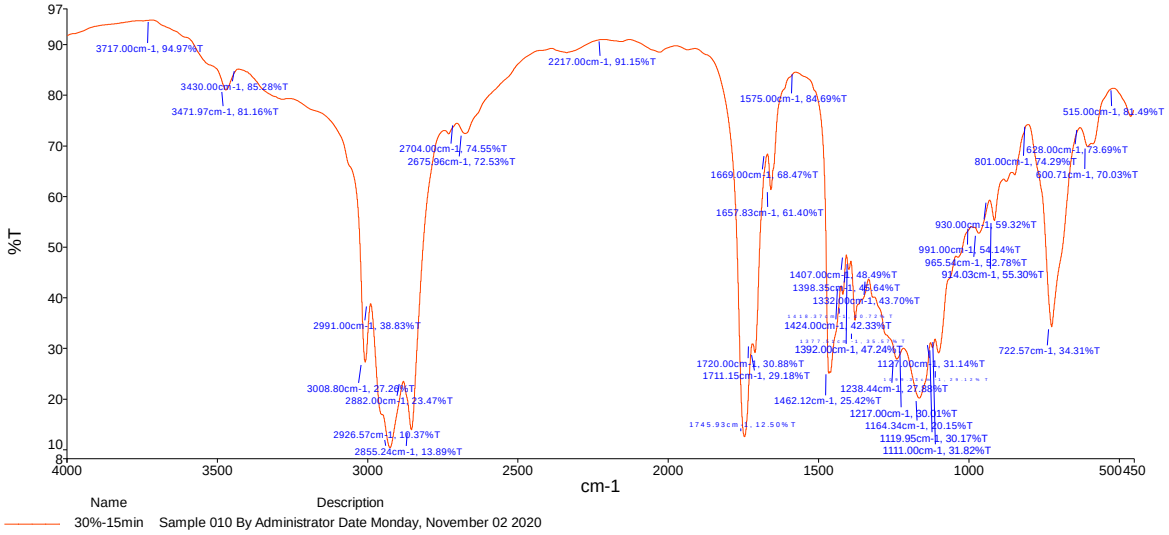

Figure (4-13) FTIR spectrum of sample (S2) at 30% -15 min compare with peaks by Fluka library.

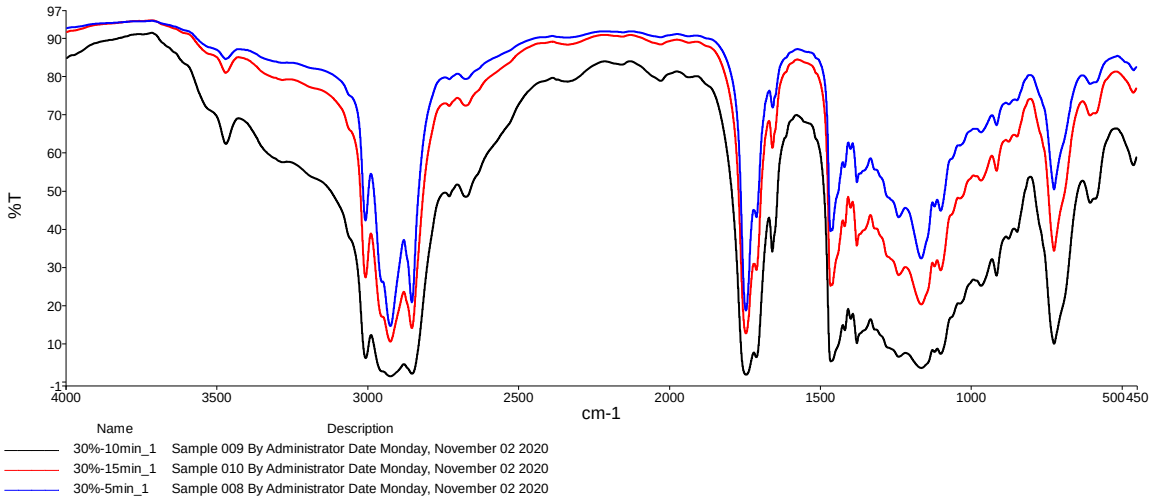

Figure (4-14) FTIR spectrum of sampled (S2) compare in different time.

Table (4-4) List of Searched Library References of sample S2, at 30% and different time.

	search reference spectrum description	search score in 5min	search score in 10 min	search score in 15 min
1	bis(1-butyphentyl) adipate	0.640684-2 cis-androsterone	0.67447	0.560167
2	(+)-camphor-10-sulfonyl chloride	0.625926	0.721536 methyl n-valerate	0.564359
3	bis(2-ethylhexyl) sebacate	0.661766	0.716513	0.575813
4	ethyl myristate	0.738957	0.679279	0.614808
5	ethyl palmitate	0.80428	0.668349	0.640955

6	dimethyl azelate 90-95%	0.73261	0.733814	0.648429
7	butyl stearate	0.809522	0.675055	0.650169
8	ethyl linoleate	0.772048	0.797126	0.718366
9	methyl elaidate gc reference	0.838258	0.716571	0.719914
10	methyl linoleate natural	0.91403 -	0.845012	0.816062

Table (4-5) The analyzed data of sample S3, at 41.5% and 100 º C

sample	humidity	temperature	sample name	time	search best hit description	search best Hit
S3	41.5%	100 °C	S3.1	5min	methyl linoleate natural	F62290
			S3.2	10min	methyl linoleate natural	F62290
			S3.3	15min	methyl linoleate natural	F62290

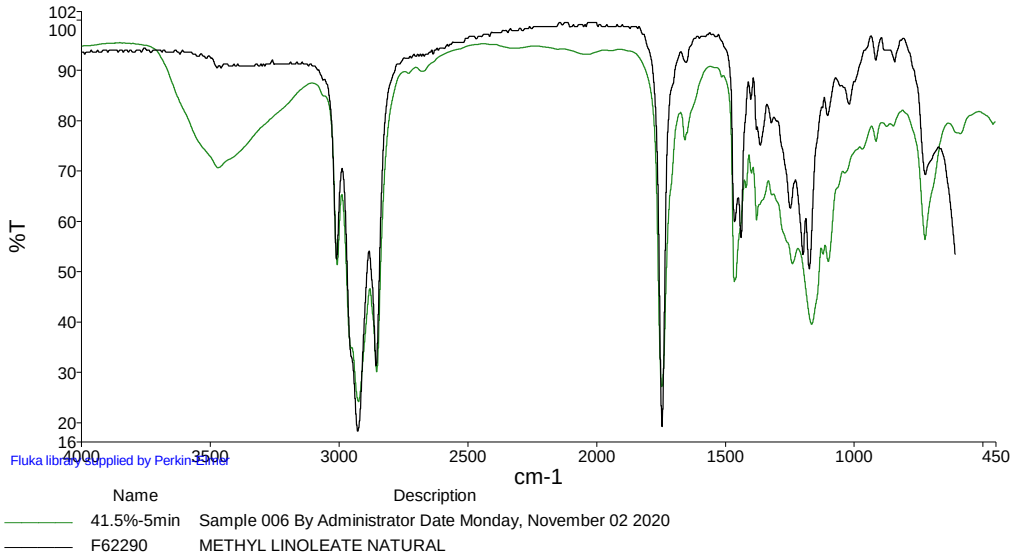

Figure (4-15) FTIR spectrum of sample (S3) at 41.5% -5min compare with Fluka library.

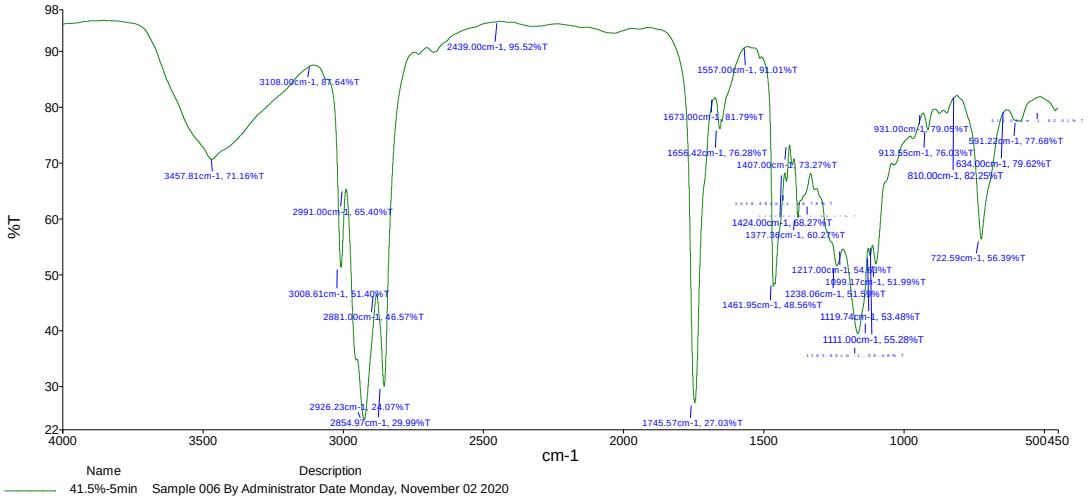

Figure (4-16) FTIR spectrum of sample (S3) at 41.5% -5min with peaks by Fluka library.

