UV-VISIBLE SPECTROSCOPIC QUANTIFICATION OF SUN SCREENING EFFICIENCY OF SOME HERBAL EXTRACTS AND COMMERCIALLY AVAILABLE BODY CREAMS AND SUNSCREENS IN ETHIOPIA

MSC IN LASER SPECTROSCOPY

BY: KENEAN DAGNE RORISA

HAWASSA UNIVERSITY, HAWASSA, ETHIOPIA

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This is to certify the thesis entitled "UV-Visible spectroscopic quantification of sun screening efficiency of some herbal extracts and commercially available body cream and sunscreens" submitted by Kenean Dagne Rorisa in partial fulfillment of the requirements for the degree of Master's with specialization in Physics (Laser spectroscopy). Therefore, I recommend that the student has fulfilled the requirements and hence can hereby submit the thesis to the department.

Name of advisor	Signature	Date
Dr. Daniel Mulugeta	______________________	______________________

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We, the undersigned members of the Board of Examiners of the final open defense by Kenean Dagne Rorisa, have read and evaluated his thesis entitled "UV-Visible spectroscopic quantification of sun screening efficiency of some herbal extracts and commercially available body cream and sunscreens" and examined the candidate. This is, therefore, certifying that the thesis has been accepted in partial fulfillment of the requirements for the degree.

Dr. Daniel Mulugeta	____________	_______________
Name of major advisor	Signature	Date
Dr. Misrak Getahun	____________	_______________
Name of internal examiner-I	Signature	Date
Woubshet Bahru (MSC)	____________	_______________
Name of internal examiner-II	Signature	Date
Dr. Yoseph Aresawem	____________	_______________
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Declaration

I hereby declare that this MSc specialty or equivalent thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

Name: Kenean Dagne Rorisa

Signature: ______________________

This MSc Specialty or equivalent thesis has been submitted for examination with my approval as thesis advisor.

Name: Dr. Daniel Mulugeta

Signature: ________________________

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List of abbreviation

UV-Visible: Ultraviolet-Visible

UV: Ultraviolet

SPF: Sun protection factor

MED: Minimal erthemal dose

Abs: Absorption

DNA: Deoxyribonucleic acid

LASER: Light amplification by stimulated emission of radiation

EMR: Electromagnetic radiation

SU: Supper white

DI: Diana

VA: Valera

DR: Dr. Rachel

DE: Demakese

GE: Gesho

GR: Grawa

TO: Tosign

AB: Abish

AC: Alternative current

DC: Direct current

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I want to start by giving thanks to the all-powerful God who enabled me to start and complete this research effectively and according to plan. Secondly, I would like to thank Dr. Daniel Mulugeta, my advisor, for his kind guidance and unwavering support, which enabled me to successfully complete the current research. He is the one who has consistently offered me assistance. Finally, I want to express my gratitude to my parents, Dagne Rorisa and Wesene Negash, as well as my sister Yordanose Dagne and her husband, Mesfin Tasew, for their unwavering support throughout my life.

Abstract

In this study, the sun protection factor (SPF) of different plant extracts, as well as commercial sunscreens and body cream, was evaluated using the UV-Visible spectroscopic approach, which is quick, simple, and inexpensive. The in vitro SPF value is estimated using the spectrophotometric method proposed by Mansur et al. After dilution with ethanol solutions, five herbal extracts, Ocimum lamifolium hochst (Damakese), Rhamnus prinoides (Gesho), Vernonia amygdalina (Grawa), Thymus schimperi (Tosign), and Trigonella foenum-graecum (Abish), were prepared, and the absorbance was measured between 290 nm and 320 nm. All of the examined herbal extracts were found to have some level of UV protection; the highest SPF value was 5.86 for Rhamnus prinoides (Gesho) extract, while the lowest was 0.93 for Ocimum lamifolium hochst (Demakese) extract. The same technique was applied to determine the SPF values of commercial body cream and sunscreens. The examined samples, Lady Diana, Valera, Dr. Rachel, and Super White's - labeled SPF values were in the range of 30 and 60. After evaluation, the results of the analysis showed that all of the selected samples had SPF values lower than what was written on the label. This discrepancy raises questions about the product's effectiveness and reliability. Commercial products shield the skin from UV rays; however, prolonged exposure may result in negative effects on the skin. The impact of chemical sunscreens must be countered by an alternative. This study examined the possible photo-protective qualities of natural substitutes, especially herbal extracts, in response to these concerns.

Keywords: Sunscreen, Sun protection factor, Body cream, Herbs, UV absorbance, UV-Visible spectroscopy

CHAPTER ONE

1. Introduction

1.1 Background study

Sunlight is important for the production of vitamin D, but excessive exposure to sunlight can cause various issues ranging from sunburn to skin cancer. UV radiation generates harmful molecules known as free radicals and reactive oxygen species, which can result in skin cancer and premature aging. Ultraviolet (UV) radiation from the sun poses a significant risk to human skin and can cause numerous health problems. More than a million people worldwide are diagnosed with skin cancer each year, and 10,000 of those cases result in death from malignant melanoma, a type of skin cancer caused by the damaging effects of UV radiation on the skin [1, 2]. There are three types of UV radiation: UV-A (400 nm-320 nm) causes premature aging of the skin, UV-B (320 nm-290 nm) causes sunburn and can lead to skin cancer, and UV-C (290 nm-200 nm) is filtered by the atmosphere before reaching the Earth [3]. The role of sunscreens in protecting the skin from these harmful effects is well-established and crucial.

Sunscreens have been manufactured and made accessible for nearly a century, gaining global recognition as an essential component of sun protection methods. By absorbing, reflecting, and scattering ultraviolet (UV) radiation, sunscreens effectively reduce skin issues caused by sun exposure, including sunburn, premature aging, and the risk of cancer [4, 5].

Sunscreens can have either organic (chemical) or inorganic (physical) active ingredients. Certain products are made up of both chemical and physical constituents. Chemical sunscreens can be further separated into two categories: UV-A and UV-B sunscreens, based on the wavelength range in which they exhibit maximal absorption [6].

A sunscreen's effectiveness is often measured by its sun protection factor (SPF), which is calculated by dividing the UV energy needed to create a minimal erythema dose (MED) on skin that is protected by sunscreen by the UV energy needed to produce a MED on unprotected skin. The smallest duration or amount of UV light exposure required to cause a mild, noticeable erythema on exposed skin is known as the minimal erythemal dose, or MED. The product's ability to prevent sunburn increases with its SPF level. Sunscreen products are often divided into three categories: minimal (SPF <12), moderate (SPF 12–30), and high (SPF ≥ 30), depending on the SPF rating [7, 8].

$$\mathrm{SPF} = \frac{\mathrm{MED(with\ sunscreen)}}{\mathrm{MED(without\ sunscreen)}} \ ,$$

It is possible to assess the photo-protection provided by topical sunscreen against exposure to solar UV radiation in vitro or in vivo. The best way to assess the in vivo determination is through photo testing on human subjects. This kind of determination has been around for a while, and it is accurate and helpful, it is also a laborious, costly, and complex process, especially when information on UV-A protection is needed. As a result, a lot of work has gone into creating in vitro methods to evaluate the photo-protective properties of sunscreen ingredients.

There are two main types of in vitro procedures: techniques that measure the transmission or absorption of UV light through sunscreen product films in quartz plates or bio-membrane, as well as techniques that use spectrophotometric analysis of diluted solutions to predict the absorption properties of the sunscreen agents [9].

Using UV-Visible spectroscopy and the following equation, Mansur et al. [10] created a relatively straightforward mathematical formula that replaces the in vitro approach suggested by Sayre et al. [11].

$$SPF = CF \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda),$$

Where: Abs (λ) is the absorbance of the sunscreen product; I (λ) is the solar intensity spectrum; and EE (λ) is the erythemal effect spectrum and correction factor (= 10) is represented by CF.

Most sunscreens are made of chemicals. The gradual penetration of the skin's epidermis by chemical sunscreens can cause harm to the skin's biology. Chemically produced sunscreens have documented responses such as photo-toxicity and photo-allergenic responses. The addition of organic compounds to some sunscreens as preservatives and scents could cause a significant allergic reaction on the skin, resulting in irritation, swelling, and severe itching.

Concerned about their skin being exposed to unknown chemicals, many individuals with sensitive skin, including those with skin hypersensitivity, refuse to use chemical sunscreens.

Despite the introduction of numerous hypoallergenic cosmetic products for clients with sensitive skin, alternatives to sunscreen agents are still limited [12].

Herbal sunscreens are more effective at blocking UV rays than synthetic ones and have fewer negative effects, if any. Herbs are free of synthetic chemicals; instead, they contain naturally occurring harmless chemicals like antioxidants and other bioactive substances [13]. Flavonoids, polyphenols, and other phytochemicals with anti-inflammatory and antioxidant properties are some of the bioactive compounds found in herbal products [14].They counteract the free radicals caused by exposure to UV light. Plants that have experienced DNA damage induced by UV radiation produce secondary metabolic products that absorb UV rays. Flavonoids and phenolic compounds have excellent antioxidant and photo-protective qualities, making them a safe, affordable, and biologically useful component for sunscreen formulations [15].The potential of certain molecules to absorb UV light makes them interesting choices for organic sunscreens [16]. The comparative effectiveness of herbal and commercially available body creams and sunscreens in terms of sun protection is still not well understood, despite the potential benefits of using herbal products.

To protect our skin from damaging UV radiation, sunscreen application is now essential. Herbal sunscreens eliminate the use of chemical sunscreens, protecting the skin from the damaging effects of UV radiation. More people are realizing how safe chemical-based sunscreens are for the skin. Chemical sunscreens soak into the skin, making it uncomfortable and itchy. Producers worldwide have started producing herbal sunscreens to avoid the negative effects of synthetic chemical products [17].The conventional use of synthetic chemicals in commercial sunscreens has raised concerns about potential negative effects on human health and the environment [18]. Natural alternatives, particularly herbal extracts, have been studied for their potential photo-protective properties in response to these concerns.

The current study will experimentally investigate the UV protective efficiencies of some herbals, such as *Ocimum lamifolium hochst* (Damakese), *Rhamnus prinoides* (Gesho), *Vernonia amygdalina* (Grawa), *Thymus schimperi* (Tosign), and *Trigonella foenum-graecum* (Abish), which are commonly used for medical purposes in Ethiopia. Previous research studies show that extracts from these herbs possess antioxidant and anti-inflammatory qualities [36-40].

In addition, this study will also determine the SPF of some commercially available body cream and sunscreens experimentally using UV-Vis spectroscopy and the value will be compared with the SPF value on the label. The commercial sunscreens used in this work are Lady Diana, Valera, Supper White, and Dr. Rachel, which are commonly used commercial sunscreens and body creams in Ethiopia.

In this thesis, one of the best methods is UV-Vis absorption spectroscopy, which is used to measure the absorption of solutions. UV-Vis absorption spectroscopy is an applied spectroscopic technique used to study the physical system when it interacts with electromagnetic radiation (EMR). Moreover, it is a spectroscopic technique that studies the absorption, transmission, and detection of light in relation to the optical properties of a material medium.

1.2 Statement of the problem

The environmental impact and safety of synthetic compounds commonly found in commercial body creams and sunscreen products offered in stores have been questioned, despite the fact that sunscreens are vital for protecting the skin from damaging UV radiation. Recent research suggests that certain chemical UV filters may trigger allergic reactions and hormonal imbalances. Moreover, these artificial components have been connected to environmental hazards such as aquatic toxicity and coral bleaching. The efficacy of commercially available body creams and sunscreens in providing adequate UV protection warrants investigation, as discrepancies between labeled and actual SPF (sun protection factor) values have been reported. This disparity calls into question the reliability and effectiveness of the products. Therefore, there is a growing interest in natural alternatives, such as herbals, which are believed to have photo-protective properties due to their bioactive components. However, there is a lack of comprehensive, measurable evidence comparing the efficacy of these natural herbs with that of conventional sunscreens.

In order to close this gap, this study compares the sun-screening effectiveness of different herbals to that of common brand-name sunscreens using quantitative UV-Vis spectroscopy. The main issue is the lack of comprehensive and reliable scientific information that may help stakeholders in business and consumers make educated judgments on the usage of herbals as safe and practical substitutes for synthetic sunscreens. This disparity impedes the creation of sun protection tactics that are safer, greener, and possibly more effective.