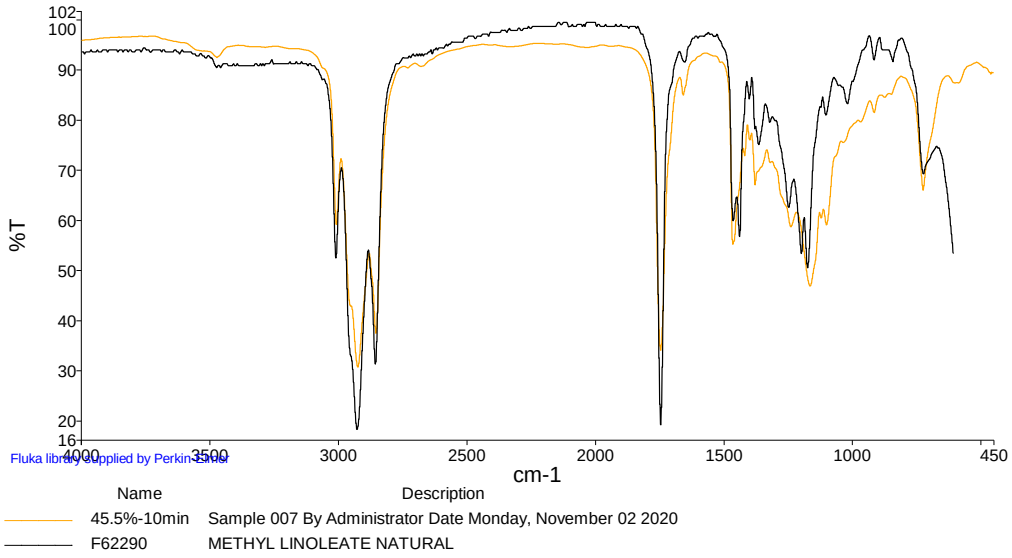

Figure (4-17) FTIR spectrum of sample (S3) at 41.5% -10 min compare with Fluka library.

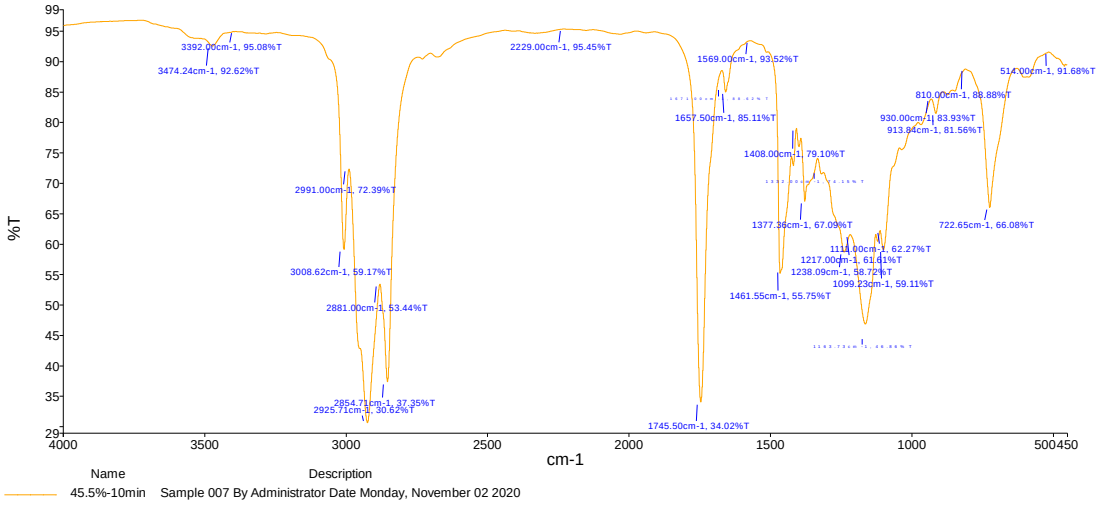

Figure (4-18) FTIR spectrum of sample (S3) at 41.5% -10 min with peaks by Fluka library.

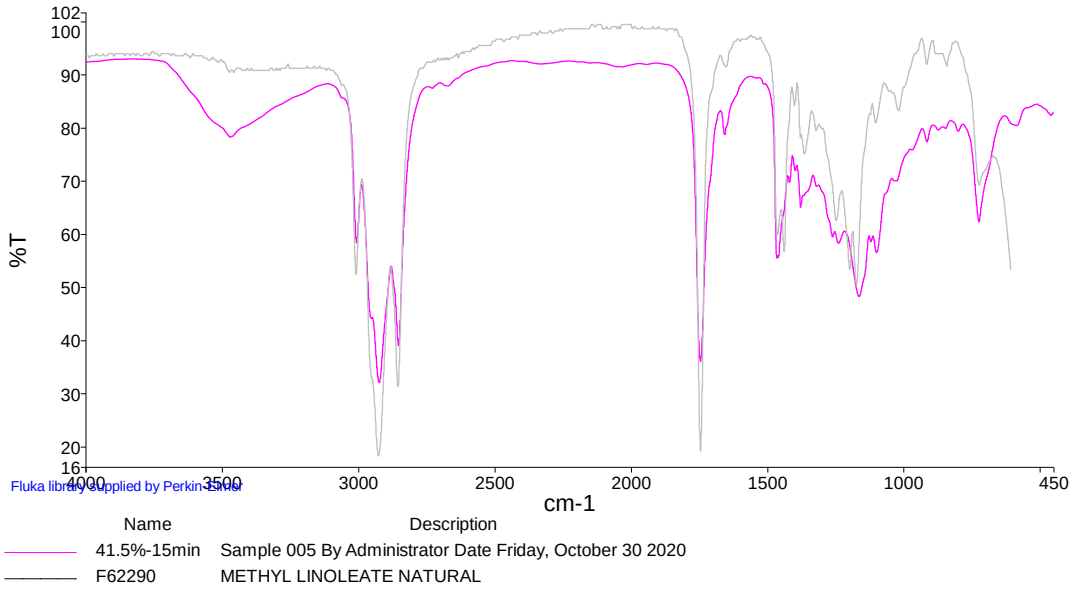

Figure (4-19) FTIR spectrum of sample (S3) at 41.5% -15 min compare with Fluka library.

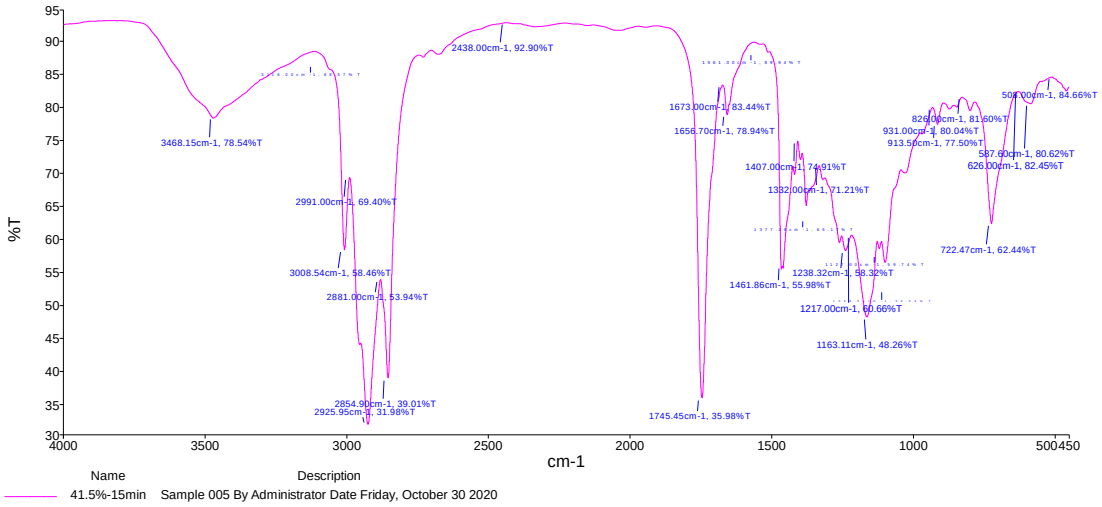

Figure (4-20) FTIR spectrum of sample (S3) at 41.5% -15 min with peaks by Fluka library.