1.3 Objective of the study

1.3.1 General objective

- ✓ The main objective of this study is to quantify the sun protection effectiveness of different herbal extracts, brand-name sunscreens, and body cream by using UV-Visible spectroscopy.

1.3.2 Specific objectives

- ✓ Measure the UV-absorbance of the samples in the UV-B (320 nm-290 nm) region of the electromagnetic spectrum.
- ✓ Determining the sun protection factor of these samples from their absorbance by using Mansur's mathematical equation.
- ✓ For commercial products, compare the sun protection factor determined in this study with the value on their label.
- ✓ Compare the sun protection factor of herbal extracts with that of commercial products.

1.4. Scope of the study

- ✓ Selection of sunscreen samples

The research will concentrate on a particular variety of herbs that have been suggested to have UV protective qualities. Common examples of these would be Demakese (*Ocimum lamifolium hochst*), *Rhamnus prinoides* (Gesho), *Vernonia amygdalin* (Grawa), *Thymus schimperi* (Tosign), and *Trigonella foenum-graecum* (Abish).

There will be a range of commercially available body creams and sunscreens, such as Dr. Rachel, Lady Diana, Valera, and Supper White. To provide a comprehensive overview, a variety of SPF ratings and chemical and physical sunscreens will be included in the selection.

- ✓ UV-Vis spectroscopic analysis

The use of UV-Vis spectroscopy to detect the absorption spectra of the chosen samples is the basis of this investigation. This investigation will be restricted to UV-B, the UV range that is important for sun protection.

- ✓ Quantitative analysis

The study will use UV absorption data to quantify the effectiveness of sun protection. Calculating particular metrics, such as absorbance at critical wavelengths, will be necessary for this.

1.5. Limitations of the study

- ✓ Scope of spectroscopic analysis

UV-Vis spectroscopy is the main method used in the study to analyze sun filtering effectiveness. Although this is a reliable approach for measuring UV absorption, it does not offer data on other aspects such as skin penetration, photo stability, or the sunscreen's long-term efficacy.

- ✓ Limited range of products tested

The study will only examine a select number of commercial sunscreens and herbal extracts. The findings may not be generalizable to all available products in the market.

- ✓ Time constraints

The research is being done in a limited amount of time, which can restrict the breadth and depth of studies that are done over one year of time, such as those on the stability of sunscreen formulas.

- ✓ Budget

Research is done on body creams and sunscreens, which are pricey products on the market.

1.6. Significance of the study

- ✓ Advancing knowledge in sunscreen efficacy

The scientific understanding of the effectiveness of different sunscreens, including both commercial formulations and herbal ones, is enhanced by this study. In studies on photo-protection and dermatology, it helps close a significant information gap by offering quantitative data on their UV absorption capacities.

- ✓ Promoting natural sunscreen alternatives

The study could support and promote the use of natural sunscreen substitutes by quantitatively evaluating the capacity of plant extracts to protect against UV rays. This is especially important given the increasing demand for natural and organic skincare products among consumers.

- ✓ Enhancing public health and safety

The results of the study can help customers make better decisions by educating them about the safety and efficacy of various sunscreen products. Given the negative effects of sun exposure on public health, including skin cancer and premature aging of the skin, this is especially crucial.

- ✓ Innovations in cosmetic industry

The knowledge gathered from this study has the potential to spur innovation in the skincare and cosmetics sectors, resulting in the creation of better, safer, and more efficient sun protection solutions.

- ✓ Global relevance

Because sun protection is a universal requirement, the results of this study are relevant worldwide. They may be especially important in areas where it is easier to obtain natural extracts than synthetic sunscreens.

- ✓ Educational value

Through the dissemination of information on sun protection and the science behind it, the study educates both the scientific community and the general public.

- ✓ Foundation for future research

This work establishes the foundation for future investigations, especially regarding the long-term stability, safety, and environmental effects of both commercial and herbal sunscreens.

CHAPTER TWO

2. Theory

2.1 Optical spectroscopy

The study of electromagnetic interactions with matter is known as spectroscopy. As a result, matter absorbs or releases energy in discrete quantities, known as quanta. The electromagnetic spectrum, from the gamma to the radio regions, is well-known for its absorption or emission processes. Optical spectroscopy is a tool for studying the structure and dynamics of molecules, as well as exploring the micro world of atoms and molecules [19]. This approach takes less time and is significantly faster.

2.2 Electromagnetic radiation

The electromagnetic spectrum is a range of energy that spans from very long radio waves to very short gamma rays. It encompasses the complete and continuous range of electromagnetic radiation, including radio waves and gamma rays, based on wavelength, frequency, and photon energies. However, the human eye is only capable of perceiving a small portion of this spectrum, which is known as visible light [20]. Electromagnetic radiation, when interacting with matter, causes transitions between different energy levels. It is the primary component used in spectroscopy.

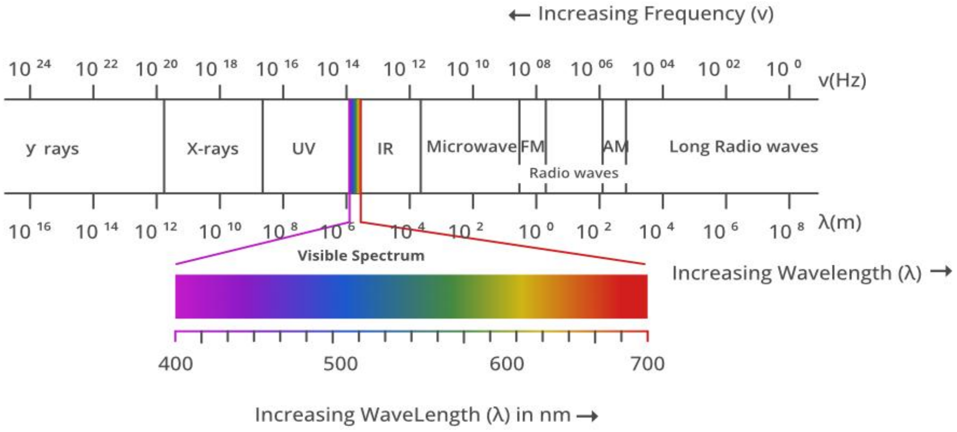


Figure2.1.Electromagnetic radiation and spectrum

Electromagnetic radiation can be broadly described as either a *wave* or a *particle*. *Particles* are referred to as photons. Each photon has a defined energy, which depends only on the frequency of the radiation.

$$E = h\nu, \text{ where h is Planck's constant } (h = 6.63\times10^{-34} \text{ J})$$

The *wave* nature of radiation reveals two components: an electric field and a magnetic field. At all times, both oscillate with the same frequency and are oriented perpendicular to each other. In polarized light the electric field oscillates in one direction only but unpolarized light has an electric field that oscillates in every direction.

Frequency ν and wavelength λ of a wave are related by

$$\nu = \frac{c}{\lambda} \ ,$$

Where, c is the speed of light. In vacuum, electromagnetic radiation has a propagation speed of $c = 3\times10^{8}$ m/s. Wavelength and frequency are commonly used to describe electromagnetic radiation. Additionally, there is the wavenumber $\tilde{\nu}$ which is expressed as follow [21],

$$\tilde{\nu} = \frac{1}{\lambda}, k = \frac{2\pi}{\lambda}, \omega = 2\pi f,$$

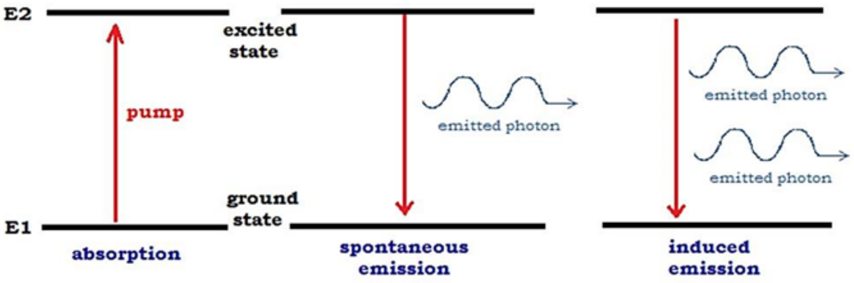
2.2.1 Laser

Laser is an electromagnetic radiation that has special characteristics such as, coherence, mono-chromaticity, unidirectional and high intensity [22].

- ✓ ***Coherent***: Two or more waves in a radiation field maintain the same phase relationship to each other at all times.
- ✓ ***Mon chromaticity***: Laser light is highly monochromatic, meaning it consists of only one color (frequency).
- ✓ ***Directional***: The output beam of a laser has a well-defined wave front, and therefore it is highly directional, except for the divergence caused by the diffraction effect.
- ✓ ***Intensity***: The laser output is highly intense.

The term "LASER" stands for "light amplification by stimulated emission of radiation". Laser is produced when ordinary light interacts with matter. There are three basic interaction processes; those are:

- ***Absorption*** of an increment $\Delta E=E_2-E_1$ of energy from the pump: The atom is raised from level 1 to level 2.
- ***Spontaneous emission*** of a photon of energy $h\nu=E_2-E_1$: The atom jumps down from level 2 to the lower level 1.
- ***Stimulated emission***: The atom jumps down from energy level 2 to the lower level 1 and, the emitted photon of energy $h\nu = E_2-E_1$ is an exact replica of a photon already present.



A (absorption) B (spontaneous) C (stimulated)

Figure2.2.Basic laser interaction processes of laser, A, absorption; B, spontaneous emission and C, stimulated emission

The laser device will amplify the light and produce highly directional, high-intensity, monochromatic light. The working principles of lasers are based on basic processes such as absorption, stimulated emission, population inversion, and amplification.

The laser devices usually have three basic components: [22]

- ✓ ***An energy pump***: The energy required for population inversion and stimulated emission in the system is provided by the pump source. There are two methods for pumping: optical and electrical discharge. Pump sources include electrical discharges, arc lamps, flash lamps, other laser lights, and chemical processes.
- ✓ ***Active/ Gain medium***: This produces an electromagnetic wave in the incident direction and amplifies it; the population inversion is caused by the external energy source,

namely the pump source. Optical gain, also known as amplification, is the result of stimulated and spontaneous photon emission occurring in the gain medium. Many materials are employed as lasing materials, such as semiconductors, organic dyes, gases (He, Ne, CO_2, etc.), solids (Nd-YAG, sapphire (ruby), etc.), and frequently the elements used as a medium are called lasers.

- ✓ ***An optical resonator/Cavity***: A portion of the emitted radiation that is concentrated within a few resonator modes is trapped using two opposing mirrors. The optical resonator plays a vital role in generating laser output as it provides high directionality to the laser beam and amplifies the gain in the active medium to offset losses caused by photons deviating from the laser medium, diffraction losses due to specific mirror sizes, and losses from absorption and scattering within the active medium.

2.3 Interaction of electromagnetic radiation with matter

Matter only interacts with electromagnetic radiation (EMR) when it possesses electric and magnetic properties and is affected by the magnetic and electric components of the EM radiation. Either the EMR is absorbed or emitted, depending on the net change in the molecule's electric or magnetic dipole moment interaction with the electrical or magnetic component of the experiment [23]. Any of these forms of energy is altered by the emission or absorption of EMR.

Quantitatively, we can determine these energies using molecular spectroscopy [24].

- ✓ ***Rotational energy***: It is due to the spinning of molecules about the axis passing through the center of gravity. Rotational levels are quantized, and the energy spacing between these quantized levels is equivalent to the energy of the EMR in the microwave region of the electromagnetic spectrum. Experimentally, the rotational energy of the molecule can be determined by rotational spectroscopy (microwave spectroscopy).
- ✓ ***Vibrational energy***: It is due to vibrations in molecules. Vibrational levels are quantized. The energy spacing between these quantized levels is in the infrared region of the EMR. Experimentally, the vibrational energy of the molecule can be characterized by IR spectroscopy (vibrational spectroscopy).
- ✓ ***Electronic energy***: Energy is due to the electronic transition between quantized electronic levels. UV-visible spectroscopy and other electronic spectroscopy techniques are usually implemented to determine electronic energies.

If E is the total energy of a molecule, it can be expressed as the sum of rotational, vibrational, and electronic contributions.

$$E = E_{(\text{rotational})} + E_{(\text{vibrational})} + E_{(\text{electronic})}$$

2.4 Molecular spectroscopy

Molecular spectroscopy discusses the interaction between electromagnetic radiation and molecules. This interaction leads to changes in vibrational and rotational energy levels, as well as electronic transitions. As a result, the spectra of molecules are much more complex compared to those of atoms. Molecular spectra can be observed across the visible, infrared, and microwave ranges. The abundance of known molecules, in comparison to free atoms, has sparked a recent increase in interest in molecular spectroscopy. The various types of spectra produced by molecular species, their corresponding ranges, and the energy changes that occur in molecules upon radiation absorption are listed below [25, 26, 4];

- ✓ ***Rotational spectra (Microwave)***

The transitions between the rotating energy levels of molecules and the absorption of radiation falling in the microwave region give rise to these spectra. Molecules with a persistent dipole moment have these spectra, for example, HCl, CO, H_2O vapor, NO, etc. These spectra are found in the (1–200) cm^{-1} spectral region.

- ✓ ***Vibrational and vibrational-rotational spectra (Infrared)***

These spectra result from transitions that are created between a molecule's vibrational energy levels and the absorption of infrared radiation. Molecules exhibit infrared spectra when their vibrational motion is accompanied by a shift in their dipole moment. These spectra are found in the (500-4000) cm^{-1} spectral region.

- ✓ ***Electronic Spectra (UV-Vis)***

Electronic transitions that occur when a molecule absorbs visible and ultraviolet light give rise to electronic spectra. Electronic spectra in the ultraviolet range from (200-400) nm, whereas those in the visible range from (400-800) nm. The electronic spectra of molecules are extremely complicated because vibrational and rotational transitions always accompany electronic transitions in molecules.

Since light is an energy form, when matter absorbs light, the energy content of the matter's molecules (or atoms) increases. The electrical, vibrational, and rotational energies of a molecule add up to its total potential energy [19].

$$E_{(total)} = E_{(rotational)} + E_{(vibrational)} + E_{(electronic)} \rightarrow \textit{Born-Oppenheimer approximation}$$

A molecule's total energy is not a continuous quantity, but rather a range of distinct levels or states. The order of the energy differences between the various states is:

$$E_{electronic} > E_{vibrational} > E_{rotational}$$

In certain molecules, incoming photons of visible and ultraviolet light possess sufficient energy to induce transitions between distinct electronic energy states. An electron must travel from a lower energy level to a higher energy level using the energy contained in the absorbed light wavelength.

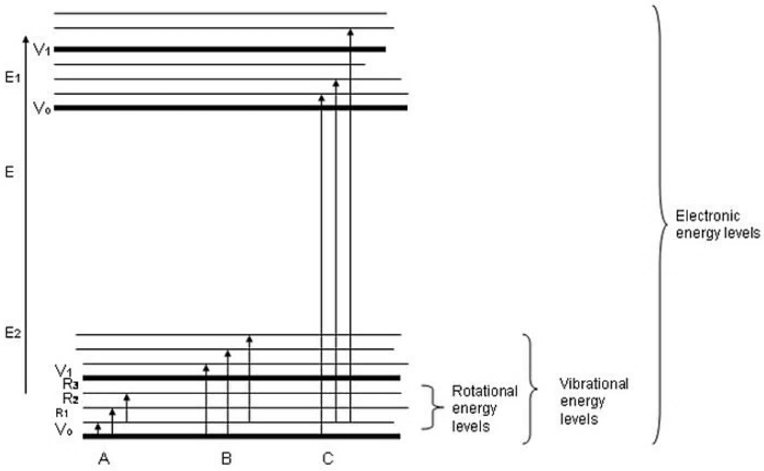


Figure2.3.Energy levels in the molecules

2.5 Nature of molecular absorption

Certain radiation may be absorbed by transparent materials due to continuous radiation passing through them. Following that, any remaining energy is passed through a prism to create an absorption spectrum, which is a spectrum with gaps in it. Energy absorption by molecules converts a lower energy state into a higher energy state.

Electromagnetic radiation is absorbed in a certain spectrum area due to transitions between electronic energy levels, as observed in UV and visible spectroscopy. As a molecule absorbs energy, one electron is gained and transferred from an occupied orbital to a vacant orbital with higher potential energy. Molecular absorption is more complex than atomic absorption because of the vast number of potential transitions. An outer electron of a molecule gets shifted when it interacts with photons in the UV-Vis region. The quantum energy, or hν, is the same as the energy difference between the two energy levels during resonance circumstances. The atom gains a quantum of energy as a result [25, 26]. The nature of molecular absorption allows scientists to interpret absorption spectra, identify molecules, characterize chemical reactions, and study molecular properties in various environments.

2.5.1 Transition probability

When a photon (hν) is absorbed by a molecule, the likelihood of the molecule changing its energy level is determined by two factors: the kind of starting and final state wave functions (Eigen states) and the degree of their interaction with the photon. Based on the predicted wave functions of the upper and lower states, the following transition probabilities are derived: The speed at which a molecule's absorption causes it to change into an excited state when it is subjected to an electric field that is shifted by the transition dipole moment. Consequently, one effective method of confirming the correctness of predicted wave functions is to use transition probabilities that have been shown by experimentation [27]. Transition probability is the likelihood that a spectroscopic transition will occur. It refers to the probability of an electron changing energy levels within an atom or molecule. This concept is crucial for comprehending the absorption and emission of electromagnetic radiation by matter.

2.5.2 Selection rule

Some transitions between energy levels are permitted according to selection rules. Based on an initial state and perturbing potential, they are defined by which final states are reachable. Though, in general, only the states with the lowest energy will be thermally inhabited, atomic and molecular species have a vast number of states in which energy can be dispersed. If electromagnetic radiation could effectively stimulate transitions between any one of these states, atomic and molecular spectra would be complex. Selection rules limit the possible transitions and make these spectra amenable to analysis.

$$D = \int \psi_1 \, \mu \, \psi_2 d\tau$$

Where Ψ_1 and Ψ_2 are the wave functions of the two states, "state 1" and "state 2", involved in the transition and μ is the transition moment operator [28]. If the value of this integral is zero, a transition between states 1 and 2 is deemed "forbidden" since it represents the propagator and, thus, the possibility of such a transition. As it happens, defining a selection rule may be done without computing the integral: It is sufficient to determine the symmetry of the transition moment function. If the transition moment function is symmetric over the whole totally symmetric representation of the point group that the atom or molecule belongs to, then the integral's value is not zero and the transition is allowed. If not, the transition is "forbidden". The transition moment integral is zero if the transition moment function is odd or anti-symmetric.

2.5.3 Einstein coefficients

Absorption, stimulated emission, and spontaneous emission are all described by the specified Einstein *A* and *B* factors for atom-photon interactions. The Einstein approach may be used to calculate B and, as a result, determine A. Think of two level systems, where n_1 is the ground state level of an atom and n_2 is the excited state level of an atom. The Boltzman distribution provides information on the atom distribution in the two levels [19].

$$\frac{n_1}{n_2} = \frac{\mathrm{e}^{(-\mathrm{E2}/\mathrm{KT})}}{\mathrm{e}^{(-\mathrm{E1}/\mathrm{KT})}} = \mathrm{e}^{[-\left(\frac{E_2-E_1}{KT}\right)]} = \mathrm{e}^{(\frac{-hv}{kT})}$$

Suppose that the molecules are in thermal equilibrium with energy of density ρ_v and that the number of atoms in the lower state, n_1, and the energy density determine the absorption rate [29].

- ***Rate of absorption***

$$\frac{dn_2}{dt}|_{absorption} = B_{12} n_1 \rho(\nu)$$ B_{12}; Einstein's coefficient of absorption

Coefficient of absorption is the coefficient that represents the absorption process. B_{12} is the symbol for it. The likelihood that an atom in energy level 1 (lower energy level) would absorb a photon of a certain frequency and be excited to energy level 2 (higher energy level) is defined as the probability per unit time per unit mean intensity at frequency.

Emissions that are both spontaneous and induced can transport molecules from a higher state to a lower state.

- ***Rate of spontaneous***

$\frac{dn_2}{dt}|_{spontaneous} = A_{21}n_2$ A_{21}: Einstein's coefficient of spontaneous emission

The term "coefficient of spontaneous emission" refers to the coefficient that corresponds to the spontaneous emission process. A_{21} represents this coefficient. It is the probability, expressed in units of time, that an atom at energy level 2 would spontaneously emit a photon and transition from energy level 2 (higher energy level) to energy level 1 (lower energy level).

- ***Rate of stimulated***

$\frac{dn_2}{dt}|_{stimulated} = B_{21}n_2\rho(\nu)$ B_{21}: Einstein coefficient of stimulated emission

The term "coefficient of stimulated emission" refers to the coefficient that corresponds to the process of stimulated emission. B_{21} represents this coefficient. In this process, two photons are emitted, along with the shift from energy level 2 to energy level 1 caused by the incoming photon.

The rate of emissions and absorption is equal under equilibrium conditions.

$$\frac{dn_2}{dt} = -A_{21}n_2 + B_{12}n_1\rho(\nu) - B_{21}n_2\rho(\nu)$$

$$n_2[-A_{21} - B_{21}\rho(\nu)] + n_1[B_{12}\rho(\nu)] = 0$$

$$\frac{n_2}{n_1} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)}$$

Generacy of state (g) can have the same energy

$\frac{n_2}{n_1} = \frac{g_2}{g_1}e^{(-hv/kt)}$ Then,

$\frac{B_{12}\rho(\nu)}{A_{21}+B_{21}\rho(\nu)} = \frac{g_2}{g_1}e^{(-hv/kt)}$ At extreme temperature, $[e^{\left(\frac{-hv}{kt}\right)} \sim 1]$

When we compare the two ρ (ν) expressions, we obtain

$$\frac{B_{21}}{B_{21}} = \frac{g_2}{g_1} \quad , \quad B_{21} = \frac{g_2}{g_1} B_{21} \rightarrow B_{21} = B_{12} \quad and \quad \rho(\nu) = \frac{8\pi v^3}{c^3} \frac{hv}{e^{(\frac{-hv}{kt})} - 1}$$

$$\frac{g_2}{g_1} B_{21} \rho(\nu) = \frac{g_2}{g_1} A_{21} e^{\left(\frac{-hv}{kt}\right)} + \frac{g_2}{g_1} B_{21} e^{(\frac{-hv}{kt})}$$

$$B_{21}(1 - e^{\left(\frac{hv}{kt}\right)})\rho(\nu) = A_{21} e^{(\frac{-hv}{kt})}$$

$$B_{21} e^{\left(\frac{-hv}{kt}\right)} \left(e^{\left(\frac{hv}{kt}\right)} - 1\right) \frac{8\pi v^3}{c^3} \left(\frac{1}{e^{\left(\frac{hv}{kt}\right)} - 1}\right) = A_{21} e^{(\frac{-hv}{kt})}$$

$$\frac{A_{21}}{B_{21}} = \frac{8\pi v^3}{c^3}$$

It demonstrates that the relationship between Einstein's coefficient of spontaneous emission and Einstein's coefficient of stimulated emission is directly proportional to the frequency cube (ν^3).

2.6 UV-Visible spectroscopy

Ultraviolet-visible spectroscopy is an optical spectroscopy technique that utilizes visible, ultraviolet, and near-infrared light as a source of radiation. These regions of the electromagnetic spectrum cover the wavelength range from around 200 nm -750 nm. The UV-Visible spectrum is generated through the interaction of electromagnetic radiation with molecules, ions, or complexes in the UV-Visible range [30].This spectroscopic method serves as a foundation for the analysis of diverse materials, encompassing organic, inorganic, and biological substances.

2.6.1 Principle of UV-Vis Spectroscopy

Spectroscopy operates on the principle that chemical substances which absorb ultraviolet or visible light produce distinct spectra. This scientific technique relies on the interaction between light and matter, where the absorption and release of light by matter lead to the formation of a spectrum. The observable spectrum shows how wavelengths interact with discrete-dimensional objects like atoms, molecules, and macromolecules. When an electromagnetic wave contacts a substance, events including transmission, absorption, reflection, and scattering can occur. When the energy difference between molecules in their excited and ground states is equal to the frequency of incoming light, absorption occurs. An electron is stimulated from its ground state to its excited state, a process known as an electronic transition. This forms the core idea of molecular spectroscopy [30].