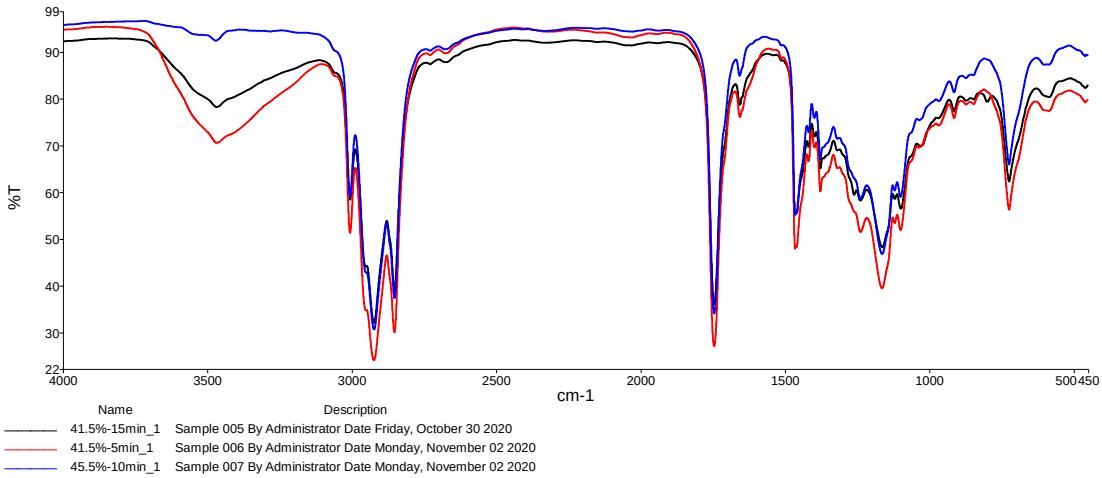

Figure (4-21) FTIR spectrum of samples (S3) compare in different time.

Table (4-6) List of Searched Library References of sample S3, at 41.5% and different time.

	search reference spectrum description	search score in 5min	search score in 10 min	search score in 15 min
1	cis-androsterone	0.641572-2 (+)-camphor-10-sulfonyl chloride	0.67447	0.637778
2	trichloroacetic acid	0.641543-1	0.641543 methyl n-valerate	0.64012
3	bis(2-ethylhexyl) sebacate	0.679553- 3	0.716513	0.670307

4	ethyl myristate	0.743258- 5	0.679279	0.738888
5	dimethyl azelate 90-95%	0.739748- 4	0.668349	0.739884
6	ethyl linoleate	0.796065- 6	0.733814	0.791
7	ethyl palmitate	0.800857- 8	0.675055	0.80035
8	butyl stearate	0.800521-7	0.797126	0.804161
9	methyl elaidate gc reference	0.845138-9	0.716571	0.838327
10	methyl linoleate natural	0.92406-10	0.845012	0.92344

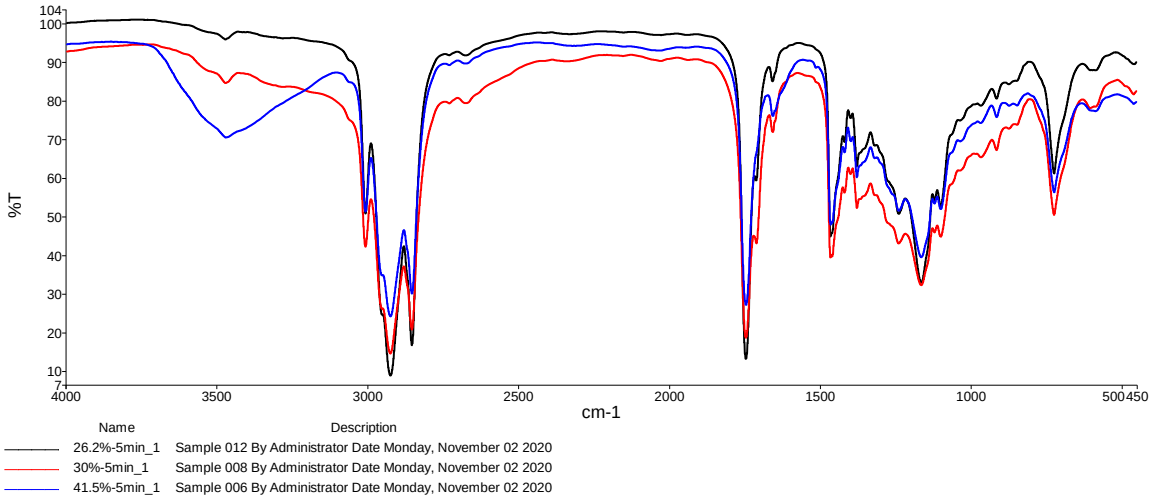

Figure (4-22) FTIR spectrum of samples compare with different humidity in 5 min.

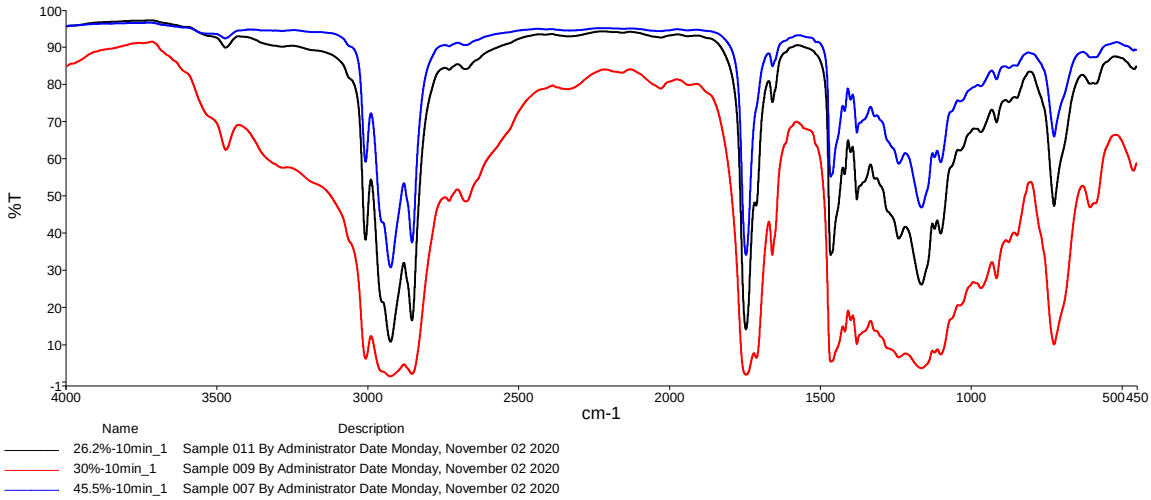

Figure (4-23) FTIR spectrum of samples compare with different humidity in 10 min.

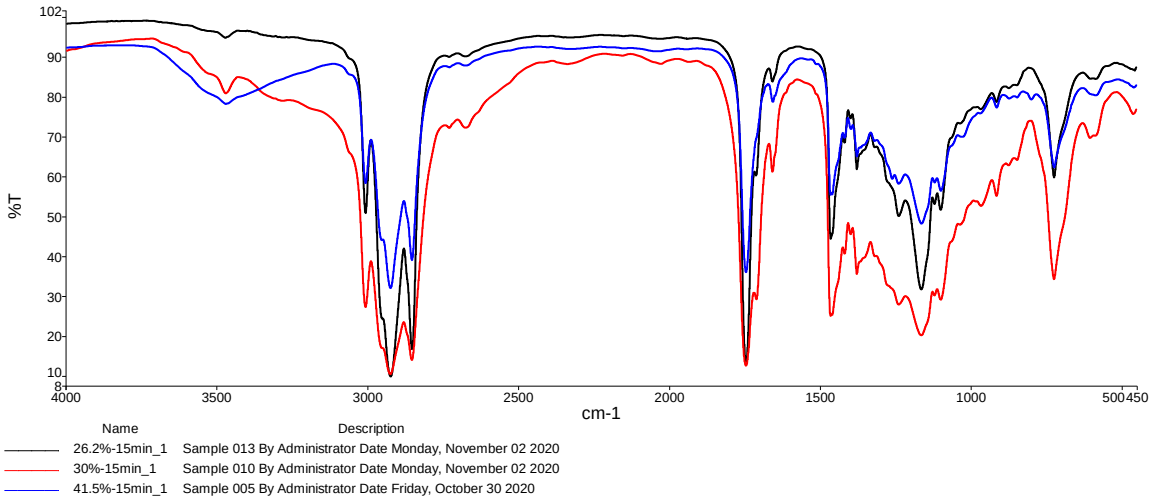

Figure (4-24) FTIR spectrum of samples compare with different humidity in 15 min.

the results of FTIR spectra have assigned the existence of a variety of sharp, strong, and weak peaks as well as crucial functional groups that correspond to C-H, -CH2, -CH3, C=O, C-O, N-H, -COOH , O-H and C=C, suggesting the presence of methyl linoleate natural and laurolactam. the major reference

spectrum description search at compounds the bottom of the tables (see Figure (4-2, 4- 4, 4- 6) after effect of humidity and temperature factor. These functional groups with their rotation and molecular movements and despite being affected by the factors of moisture and heat confirms that the black seed as a natural product was not affected by its components and natural elements according to previous studies. To the best of our knowledge, a weak absorption peak at 2991 cm^{-1} shown in the FTIR spectrum (see Figure 4-6, 4-13, 4-20) can be corresponded to the C-H stretching of the methyl group. Moreover, the two intense bands observed at 2926 cm^{-1} and 3008 cm^{-1} (see Figure (4-9,4-11,4-13) can be assigned to the C-H stretching of an aliphatic group, Meanwhile, in (Figures 4-4, 4-11, 4-18) another important strong band is observed at 1745 cm^{-1} and 1657 cm^{-1}, which can be attributed to the C=O stretching of the forester and ketone groups, respectively.