Any molecule that is subjected to light radiation experiences an electronic transition in its structure, leading to absorption in the visible or ultraviolet range. Usually, a molecule consists of one or more electrons, which can be in the form of n (non-bonding), π, or σ (bonding), or a combination of these. The energy source from light is absorbed by the electrons, allowing them to transition from a low energy state to a high energy state more easily. The structure of a molecule can be represented by its absorption peaks and the properties of its electrons [19, 31].

2.6.2 Instrumentation

The components involved in UV-Visible spectroscopy are a light source, monochromator, sample holder, detector and recording devices [30].

- ✓ ***Light source***- Sources for UV-Visible spectrometers are those found in the visible and ultraviolet spectrums. Examples include deuterium lamps and tungsten halogen lamps.
- ✓ ***Wavelength selector*** - There is an optical tool known as a monochromator that is used to select a certain restricted range of light wavelengths. It consists of a mirror, lenses, a grating/prism, and a slit.
- ✓ ***Sample cell or cuvette***- A component of the sample is introduced into the sample cell. Example: Quartz - is transparent in both UV and visible regions (200 nm -700 nm range).
- ✓ ***Detector*** - are devices that convert light / photons in to electrical signal. Example of simple detectors is photomultiplier tube.

- ✓ ***Signal Processors* -** The computer stores all the data generated and produces the spectrum of the desired compound. It converts *DC* to *AC* or vice versa.

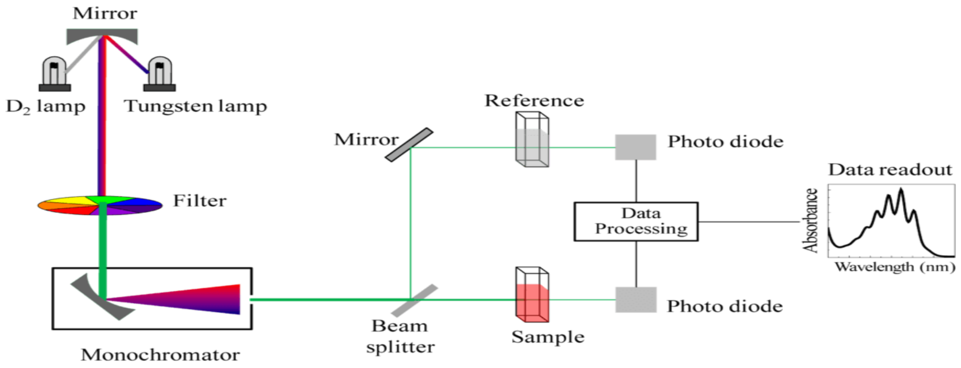


Figure2.4.Components of UV/Visible spectrometer

2.7 Absorption of sun's UV radiation by matter

The sun and other high-temperature surfaces emit ultraviolet radiation continuously. The ozone layer in the lower stratosphere is formed by oxygen in the Earth's atmosphere, which absorbs the majority of the UV radiation from sunlight. UV-A radiation makes up nearly 99% of the ultraviolet light that does reach Earth's surface. However, more UV-B radiation reaches Earth's surface when the ozone layer thins, which could be dangerous for living things. Studies have demonstrated, for instance, that UV-B radiation reaches the ocean's surface [32].

The human skin undergoes a complex series of interactions when light passes through it. The primary process of light propagation in the skin is absorption. One way to think of absorption is as the process by which photon energy is absorbed by bound electrons (subatomic particles) in atoms. According to atomic physics, matter is made up of atoms and molecules, which contain electrons [33]. Atomic orbitals can be used to characterize the energy levels of these electrons. Every orbital is separate and has a distinct state, such as energy. By producing or absorbing photons with energy equal to the energy difference between electron's orbitals, electrons can also be moved from one orbital to another. These electrons will absorb the energy of the light and transition from a ground state to an excited state when light with the same precise frequencies reaches the medium. Excited electrons are unstable and will eventually return to their ground state when electromagnetic energy is released.

2.8 UV radiation effect on skin

Sunlight exposure can cause oxidative damage to skin cells, photo-aging, sunburns, and skin cancer. There are three sections in the electromagnetic spectrum: The UV wavelength band with the least amount of power is UV-A. The ozone layer does not block this lengthy wave of black light. UV-A predominantly causes the skin's melanin pigments to oxidize, or darken, which results in a cosmetic tan. It has a limited ability to induce erythema. The wavelength range of UV-B is between 290 nm and 320 nm. It is mostly responsible for inducing enhanced melanin formation, contains the wavelengths largely linked to erythema (sunburn), and is also required for the skin to produce vitamin D [1, 2, 3].

The erythemal power of UV-B wavelengths at 305 nm is 1000 times greater than that of UV-A wavelengths. It is largely absorbed by the ozone layer and is of medium wave strength. UV-C is found in the 200 nm - 290 nm range. The ozone layer and atmosphere fully absorb shortwave radiation. Severe erythema (sunburn) can result from even a brief overexposure to UV-C, which is extremely hazardous to the eyes. The atmosphere filters UV-C radiation before it reaches the planet. Sunburn damage is caused by UV-B light, which is not entirely blocked by the ozone layer. UV-A ray cause premature skin aging by penetrating the dermis and epidermis to reach their deeper layers [34].

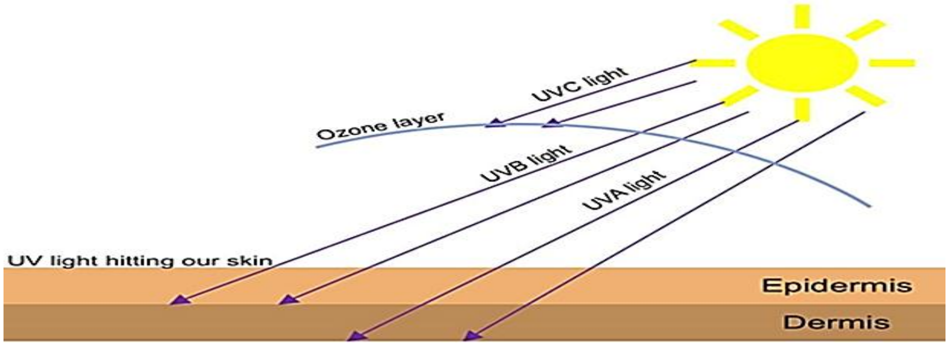


Figure2.5.The effect of UV radiation on skin

Sunscreens work by absorbing, reflecting, and scattering ultraviolet (UV) light. SPF is a measure of how effective a sunscreen is in preventing skin conditions such as sunburn, aging skin, and cancer. There are two methods for determining SPF.

- ✓ ***In vivo sun protection factor (SPF):*** The most conventional approach, recognized by authorities in a number of nations, involves using ten to twenty healthy human volunteers of both sexes with suitable skin types in each of these long-range techniques. However, the costly in vivo approach raises ethical concerns regarding the use of humans in research [35].
- ✓ ***In vitro sun protection factor (SPF):*** The total protection efficacy of a sun care product against erythemal effective UV radiation is determined using in vitro transmittance measurement. This measurement is weighted by the erythema action spectrum and the "standard" output spectrum of a UV solar simulator, which is used to assess SPF. There are two primary types of in-vitro methods: measuring UV radiation absorption or transmission through sunscreen product coatings in quartz plates or membranes, and techniques based on spectrophotometric measurements that establish the absorption properties of the sunscreen agents [9].

2.9 Chemical constituents of the sample

2.9.1 Chemical constituents of commercial sunscreens and body cream

Table2.1. Chemical constituent of commercial sunscreens and body cream

Sample	Active ingredients	Labeled SPF
SU	Turmeric and saffron	30
DI	Avobenzone($C_{20}H_{22}O_3$), methylparaben($CH_3(C_6H_4(OH)COO$), titanium dioxide(TiO_2), zinc oxide(ZnO), benzophenone-3($C_{14}H_{12}O_3$).	60
VA	Ethylhexyl methoxycinnamate($C_{18}H_{26}O_3$), diethylamino hydroxybenzoyl hexyl benzozte($C_{24}H_{31}NO_4$), sodium hydroxide($NaOH$), phenooxy ethanol($C_8H_{10}O_2$), Oxybenzon($C_{14}H_{12}O_3$)	60
DR	Phenoxyethanol($C_8H_{10}O_2$), methoxycinnamate($C_{18}H_{26}O_3$), triethanolamine($C_6H_{15}NO_3$), avobenzone($C_{20}H_{22}O_3$), polyacrylamide(-$CH_2CHCONH_2$-), methylparaben($CH_3(C_6H_4(OH)COO$)	60^{++}

2.9.2 Chemical constituent of herbs

Table2.1.Chemical constituent of herbs

Common name with family name	Technics used to identification	Chemical constituents	Part preferentially used
Demakese (*Lamiaceae*)	Chromograph	Alkaloids, sterols, carbohydrates, glycosides, tannins, flavonoids, bornyl acetate, p-cymene, camphene, a-pinene, and sabinene. [36]	Leaf
Tosign(*Lamiaceae*)	Chromograph	Flavonoids, phenolic acids, terpenes, saponins, polyphenols, tannins, iridoids, and quinones. [37]	Leaf
Gesho(*Rhamnaceae*)	Chromograph	Alkaloids, triterepenes, saponins, tannins, phenols, cardiac glycosides, anthraquinones, polyphenols and flavonoids.[38]	Leaf
Grawa(*Asteraceae*)	Chromograph	Lactone, flavonoids, terpenes, coumarins, phenolic acids, lignans, xanthones and anthraquinones. [39]	Leaf
Abish(F*abaceae*)	Chromograph	Steroids, alkaloids, saponins, polyphenols, flavonoids, lipids, carbohydrates, amino acids, and hydrocarbons.[40]	Seed

2.10 Spectroscopic determination of sunscreen's SPF

Sunscreen's ability to prevent sunburn is indicated by the number next to its SPF, or sun protection factor. In order to prevent ultraviolet (UV) light from reaching the skin, sunscreens either reflect or absorb it. For a sunscreen to be effective, it must block the UV-A and UV-B spectral bands, which are between 400 nm and 290 nm. In order to provide skin protection from UV radiation, the active ingredient, whether organic or inorganic must be present in a suitable amount and consistency [41].

The absorbance of UV-B radiation with a wavelength between 290 nm and 320 nm determines the SPF value. If light is not absorbed, it will still pass through the skin. More UV-B ray absorption by the sunscreen compounds reduces the amount of UV rays that reach the skin [42].

The SPF of sunscreens in spectroscopy is determined by Mansuer et al.'s [10] mathematical equation;

$$\mathrm{SPF} = \mathrm{CF}\sum_{290}^{320}\mathrm{EE}(\lambda) \times \mathrm{I}(\lambda) \times \mathrm{Abs}(\lambda),$$

Where: CF is the correction factor (=10); "EE (λ)", the erythemal effect of radiation at wavelength λ; I (λ), the intensity of the solar spectrum; and Abs (λ), the absorbance at wavelengths 290 nm -320 nm. EE (λ), I (λ), and Abs (λ) are values obtained or applied for every wavelength (λ). The values for each of the [EE (λ) x I (λ)] are constants that have been reported by the authors as normalized based on the work by Sayre et al. [11].

Table2.2.Sayre constants

Wavelength (nm)	EE(λ) ×I(λ)
290	0.015
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0839
320	0.0180
Total	1

2.11 Reviews of related literatures

Several experimental studies have been conducted to determine the effectiveness of herbal products and commercially available cosmetic products as sunscreens. Some of these studies, which are closely related to my research, are reviewed below.

Zayd et al. evaluated six commercial products such as creams, foundations, and lotions for sun protection factor (SPF) using Mansuer et al.'s mathematical equation to determine the SPF of sunscreen. This study was conducted using the in vitro determination method with UV-Visible spectroscopy. The selected commercial products ranged from 10 to 90. Absolute ethanol (95%) was used as the solvent. These sunscreens contain both physical and chemical sunscreens, and the active ingredients are not labeled. The absorbance of the prepared solutions was measured in the range of 290-320 nm, with each measurement changing the wavelength range by 5 nm. After evaluating the SPF of the sunscreens, they found that all of the sample products showed a lower sun protection factor compared to the labeled SPF [43].

Mbanga, L. et al. use UV spectrophotometry to measure the sun protection factor (SPF) of 10 different sunscreen creams and lotion formulations that are sold in Kinshasa. These formulations may comprise chemical or physical sunscreen. The Mansur equation was used to assess the estimated sun protection factor of ten distinct commercially available body cream and lotion formulations that were established in the Kinshasa market. The selected products were prepared with ethanol. The SPF values on the labels ranged from 15 to 60. According to the study's findings, 40% of the sunscreen samples from the ten distinct commercial formulations closely matched the SPF claimed on the label, whereas 60% of the sunscreen samples showed SPF values that were lower [41].

Dutra E.A. et al. used UV spectrophotometry to calculate the sun protection factor (SPF) of different sunscreens, creams, and foundation emulsions that contain both chemical and physical filters. They assessed ten distinct sunscreen emulsion samples that were commercially available and made by different manufacturers. This study was conducted using an in vitro determination method. The values with the SPF labels ranged from 8 to 30. Ethanol analytical grade was used as a solvent, and these sunscreens contain both physical and chemical sunscreen. After evaluating the selected products, in close accordance with the indicated SPF, 30% of the studied samples had SPF values; 30% had SPF values beyond the labeled amount, and 40% had SPF values below the labeled amount. For the in vitro assessment of sunscreen emulsion SPF values, the suggested spectrophotometric approach is quick and easy to use [3].

Malsawmtluangi, C. et al. determined the ultraviolet (UV) absorption properties of seven aqueous herbal extracts of some commonly found vegetable sources such as coconut, watermelon, aloe Vera, carrot, cucumber, papaya, and strawberry, by determining the sun protection factor (SPF) number. The in vitro SPF number is determined according to the spectrophotometric method described by Mansur JS et al. Aqueous herbal extracts were prepared, and after dilution with alcoholic solutions, the absorbance was recorded between 290 nm-320 nm using UV-Vis spectrophotometry. All of the examined herbal remedies were shown to have some value of UV protection; watermelon had the lowest SPF of 0.97 and aqueous coconut extract had the highest, at 7.38 [12].

Chandaka Madhu et al. investigated the ultraviolet absorption properties of ethanolic herbal extracts from commonly used vegetable sources by determining the sun protection factor (SPF) number. The ethanolic herbal extracts that were investigated included Acuminate Cucumis, Sativus, Carica Papaya, Vitis Vinifera, Malus Domestica, Daucus Calota, Solanum Lycoperisum, and Beta Vulgaris. After collection, they prepared the standard solution using ethanol as the solvent. The in-vitro SPF number was determined using the spectrophotometric method described by Mansur JS et al. The absorbance was recorded between 290 nm-320 nm using UV-Vis spectrophotometry. It was observed that all of the ethanolic herbal extracts showed some UV protection capability. It was found that all have almost similar UV protection capabilities, along with their many beneficial effects, ease of availability, affordability, and safety [44].

Pradhan and his associates investigated the sun-protective potential of six medicinal plants - Asparagus racemosus, Bergenia pacumbis, Melia azedarach, Murraya koenigii, Pleurospermum benthamii, and Thymus linearis - in vitro. They looked at the possibility of using specific extracts from these plants as an ingredient in sunscreen for contemporary makeup, using the Mansur equation and ultraviolet-visible spectrophotometry. When compared to store-bought sunscreen, the majority of the plant extracts had much higher SPF ratings, according to their findings. The highest SPF values were observed in Pleurospermum benthamii (34.97±0.25), Thymus linearis (24.98±0.60), and Bergenia pacumbis (24.02±0.15). These findings indicate that these plant extracts have excellent anti-solar properties [45].

CHAPTER THREE

3. Material and method

3.1 Samples

Herb samples such as *Ocimum lamifolium hochst* (Demakese), *Rhamnus prinoides* (Gesho), *Vernonia amygdalina* (Grawa), *Thymus schimperi* (Tosign), and *Trigonella foenum-graecum* (Abish) were collected from a home garden. Commercial samples such as Lady Diana, Valera, Dr. Rachel, and Supper White sunscreens and body cream were bought from pharmacies and cosmetics stores in the local market.

3.2 Chemicals and reagents

Commercially bought ethanol (96%) was used.

3.3 Instrumentation

The following are the laboratory tools that were used in the experiment: After the leaves and seeds were dried, herb grinder was used to create a fine powder. Among the items are beakers, a funnel, a graduated cylinder (100 ml and 50 ml), a wash bottle, a pipette, flasks, magnetic stirrers, analytical balances, Whatman filter paper (0.75µm), quartz cuvettes (1 cm), and a T80 UV-Visible spectroscopy. Before usage, all glassware apparatus were well cleaned, washed with water, and dried.

3.4 Preparation of standard solutions

3.4.1 Commercially available sunscreens and body cream

Commercial sunscreens and body creams were collected from pharmacies and cosmetics shops. These samples have labeled SPF values ranging from 30 to 60. After collection, one gram of each sample was weighed using an analytical balance to determine the amount of Lady Diana, Valera, Dr. Rachel, and Super White sunscreens and body creams in grams. The samples (Diana, Valera, Dr. Rachel, and Super White) were then dissolved in 100 milliliters of ethanol in a volumetric flask. They were stirred for 25 minutes with a magnetic stirrer at room temperature and filtered through 0.75µm Whatman filter paper, discarding the first 10 milliliters. Then, a volumetric flask containing a 5 ml aliquot (main solution) was diluted with 50 ml of ethanol. Lastly, a 25 ml volumetric flask was filled up with ethanol after a 5.0 ml second solution was transferred there. Using a 1 cm quartz cell and ethanol as a blank, the absorption spectra of materials in solution were measured between 290 nm and 320 nm using the in vitro determination method. Every 5 nm, three assessments were made based on the absorption data that were collected using T80 UV-Vis spectroscopy (double beam spectrophotometer) in the range of 290nm to 320nm. The Mansuer et al. mathematical equation was then applied to determine the sun protection factor (SPF) of the chosen body cream and sunscreens, in conjunction with substituting the in vitro method proposed by Sayre et al. [11].

3.4.2 Herbals

From household gardens, leaves and seeds were collected for *Ocimum lamifolium hochst* (Demakese), *Rhamnus prinoides* (Gesho), *Vernonia amygdalina* (Grawa), *Thymus schimperi* (Tosign), and *Trigonella foenum-graecum* (Abish). The herbs were carefully cleaned with water and allowed to dry for four days in a shaded place. The dried leaves were ground in a grinder. Following that, an analytical balance was used to weigh one gram of the dry powder. The samples were then dissolved in 50 milliliters of ethanol in a 100 ml volumetric flask, shaken with a magnetic stirrer for 30 minutes at room temperature, and then filtered using 0.75µm Whatman filter paper, with the first ten milliliters being discarded. The primary solution, which was a 5 ml aliquot, was then diluted with 25 ml of ethanol in a volumetric flask. After transferring a 2.5 ml second solution into a 25 ml volumetric flask, the flask was filled with ethanol. Using a 1 cm quartz cell and ethanol as a blank, the absorption spectra of materials in solution were measured between 290 nm and 320 nm. Every 5 nm, three assessments were made based on the absorption data collected using T80 UV-Vis spectroscopy in the range of 290nm to 320nm in vitro determination method. The Mansuer mathematical equation was then applied to determine the sun protection factor (SPF) of the chosen herbs.

CHAPTER FOUR

4. Result and discussion

4.1 SPF value determination of herbal extracts

Absorption: An atom in a lower level absorbs a photon of frequency hν and moves to an upper level.

T80 UV-Visible spectroscopy is used to measure the absorbance of the herbal extracts in the 290 nm - 320 nm range while using ethanol as reference. The following findings were produced.

Table4.3.Absorbance data of herbal extracts

Herbs	Wavelength with absorbance						
	290nm	295nm	300nm	305nm	310nm	315nm	320nm
DE	0.112±0.001	0.096±0.001	0.089±0.001	0.091±0.001	0.093±0.001	0.101±0.001	0.102±0.001
TO	0.186±0	0.163±0.001	0.149±0.001	0.138±0.001	0.131±0.001	0.13±0	0.129±0
GE	0.665±0.001	0.663±0.001	0.623±0.001	0.564±0	0.568±0.001	0.523±0.001	0.479±0.001
GR	0.187±0	0.184±0	0.183±0.001	0.185±0.001	0.19±0	0.202±0.001	0.212±0
AB	0.362±0.001	0.348±0.001	0.343±0.001	0.347±0.001	0.362±0.001	0.409±0.001	0.455±0.001

4.1.1 SPF of *Ocimum lamifolium hochst* (Demakese)

We calculated the sun protection factor of *Ocimum lamifolium hochst* (Demakese) leaf extract using Mansuer's mathematical equation.

$$SPF = CF \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda) \rightarrow mansuer\ equation$$

The value of CF=10 and $\sum_{290}^{320} EE(\lambda) \times I(\lambda)$ is also known and we got the value from Table 2.3.

And the results of the SPF at individual wavelengths (at every 5nm interval between 290 nm and 320 nm) are shown in Table 4.5 below.

Table4.4.Submission part value of *Ocimum lamifolium hochst* (Demakese**)**

D	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda) \times I(\lambda) \times Abs(\lambda)$
e	290	0.015	0.112±0.001	0.00168
m	295	0.0817	0.096±0.001	0.0078432
a	300	0.2874	0.089±0.001	0.0255786
k	305	0.3278	0.091±0.001	0.0298298
e	310	0.1864	0.093±0.001	0.0173352
s	315	0.0837	0.101±0.001	0.0088779
e	320	0.0180	0.102±0.001	0.001836

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{demakese} = 10 \times (\,0.00168 + 0.0078432 + 0.0255786 + 0.0298298 + 0.0173352 + \;0.0088779 + 0.001836\,)$$

$$SPF_{demakese} = 10 \times (0.093)$$

$$SPF_{demakese} = 0.93$$

- *SPF coverage (amount of UV protection ability in %)*[46]

  $\left(1 - \frac{1}{SPF}\right) 100\%$

- *SPF coverage* $_{demakese}$

  = $\left(1 - \frac{1}{0.93}\right) 100\%$

  → $(-0.075)100\% = -7.5\%$, *Demakese has less blocking capacity.*

4.1.2 SPF of *Rhamnus prinoides* (Gesho)

The SPF value of *Rhamnus prinoidesn* (Gesho) leaf extract is calculated using the Mansuer mathematical equation.

And the results of the SPF at individual wavelengths (at every 5nm interval between 290 nm and 320 nm) are shown in Table 4.6 below.

Table4.5.Submission part value of *Rhamnus prinoides* (Gesho)

	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda) \times I(\lambda) \times Abs(\lambda)$
Gesho	290	0.015	0.665±0.001	0.009975
	295	0.0817	0.663±0.001	0.0541671
	300	0.2874	0.623±0.001	0.1790502
	305	0.3278	0.564±0	0.1848792
	310	0.1864	0.568±0.001	0.1058752
	315	0.0839	0.523±0.001	0.0438797
	320	0.0180	0.479±0.001	0.008622

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{gesho} = 10 \times (0.009975 + 0.0541671 + 0.1790502 + 0.1848792 + 0.1058752 + 0.0438797 + 0.008622)$$

$$SPF_{gesho} = 10 \times 0.586$$

$$SPF_{gesho} = 5.86$$

- *SPF coverage (amount of UV protection ability in %)*[46]

  $$\left(1 - \frac{1}{SPF}\right) 100\%$$

- *SPF coverage* $_{gesho}$

$$= \left(1 - \frac{1}{5.86}\right) 100\%$$

→ $(0.82935)100\% = 82.935\%$ *, Gesho can block 82.935% of UV-B radiation.*

4.1.3 SPF of *Vernonia amygdalina* (Grawa)

The sun protection factor (SPF) of *Vernonia amygdalina* (Grawa) leaf extract can be calculated using Mansuer's mathematical equation.