In addition, (see Figure 16-18-20) a further remarkable absorption band was observed at 1500 cm^{-1} belonging to the C=O stretching of because of the appearance of N-H in 3473 cm^{-1} the resonance frequency effect of the carbonyl group. The two peaks at 1500 and 1700 cm^{-1} can be related to N-H absorption scissoring and methyl rock in 2960 cm^{-1}, respectively. In the end, a weak peak at 1332 cm^{-1} owing to the C-N group and a band.

All these results are very similar to those in the literature [12]. These results refer to the fact that humidity and heat factor do not affect much in changing and determining the structure of organic black seeds. Therefore, the pharaohs used them in embalming materials. We also conclude that this material can preserve its properties under changing weather conditions.

* To other side compare the results of the experiment, it is necessary to note the changes that appeared at the same time and at the same degree of

humidity, then move to compare between different times and with the same humidity, so through Figures (4-2,4-9,4-6) and (4-4,4-18,4-13) and (4-16,4-18,4-20) through the tables (4-3,4-5,4-7) which shows a clear comparison between the peaks at the same time (4-5,4-10,4-15 min) that change the result in tables (4-3,4-5,4-7).

For example, at the peak of 2991, we found that the absorption intensity was very close, with an average of (69.19, 54.62, 65.4) = 63.07 at the same time.

* We note the difference in the peaks at a rate of (0.1 to 1.5) with an average absorption of approximately 53.4

For example, at the peak of (3008.73 cm^{-1} ,3008.87 cm^{-1} ,3008.61cm^{-1}), we found that the absorption intensity was very close, with an average of (50.96, 42.27, 51.4) = 48.21

This is another indication that the black seed is not affected by humidity and heat.

4.3 Results of plasma parameters of Calcium ion in Nigella sativa by laser induced breakdown spectroscopy (LIBS)

4.3.1 Spectral Analysis

The LIBS spectrum consists of spectral lines that provide information about the components of the sample. A typical laser-induced plasma spectrum was generated by 10 ns laser pulses focused at 1064 nm with an energy of 120 mJ, and the laser shots were assembled on an ICCD array.

The spectral range of the emission lines of calcium (Ca), iron (Fe), sulfur (S) and potassium (K) from 393 to 660 nm was shown using the black seed sample. In this spectral range it is possible to observe the emission of calcium ion lines (Ca II) at 393.49 nm and 396.97 nm, the lines of (Ca I) at 422.85

and 649.72 nm elements, as well as their spectral parameters are taken from the NIST - Database extracted [9,11] are given in Table -1. The high density of calcium lines was observed in comparison to the remaining elements, which confirms the richness of the elements black seeds in this element, see Figures (4-1 - 4-9).

Table (4-7) Spectroscopic data used for the determination of the plasma temperature

no	elements	wavelength (nm)	intensity (au)	relative intensity	A_{ki} X 10^8 s	g	E_u *e.V*
1	Ca II	393.47	0.38401	1	1.35	4	3.15
2	Ca I	422.85	0.2744	0.549206413	2.2	3	2.9
3	K II	430.38	0.072216	0.166391129	0.013	5	20
4	S I	551.07	0.11842	0.35776435	0.73	2	15.8
5	Na II	445.58	0.12363	0.247443108	0.0281	4	3.8

Tables (4-8 to 4-16) show the results of different values of the effect of temperature and humidity on samples using libs spectroscopy. Figures (4-25 to 4-32) list the results of the search for the element included in the composition of the samples after the influence of temperature and humidity on them.

Table (4-8) The analyzed data of sample S1, at 26.2% and 100º C

Sample S1 at 5 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.38401	Ca II
2	396.97	0.31483	Ca II
3	422.85	0.22164	Ca I
4	430.38	0.072216	K II
5	443.59	0.087064	Ca I
6	445.58	0.10361	Na II
7	504.35	0.067689	Si II
8	526.98	0.07969	Ca I
9	558.95	0.089439	Ca I
10	589.15	0.17838	Na I
11	612.46	0.08906	Ca I
12	616.49	0.11646	Ca I
13	644.22	0.077131	Ca I
14	646.56	0.068338	Ca I

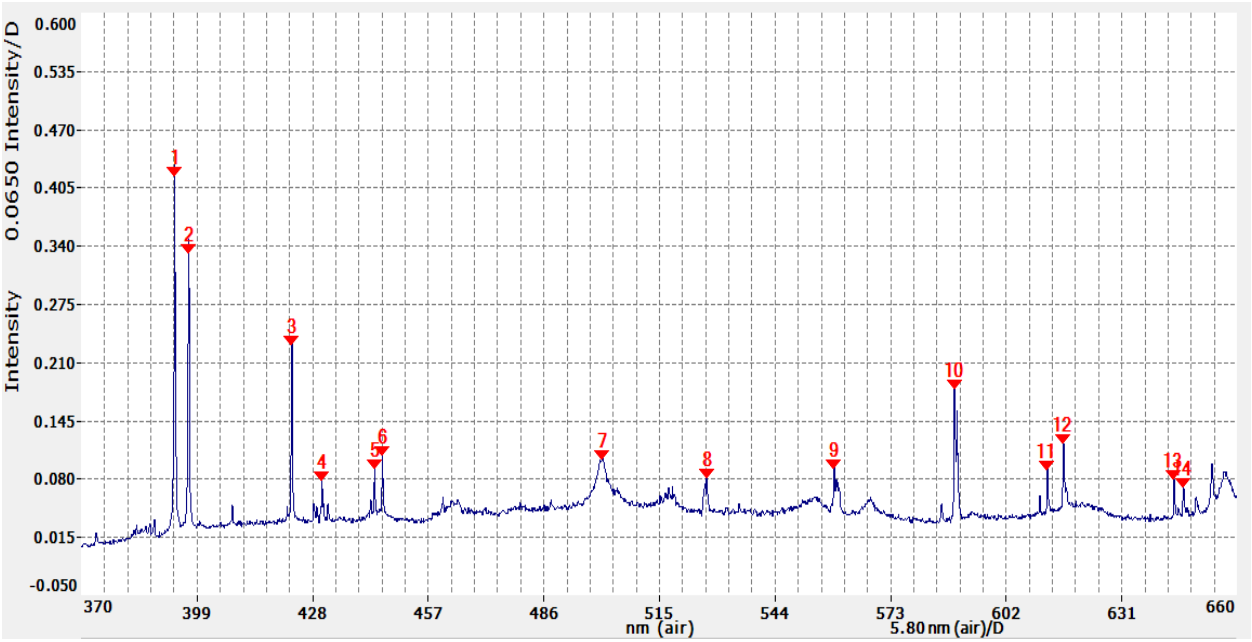

Figure (4-25) LIBS spectrum of sample (S1) at 26.2% -5min.

Table (4-9) The analyzed data of sample S1, at 26.2% and 100º C

Sample S1 at 10 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.5066	Ca II
2	396.97	0.40996	Ca II
3	422.86	0.27583	Ca I
4	445.58	0.17296	Na II
5	509.51	0.0955	K I
6	526.99	0.12954	Ca I
7	558.97	0.14502	Ca I
8	589.15	0.14287	Na I
9	616.5	0.18483	Ca I

10	644.22	0.11951	Ca I
11	646.56	0.068338	Ca I
12	649.73	0.098941	Ca I

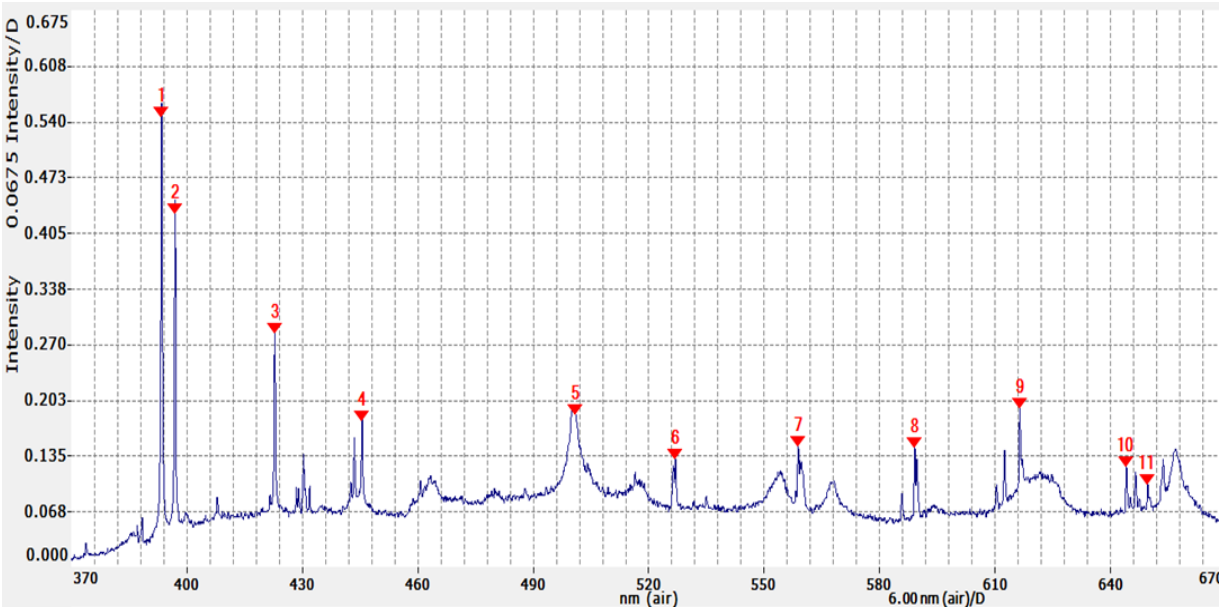

Figure (4-26) libs spectrum of sample (S1) at 26.2% -10 min.

Table (4-10) The analyzed data of sample S1, at 26.2% and 100º C

Sample S1 at 15 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.49	0.35004	Ca II
2	396.97	0.2772	Ca II
3	422.85	0.21531	Ca I
4	430.38	0.067612	K II
5	445.57	0.087933	Na II

6	526.99	0.068482	Ca I
7	589.14	0.11586	C II
8	612.47	0.068237	Ca I
9	616.5	0.089925	Ca I

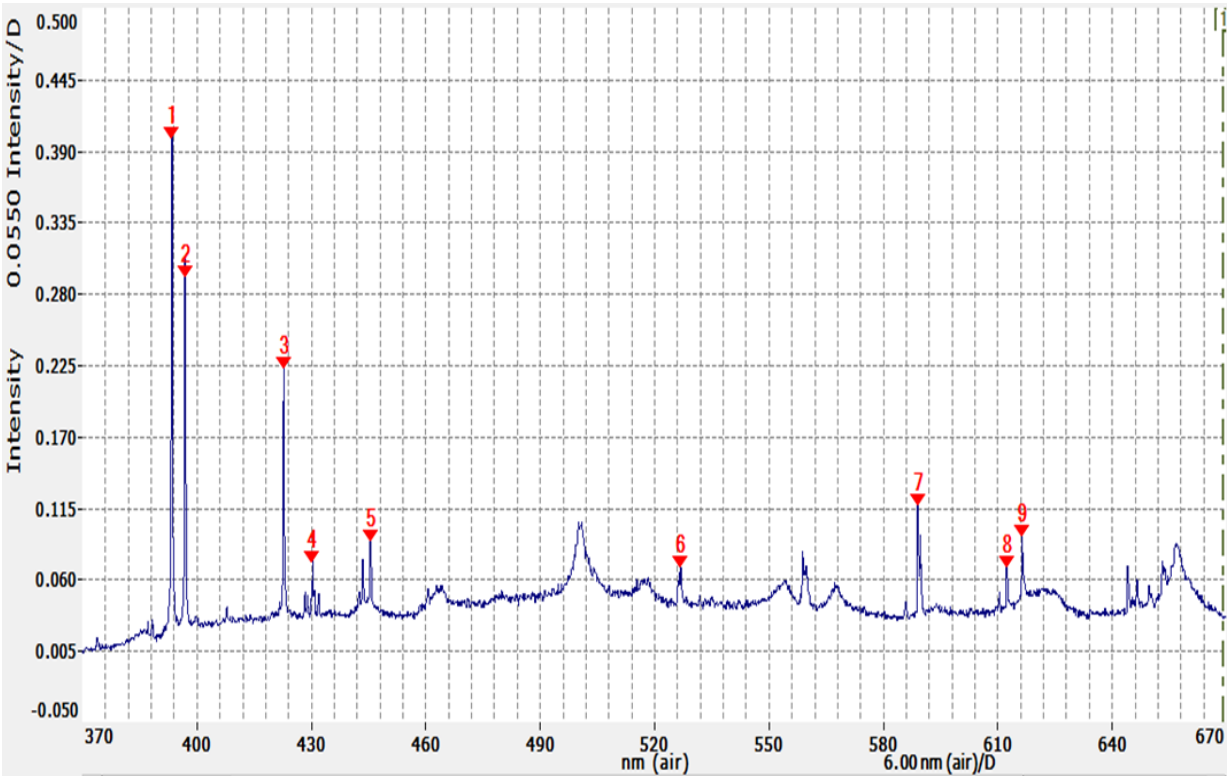

Figure (4 -27) LIBS spectrum of sample (S1) at 26.2% -15min.

Table (4-11) The analyzed data of sample S2, at 30% and 100º C

Sample S2 at 5 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.46	0.29089	Ca II
2	396.97	0.24071	Ca II
3	407.91	0.063125	Y I
4	422.85	0.15336	Ca I
5	431.92	0.051122	O II
6	443.59	0.092827	Ca I
7	445.58	0.10366	Na II
8	589.14	0.083702	C II
9	616.5	0.089925	Ca I
10	649.66	0.075544	Ca I

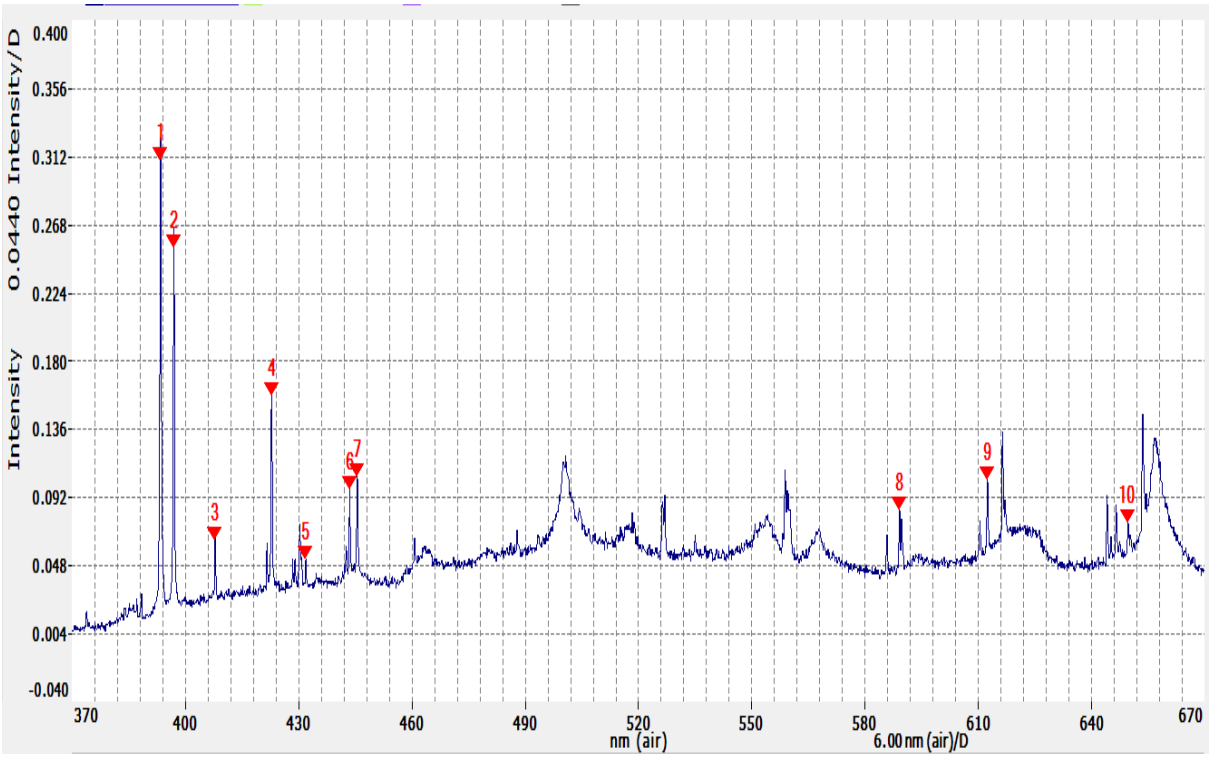

Figure (4-27) LIBS spectrum of sampled (S2). at 30% -5min

Table (4-12) The analyzed data of sample S2, at 30% and 100º C

Sample S2 at 10 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.46	0.60566	Ca II
2	396.97	0.47882	Ca II
3	407.9	0.11122	Y I
4	422.84	0.28706	Ca I
5	430.38	0.12245	K II
6	506.69	0.10464	Ti I
7	526.99	0.11925	Ca I