And the results of the SPF at individual wavelengths (at every 5nm interval between 290 nm and 320 nm) are shown in Table 4.7 below.

Table4.6.Submission part value of *Vernonia amygdalina* (Grawa)

	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda) \times I(\lambda) \times Abs(\lambda)$
Grawa	290	0.015	0.187±0	0.002805
	295	0.0817	0.184±0	0.0150328
	300	0.2874	0.183±0.001	0.0525942
	305	0.3278	0.185±0.001	0.060643
	310	0.1864	0.19±0	0.035416
	315	0.0839	0.202±0.001	0.0169478
	320	0.0180	0.212±0	0.003816

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{grawa} = 10 \times (0.002805 + 0.0150328 + 0.0525942 + 0.060643 + 0.035416 + 0.0169074 + 0.003816)$$

$$SPF_{grawa} = 10 \times 0.187$$

$$SPF_{grawa} = 1.87$$

- *SPF coverage (amount of UV protection ability in %)*[46]

$$\left(1 - \frac{1}{SPF}\right)100\%$$

- *SPF coverage* $_{grawa}$

$$= \left(1 - \frac{1}{1.87}\right)100\%$$

→ $(0.4652)100\%$ = *46.52%, Grawa can block 46.52% of UV-B radiation.*

4.1.4 SPF of *Thymus schimperi* (Tosign)

In order to calculate the SPF value of *Thymus schimperi* (Tosign) leaf extract, we used the Mansuer mathematical equation.

And the results of the SPF at individual wavelengths (at every 5nm interval between 290 nm and 320 nm) are shown in Table 4.8 below.

Table4.7.Submission part value of *Thymus schimperi* (Tosign)

	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda) \times I(\lambda) \times Abs(\lambda)$
Tosign	290	0.015	0.186±0	0.00279
	295	0.0817	0.163±0.001	0.0133171
	300	0.2874	0.149±0.001	0.0428226
	305	0.3278	0.138±0.001	0.0452364
	310	0.1864	0.131±0.001	0.0244184
	315	0.0839	0.13±0	0.010907
	320	0.0180	0.129±0	0.002322

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{tosign} = 10 \times (0.00279 + 0.0133171 + 0.0428226 + 0.0452364 + 0.0244184 + 0.010907 + 0.002322)$$

$$SPF_{tosign} = 10 \times 0.142$$

$$SPF_{tosign} = 1.42$$

- ➢ *SPF coverage (amount of UV protection ability in %)*[46]

$$\left(1 - \frac{1}{SPF}\right)100\%$$

- *SPF coverage* $_{tosign}$

$$= \left(1 - \frac{1}{1.42}\right)100\%$$

→ $(0.296)100\%$ = *29.6%, Tosign can block UV-B radiation by about 29.6%.*

4.1.5 SPF of *Trigonella foenum-graecum* (Abish)

The extract of *Trigonella foenum-graecum* (Abish) seed SPF can be calculated using Mansuer's mathematical equation.

And the results of the SPF at individual wavelengths (at every 5nm interval between 290 nm and 320 nm) are shown in Table 4.9 below.

Table4.8.Submission part value of *Trigonella foenum-graecum* (Abish)

	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda) \times I(\lambda) \times Abs(\lambda)$
Abish	290	0.015	0.362±0.001	0.00543
	295	0.0817	0.348±0.001	0.0284316
	300	0.2874	0.343±0.001	0.0985782
	305	0.3278	0.347±0.001	0.01137466
	310	0.1864	0.362±0.001	0.0674768
	315	0.0839	0.409±0.001	0.0343151
	320	0.0180	0.455±0.001	0.00819

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{abish} = 10 \times (0.00543 + 0.0284316 + 0.0985782 + 0.01137466 + 0.0674768 + 0.0343151 + 0.00819)$$

$$SPF_{abish} = 10 \times 0.25$$

$$SPF_{abish} = 2.5$$

- *SPF coverage (amount of UV protection ability in %)*[46]

$$\left(1 - \frac{1}{SPF}\right) 100\%$$

- *SPF coverage* $_{abish}$

$$= \left(1 - \frac{1}{2.5}\right) 100\%$$

→ $(0.60)100\%$ = *60%, Abish can block 60% of UV-B radiation.*

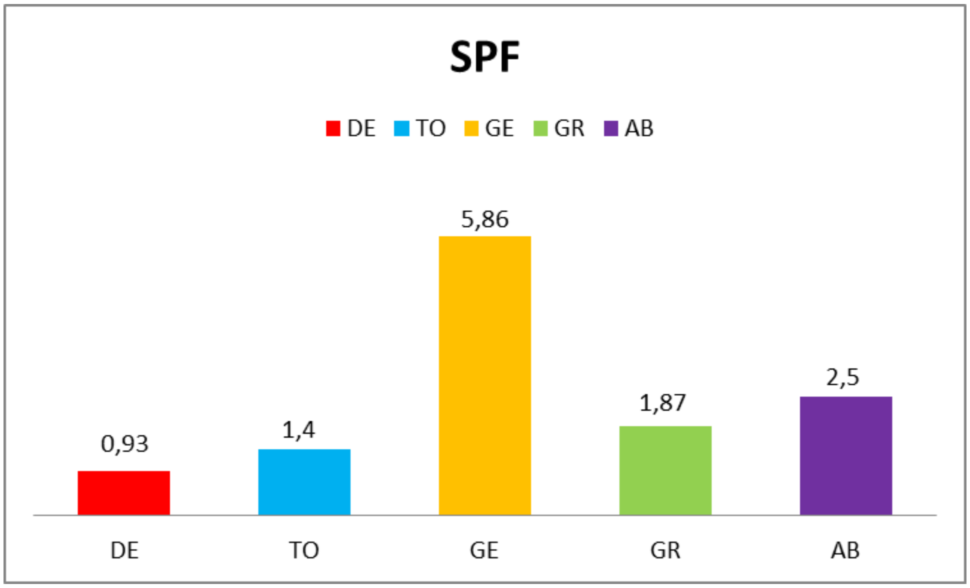


Figure4.6. The difference between five herbal extracts SPF.

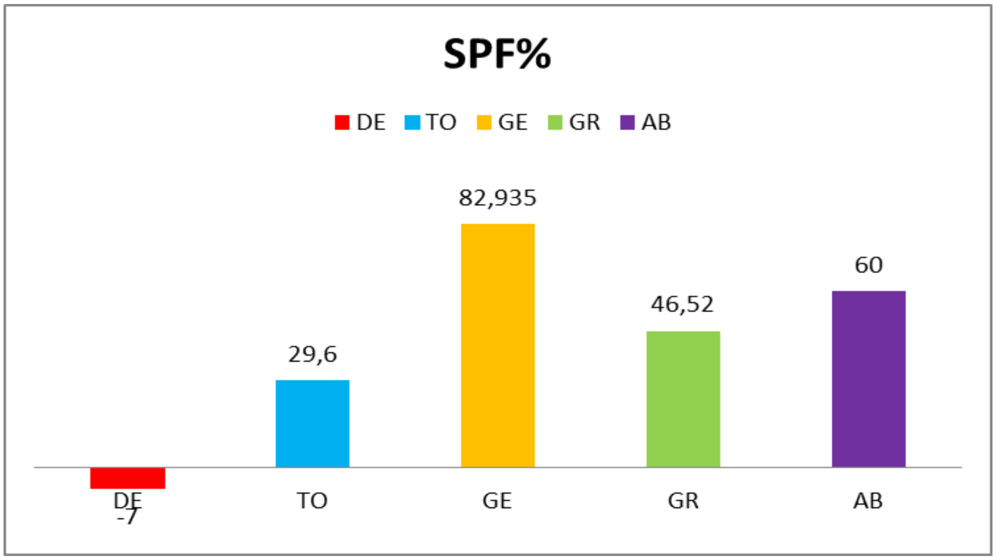


Figure4.7. SPF coverage (SPF %) of herbal extracts

4.2 SPF value determination of commercial sunscreens and body cream

T80 UV-Visible spectroscopy is used to measure the absorption of commercial sunscreens and body cream in the 290 nm- 320 nm range. Using ethanol as a reference produced the following findings.

Table4.9.The absorbance data of commercial sunscreens and body cream

Sample	Wavelength with absorbance						
	290nm	295nm	300nm	305nm	310nm	315nm	320nm
DR	0.99±0.001	1.102±0.01	1.073±0.001	1.041±0.001	1.118±0	0.988±0.001	0.944±0.001
SU	0.201±0.023	0.179±0.023	0.157±0.022	0.141±0.021	0.123±0.021	0.1±0.027	0.09±0.021
VA	2.364±0,007	1.611±0,077	2.276±0,003	1.489±0,062	2.273±0,008	1.46±0,027	2.198±0,009
DI	2.37±0.002	1.608±0.032	2.284±0.003	1.509±0.039	2.288±0.011	1.38±0.068	2.204±0.006

4.2.1 SPF of commercial sunscreen Dr. Rachel

In order to determine the SPF of Dr. Rachel's sunscreen, Mansuer mathematical equation was used.

$$SPF = \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda) \rightarrow mansuer\ equation$$

The Seyer's constant, the absorbance, and the product of Seyer's constant and absorbance at individual wavelengths in the range between 290 nm to 320 nm (at every 5nm interval) are shown in Table 4.11 below.

Table4.10.Submission part value of Dr. Rachel sunscreen

	λ(nm)	EE(λ)×I(λ)	Absorption	$EE(\lambda) \times I(\lambda) \times Abs(\lambda)$
Dr. Rachel	290	0.015	0.99±0.001	0.01485
	295	0.0817	1.102±0.01	0.095874
	300	0.2874	1.073±0.001	0.31823802
	305	0.3278	1.041±0.001	0.3412398
	310	0.1864	1.118±0	0.2083953
	315	0.0839	0.988±0.001	0.0828932
	320	0.0180	0.944±0.001	0.016992

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{rachel} = 10 \times (0.01485 + 0.095874 + 0.31823802 + 0.3412398 + 0.2083953 + 0.0826956 + 0.016992)$$

$$SPF_{rachel} = 10 \times 1.08$$

$$SPF_{rachel} = 10.8$$

- *SPF coverage (amount of UV protection ability in %)*[46]

  $\left(1 - \frac{1}{SPF}\right) 100\%$

- *SPF coverage* $_{rachel}$

  $= \left(1 - \frac{1}{10.8}\right) 100\%$

→ $(0.9074)100\% = 90.74\%$; *Dr. Rachel's sunscreen can block UV-B radiation by about 90.74%.*

4.2.2 SPF of commercial Supper white body cream

The SPF of Supper white can be calculated using Mansuer's mathematical equation.

The Seyer’s constant, the absorbance, and the product of Seyer’s constant and absorbance at individual wavelengths in the range between 290 nm to 320 nm (at every 5nm interval) are shown in Table 4.12 below.

Table4.11.Submission part of Supper White body cream

Supperwhite	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda)\times I(\lambda)\times Abs(\lambda)$
	290	0.015	0.201±0.023	0.003015
	295	0.0817	0.179±0.023	0.0146243
	300	0.2874	0.157±0.022	0.0451218
	305	0.3278	0.141±0.021	0.0462198
	310	0.1864	0.123±0.021	0.0229272
	315	0.0839	0.1±0.027	0.00839
	320	0.0180	0.09±0.021	0.00162

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm $\sum_{290}^{320} EE(\lambda)\times I(\lambda)\times Abs(\lambda)$ and multiply it by correction factor (CF) =10.

$$SPF_{supperwhit} = 10\times(0.003015+0.0146243+0.0451218+0.0462198+0.0229272 \\ +0.00837+0.00162)$$

$$SPF_{supperwhite} = 10\times 0.142$$

$$SPF_{supperwhite} = 1.42$$

- *SPF coverage (amount of UV protection ability in %)*[46]

  $\left(1-\frac{1}{SPF}\right)100\%$

- $SPF\ coverage_{\textbf{super white}}$

$= \left(1-\frac{1}{1.42}\right)100\%$

$\rightarrow (0.296)100\%$*=29.6%; Supper white body cream can block UV-B radiation by about 29.6%.*

4.2.3 SPF of commercial Valera sunscreen

The sun protection factor (SPF) of Valera sunscreen can be calculated using Mansuer's mathematical equation.