8	558.96	0.13588	Ca I
9	589.15	0.16389	Na I
10	616.49	0.16176	Ca I

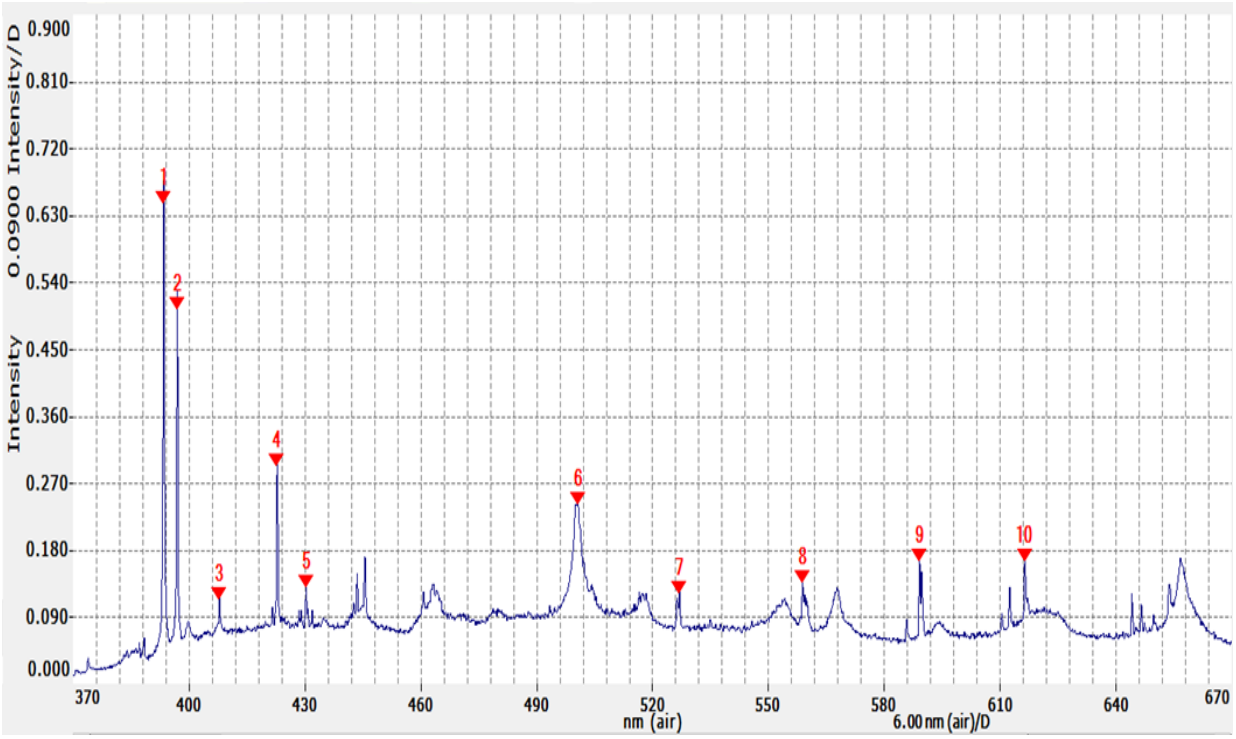

Figure (4-28) LIBS spectrum of sample (S2) at 30% -10 min.

Table (4-13) The analyzed data of sample S2, at 30% and 100º C

Sample S2 at 15 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.46	0.49054	Ca II
2	396.97	0.39236	Ca II
3	422.85	0.25232	Ca I
4	428.43	0.080626	Ti I

5	445.58	0.15521	Na II
6	527	0.11528	Ca I
7	558.96	0.13102	Ca I
8	589.14	0.11677	C II
9	612.46	0.13328	Ca I
10	646.56	0.10228	Ca I

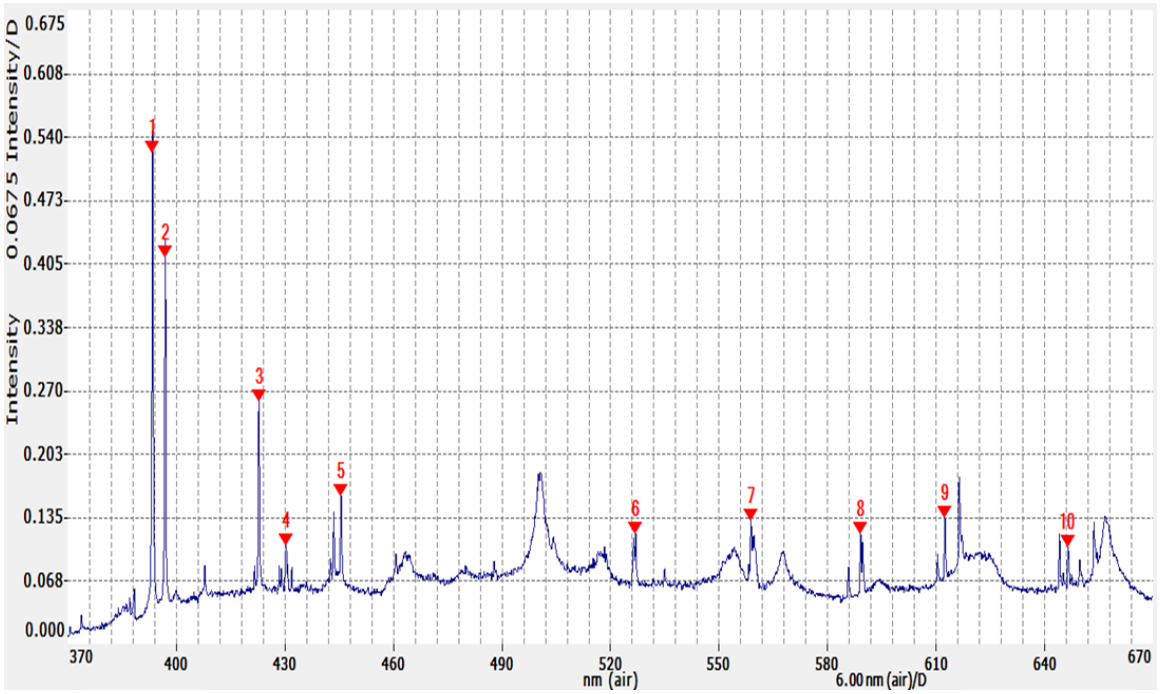

Figure (4-29) LIBS spectrum of sample (S2) at 30% -15 min.

Table (4-14) The analyzed data of sample S3, at 41.5% and 100º C

Sample S3 at 5 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.49963	Ca II
2	396.97	0.39214	Ca II
3	422.85	0.2744	Ca I
4	430.37	0.091486	K II
5	443.59	0.10747	Ca I
6	445.58	0.12363	Na II
7	460.73	0.083134	K II
8	504.23	0.086495	Si II
9	527	0.093873	Ca I
10	558.96	0.11604	Ca I
11	612.47	0.11655	Ca I
12	616.49	0.15655	Ca I
13	644.22	0.10019	Ca I

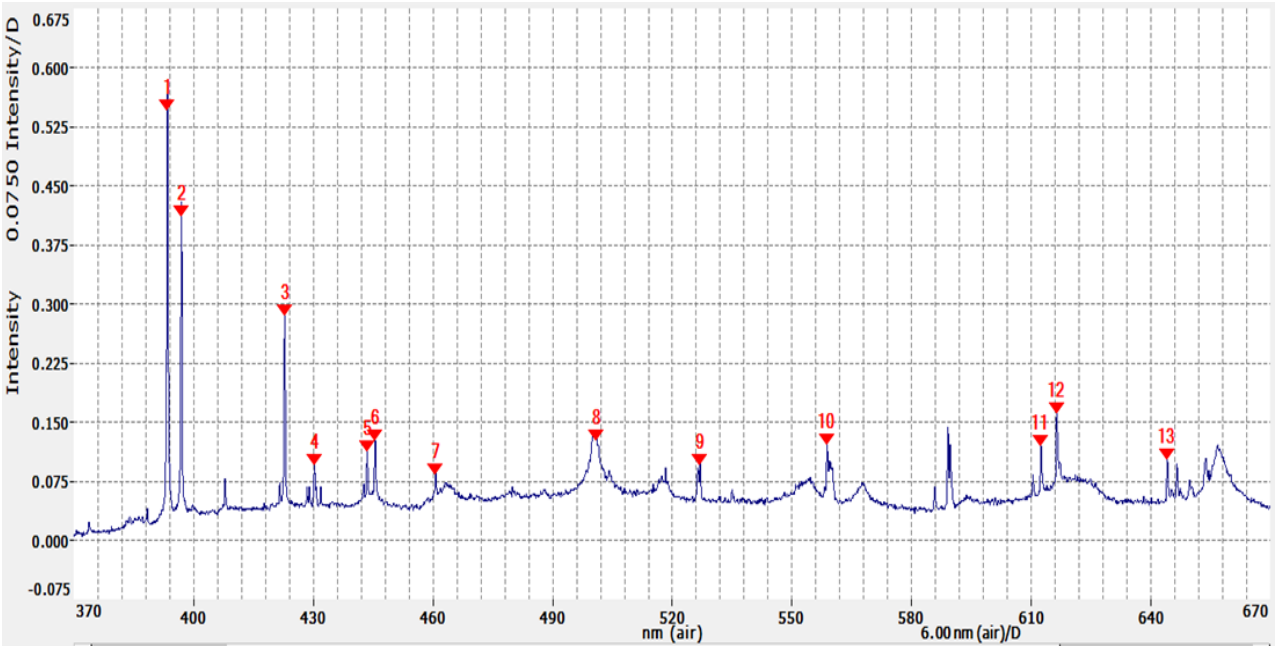

Figure (4-30) LIBS spectrum of sample (S2) at 41.5% -5 min.

Table (4-15) The analyzed data of sample S3, at 41.5% and 100º C

Sample S3 at 10 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.47	0.79453	Ca II
2	396.97	0.66147	Ca II
3	422.85	0.38067	Ca I
4	516.51	0.16207	Fe I
5	527	0.16851	Ca I
6	558.98	0.18764	Ca I
7	589.16	0.16048	C II
8	646.56	0.14739	Ca I
9	649.68	0.13275	Ca I

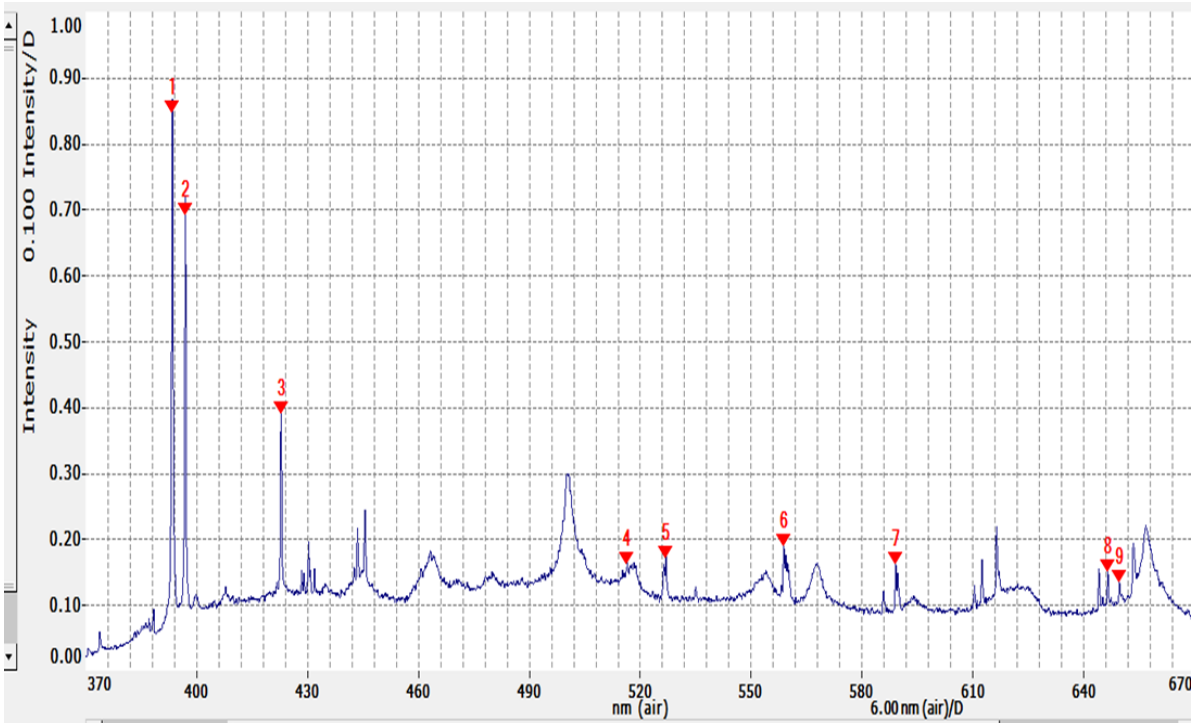

Figure (4-31) LIBS spectrum of sample (S2) at 41.5% -10 min.

Table (4-16) The analyzed data of sample S3, at 41.5% and 100º C

Sample S3 at 15 minutes			
NO	Wavelength (nm)	Intensity (au)	Peak assignment
1	393.49	0.331	Ca II
2	396.97	0.26837	Ca II
3	422.85	0.22024	Ca I
4	551.07	0.11842	S II
5	589.15	0.17469	Na I
6	649.72	0.11144	Ca I

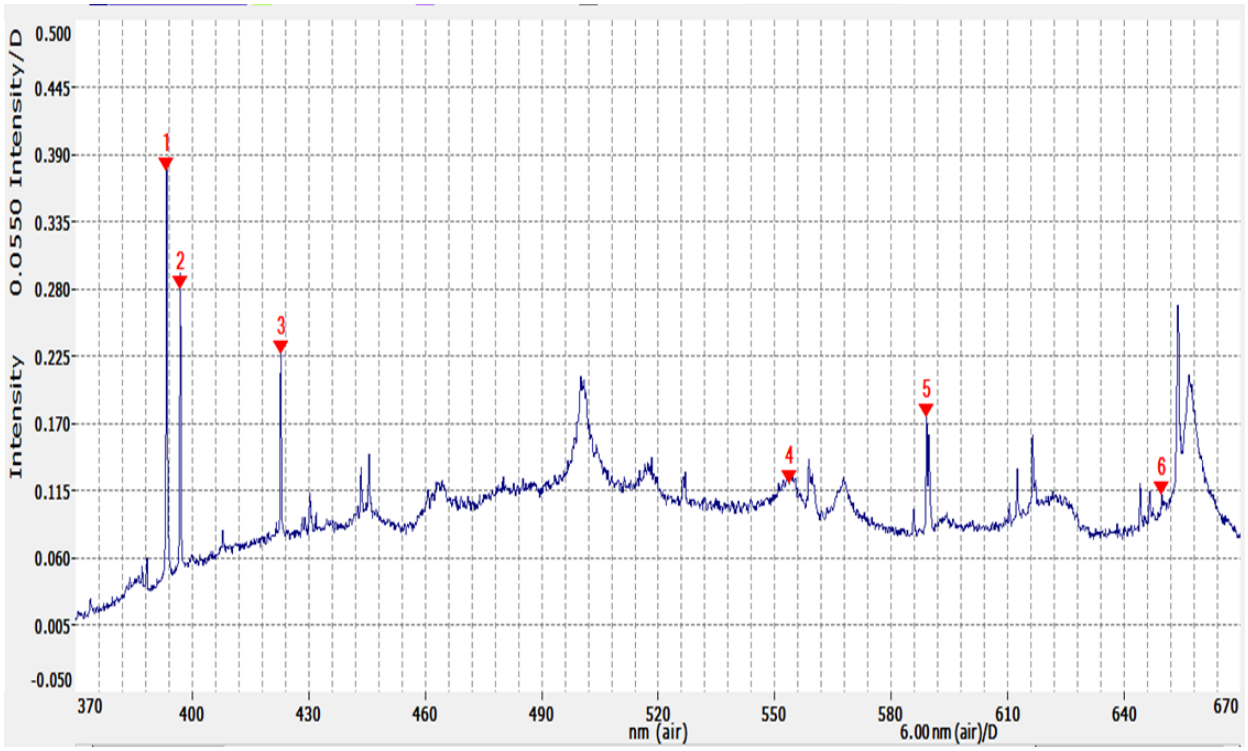

Figure (4-32) LIBS spectrum of sample (S2) at 41.5% -15 min.