The Seyer’s constant, the absorbance, and the product of Seyer’s constant and absorbance at individual wavelengths in the range between 290 nm to 320 nm (at every 5nm interval) are shown in Table 4.13 below.

Table4.12.Submission part value of Valera sunscreen

	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda)\times I(\lambda)\times Abs(\lambda)$
Valera	290	0.015	2.364±0,007	0.03546
	295	0.0817	1.611±0,077	0.1316187
	300	0.2874	2.276±0,003	0.6541224
	305	0.3278	1.489±0,062	0.4880942
	310	0.1864	2.273±0,008	0.4236872
	315	0.0839	1.46±0,027	0.122494
	320	0.0180	2.198±0,009	0.039564

From the above information, we obtained the submission value. Now multiply it by the correction factor (CF) =10, making it easy to calculate the SPF of Valera sunscreens.

$$SPF_{valera} = 10 \times (0.03546 + 0.1316187 + 0.6541224 + 0.4880942 + 0.4236872 + 0.122494 + 0.039564)$$

$$SPF_{valera} = 10 \times 1.895$$

$$SPF_{valera} = 18.95$$

- *SPF coverage (amount of UV protection ability in %)*[46]

$$\left(1-\frac{1}{SPF}\right)100\%$$

- *SPF coverage* $_{Valera}$

$$=\left(1-\frac{1}{18.95}\right)100\%$$

$\rightarrow (0.9472)100\%$ = *94.72%; Valera's sunscreen can block UV-B radiation by about 94.72%.*

4.2.4 SPF value of Lady Diana commercial sunscreens

We calculate the value of Lady Diana sunscreens using Mansuer's mathematical equation.

The Seyer's constant, the absorbance, and the product of Seyer's constant and absorbance at individual wavelengths in the range between 290 nm to 320 nm (at every 5nm interval) are shown in Table 4.14 below.

Table4.13.Submission part value of Lady Diana sunscreen

	λ(nm)	EE(λ)×I(λ)	Absorbance	$EE(\lambda)\times I(\lambda)\times Abs(\lambda)$
Diana	290	0.015	2.37±0.002	0.03306
	295	0.0817	1.608±0.032	0.1313736
	300	0.2874	2.284±0.003	0.6564216
	305	0.3278	1.509±0.039	0.4946502
	310	0.1864	2.288±0.011	0.4264832
	315	0.0839	1.38±0.068	0.115782
	320	0.0180	2.204±0.006	0.039672

Then, now we can sum up all the values obtained at individual wavelengths at every 5nm interval between the range of 290 nm - 320 nm ($\sum_{290}^{320} EE(\lambda)\times I(\lambda)\times Abs(\lambda)$) and multiply it by correction factor (CF) =10.

$$SPF_{diana} = 10\times(0.03306+0.1313736+0.6564216+0.4946502+0.4264832 \\ +0.0115782+0.039672)$$

$$SPF_{diana} = 10\times 1.9$$

$SPF_{diana} = 19$

- *SPF coverage (amount of UV protection ability in %)*[46]

  $\left(1 - \frac{1}{SPF}\right)100\%$

- *SPF coverage* $_{diana}$

  $= \left(1 - \frac{1}{19}\right)100\%$

  $\rightarrow (0.9474)100\%$ = *94.74%; Lady Diana's sunscreen can block UV-B radiation by about 94.74%.*

The sunscreens and body cream used in this study have their own labeled sun protection factor (SPF), and during this study, an experimental SPF was also determined.

Table4.14. Comparison between labeled SPF and experimentally found SPF value

Sample	Labeled SPF	Experimentally found SPF
Dr. Rachel(sunscreen)	60++	10.8
Supper white(body cream)	30	1.42
Valera(sunscreen)	60	18.95
Lady Diana(sunscreen)	60	19

Table 4.15.Comparison between the commercial product's labeled SPF coverage and the experimentally found SPF

Sample	Labeled SPF%	Experimentally found SPF%
Dr. Rachel(sunscreen)	98.33%	90.74%
Supper white(body cream)	96.67%	29.6%
Valera(sunscreen)	98.33%	94.72%
Lady Diana(sunscreen)	98.33%	94.74%

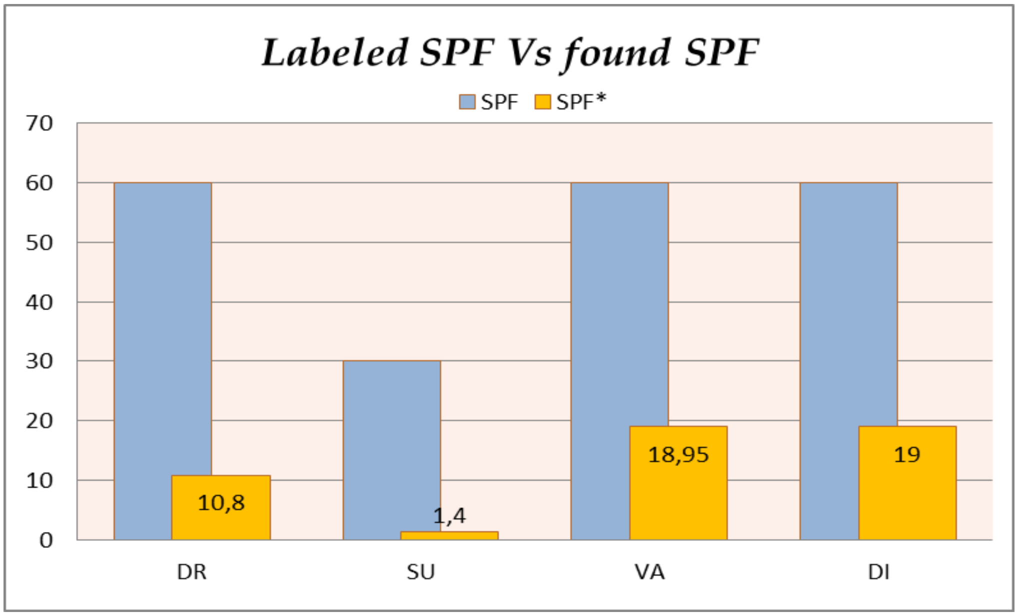
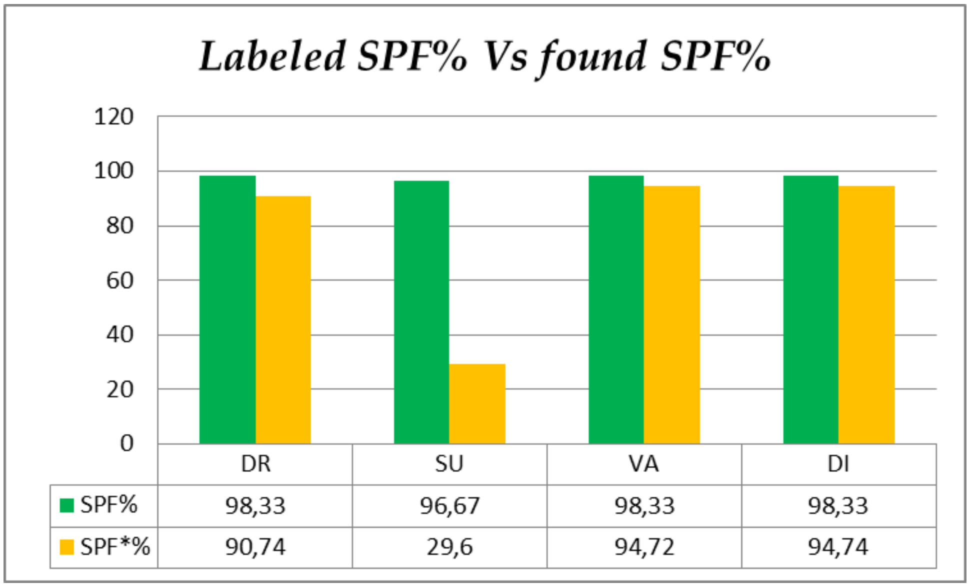


Figure4.8.Comparison between labeled SPF (SPF) and experimentally found SPF (SPF*)



	DR	SU	VA	DI
🟩 SPF%	98,33	96,67	98,33	98,33
🟨 SPF*%	90,74	29,6	94,72	94,74

Figure4.9.Comparison between the commercial product's labeled SPF coverage (SPF %) and the experimentally found SPF (SPF* %).

4.3 Discussion

The SPF rating tells us how long sunscreen will shield our skin from sunburn. In this investigation, UV-visible spectroscopy was used to analyze nine materials in vitro using the Mansuer equation. *Thymus schimperi* (leaf), *Rhamnus prinoides* (leaf), *Vernonia amygdalin* (leaf), *Ocimum lamifolium hochst* (leaf), and *Trigonella foenum-graecum* (seed) are among the herbal extracts whose SPF values are displayed in Fig. 4.6. In addition, Table 4.15 displays the SPF values of four commercial products, including body cream Supper White, sunscreen Lady Diana, sunscreen Valera, and sunscreen Dr. Rachel. The SPF numbers on the labels of these commercial products range from 30 to 60.

The SPF ratings for herbal extracts vary from 5.86 to 0.93. Sample GE had the greatest SPF value, around 5.86, while sample DE had the lowest SPF value, approximately 0.93. SPF values of 1.87, 1.4, and 2.5 on samples GR, TO, and AB, respectively, were discovered. This finding raises the possibility that these botanicals contain organic sunscreen compounds. They shield the skin from UV rays and have anti-inflammatory and antioxidant qualities. Herbal sunscreen formulas are multipurpose solutions that enhance the general health and attractiveness of the skin by providing extra skincare advantages, including hydration, antioxidant protection, and anti-aging qualities. Additionally, they are appropriate for people of all ages, including young children, old people, and babies. In their work *Pradhan et al.* [45], *Malsawmtluangi C et al.* [12] and *Chandaka et al.* [44] obtained significant results that herbal extracts have SPF values.

When it came to commercial items, sample SU showed the largest SPF value disparity. Sample SU's listed SPF was 30, but our test findings indicate that this product's SPF is actually only 1.4. Sample DI showed the least amount of variation in SPF values. This sample's advertised SPF was 60, yet the SPF determined after experimentation was 19. The values of the remaining samples (Valera and Dr. Rachel; 18.93 and 10.8) were within the DI and SU SPF ranges. Therefore, there is some discrepancy between the experimental SPF values of these samples and the SPF ratings listed on the product bottles' labels. In addition to casting doubt on the product's efficacy and dependability, this discrepancy also emphasizes the significance of clear and accurate sunscreen labels, strict quality control procedures throughout the manufacturing process, and the ways in which these elements raise the risk of sunburn, early aging, sun-related skin conditions, and skin cancer. Variations in sunscreen formulations can result in people's lack of proper protection from UV radiation, raising the risk of skin damage and skin cancer, particularly melanoma, the most fatal kind of the disease. Furthermore, certain sunscreen variations could not provide enough antioxidant defense, exposing the skin to the damaging effects of free radicals produced by exposure to UV light. Unstable chemicals called free radicals may harm DNA, proteins, and skin cells. They can cause oxidative stress, inflammation, and premature aging. This increases the likelihood of degradation, poor ingredient quality, or formulation issues. The results of the study by ***Zayd et al***. show that when they tested six different sunscreens, the SPF of each sample was lower than the SPF listed on the label. [43].

Chemical sunscreens aren't always helpful for some skin types since they contain chemicals like oxybenzone, benzophenone, and avobenzone that are bad for skin and expensive. Therefore, using products with a herbal base is the best alternative method of shielding the skin from the damaging effects of sun exposure. Comparing herbal extracts to synthetic sunscreens reveals several advantages. Because they come from botanical origins, herbs have been shown to be a safer and more natural option for sun protection. Also herbal formulations contain vitamins, antioxidants, and herbal extracts that help support skin health and vitality. Over time, this can result in a more radiant complexion. *Thymus schimperi, Rhamnus prinoides, Ocimum lamifolium hochst, Vernonia amygdalin, and Trigonella foenum-graecum* are among the medicinal herbs that Ethiopians have long used. This study suggests that these plants may provide some protection against solar radiation. As a result, sunscreen made of herbs is thought to be safer than one made of chemicals.