The emission spectra of the respective elements were obtained as complete as in Figures (4-25 , 4-32) Seven major micronutrients were found in the three types of black seed samples (mainly Ca, Na, Fe, Si, Ti, S and K).

4-3-2: Selection of the spectral line:

To determine the temperature of the plasma and the electron density, the chosen spectral line must be isolated from the spectra and have a good profile. Because these parameters depend on the integrated density of the spectral lines. By analyzing temperature, electron density, and concentration.

spectral data was taken from the NIST (National Institute of Standards and Technology), (Atomic Spectra Database)

(http://www.nist.gov/srd/index.htm).

Neutral and simple ionization ions are the main source of finite element lines.

4.4 Boltzmann Plasma Method Plasma Temperature (T):

If the plasma is in local thermodynamic equilibrium (LTE), then the population density of the atomic and ionic states will be described by the Boltzmann distribution. By measuring the relative intensity of the line, it is possible to estimate the temperature of the electron across the slope of a straight line in the Boltzmann diagram. Plasma temperature was calculated according to the equation (1,2)

Table (4-17) The electron density calculated using Saha-Boltzmann equation for the samples

element	Plasma temperature (K)	Electron density (/cm3)
Ca I	3354.2	2.34×10^{18}
Ca II	2655.4	2.91×10^{18}

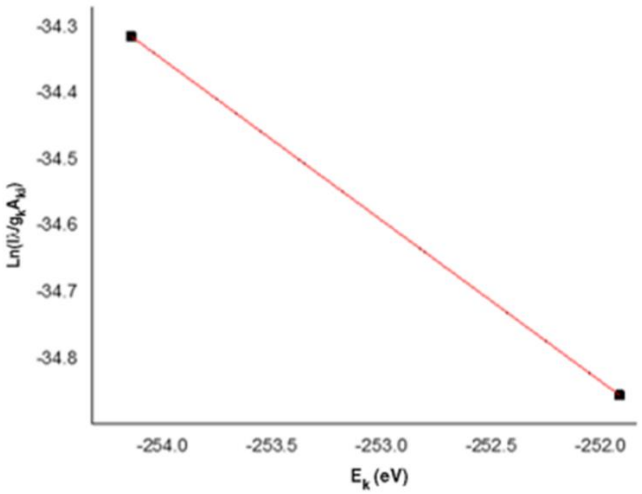

Figure (4-33) Boltzmann plot made using two Cu I lines, considering the intensities.

4.5 Conclusions

From obtained results we conclude:

*Among the basic compounds that were found when the temperature and humidity differed and were not affected by them is a compound (Natural methyl linoleate) is a type of linoleic acid that helps in the fat burning process [6].

*Linoleic Acid Methyl Ester is classified under CAS No.112-63-0[11].

*Linoleic Acid Methyl Ester is also known as Methyl Linoleate, Linoleic Acid Methyl Ester, Methyl Ester of Linoleic Acid [9].

*Linoleic Acid Methyl Ester is colorless to pale yellow liquid which is soluble in alcohol and ether. Linoleic Acid Methyl Ester is a common methyl ester produced from soybean or canola oil and methanol [12].

* Through the observation results, we find that the black seed is rich in Linoleic Acid methyl ester$C_{19}H_{34}O_2$, which applications in cosmetic, flavor and fragrances used as plasticizers, solubilizer, antistatic lubricant & rust inhibitors [8].

*Through the results of the observation and discussion, we found that the black seed was not significantly affected by the humidity and temperature factor, as it can thus be preserved in different storage conditions and makes it not affected by the climatic conditions.

*LIBS technology has been applied to black seeds to identify specific micronutrients. Major, minor and trace elements (Ca, Na, Fe, Si, Ti, S and K). were identified and counted. A procedure based on the Saha-Boltzmann multi-element diagram was used, allowing the temperature and electron density to be determined. Based on our study, the concentration of calcium

in black seeds is very high. On the contrary, it contains less sodium. The other micronutrients are almost the same in all types. Due to the high concentration of calcium in the black seed, the black seed has better nutritional content in terms of the presence of calcium.

* LIBS technology is seen to be a fast and attractive tool to identify micro-nutrients in cereal crops.

*Through the results of the observation and discussion, we found that the black seed was not significantly affected by the humidity and temperature factor, as it can thus be preserved in different storage conditions and makes it not affected by the climatic conditions.

4.6 Recommendations

Thanks to our results, which showed that the nigella sativa did not change much with the humidity degrees taken in the study and the temperature specified up to 100 degrees Celsius, it was therefore suggested in future studies that the study is done in the same way and with a difference in humidity and temperature degrees which should exceed 100 degrees Celsius, because some foods, such as pastries, can be exposed to temperatures above 100, and thus follow the evolution of their nutritional value.

I also hope that future research will be exhibited to discover the effect of humidity at room temperature and its effect on the nutritional and pharmacological value of black seed.

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erythrocyte during colon postinitiation carcinogenesis. Oxid Med Cell Longev. 2012; 2012:854065. [PMC free article] [PubMed] [Google Scholar]

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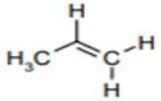
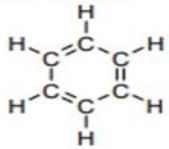
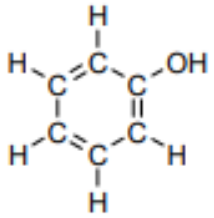
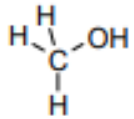
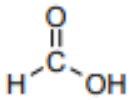
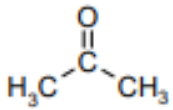
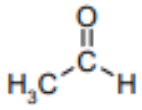
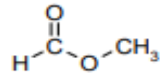
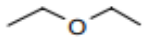
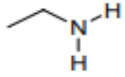
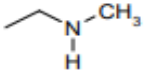
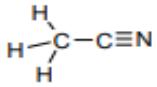
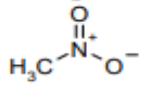
Appendix

Principal IR Absorptions for Certain Functional Groups

Functional Group Names & Example compounds	**Absorption Ranges(cm^{-1})** [Look for a single absorption in these regions, unless stated otherwise.]	**Type of Vibration causing IR absorption**
Alkanes:  Methane	**3000-2800** (Note: The absorptions can be seen as several distinct peaks in this region.)	H-C-H Asymmetric & Symmetric Stretch
	1500-1440	H-C-H Bend
Alkenes:  1-Propene	**3100-3000**	C=C-H Asymmetric Stretch
	1675-1600	C-C=C Symmetric Stretch
Alkynes: $HC\equiv C-CH_3$ Propyne	**3300-3200**	$\equiv C-H$ Stretch
	2200-2100	$C\equiv C$ Stretch
Aromatic Rings:  Benzene	**3100-3000**	C=C-H Asymmetric Stretch
	1600-1580	C-C=C Symmetric Stretch
	1500-1450	C-C=C Asymmetric Stretch

Phenols & Alcohols:  Phenol  Methanol (Alcohol)	**3600-3100** (Note: Phenols MUST have Aromatic Ring Absorptions too.)	Hydrogen-bonded O-H Stretch (This peak usually appears much broader than the other IR absorptions.
Carboxylic Acids:  Formic Acid	**3400-2400** *(This peak always covers the entire region with a **VERY BROAD** peak.)*	Hydrogen-bonded O-H Stretch *[Note: This peak can obscure other peaks in this region.]*
	1730-1650	C=O Stretch
Ketones:  Acetone	**1750-1625**	C=O Stretch
Aldehydes:  Ethanal	**1750-1625**	C=O Stretch
	2850-2800	C-H Stretch off C=O
	2750-2700	C-H Stretch off C=O

Functional Group Names & **Example compounds**	**Absorption Ranges(cm^{-1})** [Look for a single absorption in these regions, unless stated otherwise.]	**Type of Vibration** **causing IR absorption**
Esters:  Methyl Formate	**1755-1650**	C=O Stretch
	(1300-1000)	(C-O Stretch)
Ethers:  Diethyl Ether (aka-Ethyl Ether)	**(1300-1000)**	(C-O Stretch)
Amines—Primary:  Ethylamine	**3500-3100 (TWO PEAKS!)**	N-H Stretch
	1640-1560	N-H Bend
Amines—Secondary:  N-Methylethylamine	**3500-3100 (ONE PEAK!)**	N-H Stretch
	1550-1450	N-H Bend
Nitriles:  Methanenitrile	**2300-2200**	C≡N Stretch
Nitro Groups:  Nitromethane (Note: Both peaks are <200 cm-1 apart.)	**1600-1500**	N=O Stretch
	1400-1300	N=O Bend