CHAPTER FIVE

5. Conclusion and recommendation

5.1 Conclusion

Sunscreens that contain chemicals are not good for all skin types because they are too expensive and contain chemicals that harm the skin. As a result, developing herbal sunscreens and assessing their ability to protect against sun damage are crucial tasks in the cosmetics industry. Excessive exposure to sunlight can also result in photo-aging, sunburns, oxidative damage to skin cells, and skin cancer. The UV-visible spectroscopy in vitro technique was used in this work to measure the sun protection factor of body cream, commercial sunscreens, and herbal extracts. Topical compounds called sunscreens can be applied to the skin to provide UV protection. The SPF value is used to quantify the effectiveness of sunscreen. When the computed SPF of the fully examined commercial sunscreen product was compared to the SPF numbers on the label, the findings were lower. Samples evaluated in this study were Lady Diana, Valera, Dr. Rachel, and Super White. Their SPF values were in the range of 30 and 60. However, after evaluating those samples, their experimental results were found to be 19, 18.95, 10.8, and 1.42. The results showed a discrepancy between the labeled SPF and the experimental SPF found. Imported sunscreens and body creams' efficacy varies, raising doubts about their consistency and effectiveness. As a result, herbal extracts can serve as a safer and natural alternative to artificial (chemical) sunscreens. It is noted that every herbal supplement examined shows some level of UV protection. In addition to potentially providing additional skin benefits, they also offer excellent UV protection. The wide range of bioactive components found in herbal extracts, such as flavonoids, phenolic compounds, and antioxidants, naturally have UV-absorbing and photo-protective properties, which are responsible for the reported effectiveness of these extracts. The suggested UV-visible spectrophotometric approach can be used to determine the SPF values in vitro in various cosmetic formulations. It is a simple, quick, and cost-effective method that requires inexpensive reagents.

5.2 Recommendation

- ✓ Herbs are the safest ingredients to block UV radiation and are more effective than synthetic ones. Therefore, in order to manufacture sunscreens at a reasonable price, Ethiopia needs to have cosmetic factories that use herbal ingredients.
- ✓ In Ethiopian markets, there should be quality control for sunscreen efficacy. EFDA (National Regulatory Body of Ethiopia), which is under the Ministry of Health and is in charge of ensuring the quality, safety, and efficacy of medications, food, cosmetics, and medical devices, must act appropriately in order to reduce the impact of sunscreen discrepancies.
- ✓ Apply a combination strategy: Create sunscreen formulations that incorporate herbal extracts with sunblock ingredients in an effort to potentially increase the effectiveness of sun protection while upholding safety and legal requirements.

Reference

[1] Mishra, A., Mishra, A.K., & Chattopadhyay, P. (2011). Herbal Cosmeceuticals for Photoprotection from Ultraviolet B Radiation: A Review. Tropical Journal of Pharmaceutical Research, 10(3), 351-360.

[2] Sax B.W. (2000). Educating Consumers about sun protection. Pharmacy Times, 66(5), 48-50.

[3] Dutra E-A., Oliveira D-A., Kedor Hackmann E-R., Santoro M.I. (2004). Determination of sun protection factor (SPF) of sunscreens by ultraviolet spectrophotometry. Brazilian journal of pharmaceutical sciences, 40(3), 381-385.

[4] Nitulescu G, Lupuliasa D, Adam-Dima I, Nitulescu GM.(2023). Ultraviolet filters for cosmetic applications. Cosmetics, 10(4), 101.

[5] Guan L.L., Lim H.W., Mohammad T.F. (2021). Sunscreens and photo aging: A review of current literature. American Journal clinical dermatology, 22(6), 819-828.

[6] Draganita, Ana Maria & Tiplica, George. (2012). Actualitati in potoprotectie advances in sunscreen products industry. DermatoVenerol., 57, 273-284.

[7] Wood C., Murphy E. (2000). Sunscreens efficacy. Global cosmetics industry, 167, 38-44.

[8] Harrison, S. C., & Bergfeld, W. F. (2009). Ultraviolet light and skin cancer in athletes. Sports health, 1(4), 335-340.

[9] Walters C., Keeney A., Wigal C.T., Johnstom C.R., Cornelius R.D. (1997). UV spectra and cost analysis of suntan lotions: A simple introduction to the use of recording spectrophotometers. Journal of chemistry education, 74, 99-101.

[10] Mansur, J. D. S., Breder, M. N., Mansur, M. C., & Azulay, R. D. (1986). Determination of sun protection factor by spectrophotometry. An Bras Dermatol, 61(3), 121-124.

[11] Sayre, R. M., Agin, P. P., LeVee, G. J., & Marlowe, E. (1979). A comparison of in vivo and in vitro testing of sun screening formulas. Photochemistry and Photobiology, 29(3), 559-566.

[12] Malsawmtluangi, C., Nath, D. K., Jamatia, I., Zarzoliana, E., & Pachuau, L. (2013). Determination of Sun Protection Factor (SPF) number of some aqueous herbal extracts. Journal of applied pharmaceutical science, 3(9), 150-151.

[13] Chaithanya, & Haneena, Ayshath & Azmeena, Kadeejath & Varghese, Sebastin. (2023). Characterization of Herbal Sunscreen Formulation, 11(7), 2455-6211.

[14] Scalbert, A., Manach, C., Morand, C., Rémésy, C., & Jiménez, L. (2005). Dietary polyphenols and the prevention of diseases. Critical reviews in food science and nutrition, 45(4), 287-306.

[15] Ye, Y., Sun- Waterhouse, D., You, L., & Abbasi, A. M. (2017). Harnessing food- based bioactive compounds to reduce the effects of ultraviolet radiation: A review exploring the link between food and human health. International Journal of Food Science & Technology, 52(3), 595-607.

[16] Nichols, J. A., & Katiyar, S. K. (2010). Skin photoprotection by natural polyphenols: anti-inflammatory, antioxidant and DNA repair mechanisms. Archives of dermatological research, 302(2), 71-83.

[17] Sander, M., Sander, M., Burbidge, T., & Beecker, J. (2020). The efficacy and safety of sunscreen use for the prevention of skin cancer. Cmaj, 192(50), E1802-E1808.

[18] Fourtanier, A., Moyal, D., Maccario, J., Compan, D., Wolf, P., Quehenberger, F., ... & Young, A. R. (2005). Measurement of sunscreen immune protection factors in humans: a consensus paper. Journal of investigative dermatology, 125(3), 403-409.

[19] B.K. Sherma. (2005). Instrumental methods of chemical analysis. GOEL, publishing house Meerut, 11-47.

[20] Hamouda, S. A., Ibrahim, M. K., & Mohamed, M. B. (2021). The Electromagnetic Spectrum: Knowledge and Experimental Techniques. Engineering and Scientific International Journal, 8(4), 156-158.

[21] Campbell, I. D., & Dwek, R. A. (1984). Biological Spectroscopy Benjamin. Cummings: Menlo Park CA, 102-106.

[22] W. Demtröder. (2014). Laser spectroscopy: basic principle.5th edition, 1, 234-235.

[23] Douglas, A.S., Donald, M.W., James, F.H. and Stanley, R.C. (2004). Fundamentals of Analytical Chemistry, 8th Edition.

[24] Robert, M.S., Clayton, G.B. and Terence, C.M. (1996). Spectrometric identification of organic compounds, 6th Edition, Wiley International.

[25] Banwell, C. N., & McCash, E. M. (2017). Fundamentals of molecular spectroscopy. Indian Edition.

[26] Kalsi, P. S. (2007). Spectroscopy of organic compounds. New age international.

[27] P. Gupta, S.S. Das, N. B. (2023). Singh. Spectroscopy, 12-13.

[28] Harris, D. C., & Bertolucci, M. D. (1989). Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy. Courier Corporation, 1, 130.

[29] Brooker, Geoffrey. (2021). The 'Einstein A and B coefficients', essays in physics: Thirty-two thoughtful essays on topics in undergraduate-level physics. Oxford, 228-239.

[30] Skoog, D.A. Holler, F.J., Nieman, D.A. (2004). Introduction to UV spectroscopy in, principle of instrumental analysis. 5th edition, Cole publication, 336-360.

[31] Smit P., Aniket R., Diya P., Diya P.,Mitali D.,Umesh U. (2022). A review on "Uv-Visible spectroscopy". International journal of pharmaceutical research and applications, 7, 1144-1151.

[32] Casadiego, R. P. (2022). Observing the absorption of ultraviolet radiation from the sun by oxygen from the atmosphere as the cause of global warming. Technology audit and production reserves, 5(3 (67)), 29-33.

[33] Li, S. (2021). Human skin characterization and analysis based on hyperspectral reflectance using machine learning (Doctoral dissertation, Université de Lyon), 13-14.

[34] Allen M.W. and Bain G. (2014). Measuring the UV protection factor of fabrics. Journal of natural fabrics, 6(4), 319-330.

[35] Santos, E. P., Freitas, Z. M., Souza, K. R., Garcia, S., & Vergnanini, A. (1999). In vitro and in vivo determinations of sun protection factors of sunscreen lotions with octylmethoxycinnamate. International journal of cosmetic science, 21(1), 1-5.

[36] Sahalie, N. A., Abrha, L. H., & Tolesa, L. D. (2018). Chemical composition and antimicrobial activity of leave extract of Ocimum lamiifolium (Damakese) as a treatment for urinary tract infection. Cogent Chemistry, 4(1), 1440894.

[37] Özgen, U., Mavi, A., Terzi, Z., Kazaz, C., Asçi, A., Kaya, Y., & Seçen, H. (2011). Relationship between chemical structure and antioxidant activity of luteolin and its glycosides isolated from T. sipyleus subsp. sipyleus var. sipyleus. Records of Natural Products, 5(1), 12.

[38] Amabye, T. G. (2015). Evaluation of phytochemical, chemical composition, antioxidant and antimicrobial screening parameters of Rhamnus prinoides (Gesho) available in the market of Mekelle, Tigray, Ethiopia. Nat. Prod. Chem. Res, 3(6), 1-5.

[39] Wall, M. E., Wani, M. C., Manikumar, G., Abraham, P., Taylor, H., Hughes, T. J.m& McGivney, R. (1988). Plant antimutagenic agents,Flavonoids. Journal of Natural Products, 51(6), 1084-1091.

[40] Zameer, S., Najmi, A. K., Vohora, D., & Akhtar, M. (2018). A review on therapeutic potentials of Trigonella foenum graecum (fenugreek) and its chemical constituents in neurological disorders: Complementary roles to its hypolipidemic, hypoglycemic, and antioxidant potential. Nutritional Neuroscience, 21(8), 539-545.

[41] Mbanga, L., Mulenga, M., Mpiana, P. T., Bokolo, K., Mumbwa, M., & Mvingu, K. (2014). Determination of sun protection factor (SPF) of some body creams and lotions marketed in Kinshasa by ultraviolet spectrophotometry. Int. J. Adv. Res. Chem. Sci, 1(8), 7-13.

[42] Chou, J., Robinson, T. J., & Doan, H. (2017). Rapid comparison of UVB absorption effectiveness of various sunscreens by UV-Vis spectroscopy. Journal of analytical & bioanalytical techniques, 8(2), 355.

[43] Zayd, H., Alsaeh, I. A., Mosa, F. A., & Ben-Hander, G. M. (2019). In-Vitro Evaluation of Sun Protection Factors of Sunscreens Marketed in Sirte by Ultraviolet Spectrophotometry. Journal Of Pure & Applied Sciences, 18(4), 2521- 9200.

[44] Chandaka Madhu, Abhakumari, G. Durga Sudeepthi, M. Chandra Shekhar, J. Vamshidhar Reddy, Madhuri Venigalla. (2015). Estimation of phytochemicals and sun protection factor (SPF) number in commonly used ethanolic herbal extracts. PHARMANEST, 6(2), 2754 - 2756.

[45] Pradhan, S. P., Adhikari, K., Nepal, S., & Pandey, B. P. (2020). Determination of sun protective factor of selected medicinal plants from Western Nepal. Journal of Nepal Chemical Society, 41(1), 51-55.

[46] Osterwalder, U., & Herzog, B. S. P. F. (2009). Sun protection factors: Worldwide confusion. British Journal of Dermatology, 161(3), 13-24.