

**EXTRACTION AND APPLICATION OF NATURAL DYES FROM
ROTHMANNIA WHITFIELDII (URI) AND *BAPHIA NITIDA* (UHIE)**

BY

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TEXTILE SCIENCE AND TECHNOLOGY**

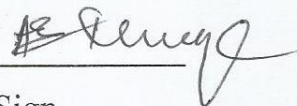
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CERTIFICATION

This is to certify that this work, “Extraction and Application of Natural Dyes from *Rothmannia whitfieldii* (Uri) and *Baphia nitida* (Uhie) was carried out by Nnorom, Onyekachi Onyinyechi (20134877718) in partial fulfillment for the award of the degree of Ph.D in Textile Science and Technology in the Department of Polymer and Textile Engineering, Federal University of Technology, Owerri.

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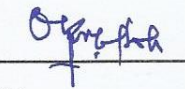
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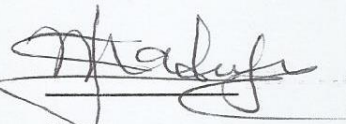
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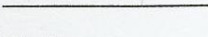

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DEDICATION

I dedicate this work to Almighty God who alone saw me through this work

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ABSTRACT

The renewed interest in natural dyes across the globe is due to some discoveries of environmental hazard and toxic effect of synthetic dyes to humans. Unfortunately, most natural dye yielding plants and their properties are neither known nor documented. In this research work dyes were extracted from locally prepared *Baphia nitida* plant cakes (*uhie*) and dry *Rothmannia whitfieldii* fruit (*uri*). Extraction methods used are water, alkali, organic acid and organic solvent at room temperature and at 65°C with a material to liquor ratio of 1:50. It was found that only alkali solution extracted dye from both plant sources while organic solvent extracted only from *uhie*. More dye was extracted at 65°C and the spectrophotometer results of wavelength of maximum absorption of the dye extracted by alkali were 620nm for *uhie* dye and 670nm for *uri* dye. Analysis of dye extracts in the area of fabric dyeing using alum ($\text{kAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) as mordant and sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) as reducing agent, FTIR spectroscopy and colour fastness to washing and rubbing indicated that both *uri* and *uhie* dyes tend to be direct dyes. Both dyes do not necessarily require mordant and reducing agent to dye a cotton fabric at room temperature and at 60°C. *Uri* dyes better at temperatures above room temperature. From FTIR spectroscopy the possible presence of conjugated double bonds were observed in both dyes and tannins only in *uri* dye. *Uri* dye had a better wet and rub fastness than *uhie* dye but similar wash fastness. Also both dyes did not stain adjacent cotton fabric during washing. However, there is a need to further purify both dyes and study their interactions with other fibres.

Key words: natural dye, FTIR spectroscopy, *uhie*, *uri*, colour fastness, maximum absorption, dye extraction.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Before the advent of synthetic dyes, natural dyes were used primarily for cloth dyeing. However, with the mass production of synthetic dyes and availability of different colour shades not found in natural dyes, the use of natural dyes reduced drastically. Also lack of documentation and less information available on database of dye yielding plants or their products affected the use of natural dyes especially in commercial scale (Singh & Purohit, 2012).

As a result of the toxic nature of some synthetic dyes, there have been renewed efforts to study and implement the use of the various natural dyes in the dyestuff industry. Natural dyes can be divided into three classes depending on their source. These include: animal, mineral, and plant dyes (some investigators add the fourth to include microbial dyes) although plant is the major source of natural dyes (Saxena & Raja, 2014). Irrespective of the source, natural dyes have been grouped into three application categories (Asian Secrets, 2012) namely:

- i. Substantive (or direct) dyes: these are dyes that do not require any mordant to fix them on the fibre.

- ii. Vat dyes: these are dyes that require reduction and oxidation to fix the dyes on the fibre.
- iii. Mordant (or adjective) dyes: these are dyes that require metal salts (especially salts of iron, copper, tin, aluminium and chromium) to fix them to the fibre.

This categorization is based on application of the dyes. Most natural dyes however belong to the group of mordant dye (Sequin-Frey, 1981). Natural dyes have complex chemical constituents and can be classified into six categories on the basis of chemical constituent as follows (Saxena & Raja, 2014):

- i. Indigoid dyes
- ii. Anthraquinone dyes
- iii. Naphthoquinone, benzoquinone dyes
- iv. Flavonoid dyes
- v. Carotenoid dyes
- vi. Tannin-based dyes

It has also been pointed out that natural dyes can be classified based on hue, that is colour (Saxena & Raja, 2014):

- i. Red colour dyes

ii. Yellow colour dyes

iii. Blue colour dyes

iv. Black colour dyes

There are about 500 plant species identified as dye source (Mishra, 2014). Some ancient plant dyes that are well-known include madder, a red dye from the roots of the *Rubia tinctorum*. Others are blue (indigo) extracted from the leaves of *Indigofera tinctoria*, yellow from the stigmas of the saffron plant, and dogwood, extracted from the pulp of dogwood tree (Practical Action, 2014). Those of animal source include secretions from insects like cochineal, dyes Fasan, from cow urine and secretions from shellfish. Mineral dyes are considered poisonous e.g. “geru” and are not in use anymore (Mishra, 2014).

In Nigeria, most natural dyes come from plants and have been extracted and used locally by local dye users (Osemeobo & Ujor., 1999). Nigeria has abundant resources in terms of plants which contain dyes in parts such as the roots, barks, leaves, seeds, fruits and flowers. Most of these plants have medicinal and dye potentials (Osabohien, 2009).

Two plants in Nigeria *Rothmannia whitfieldii* and *Baphia nitida* have been chosen for this research. *Rothmannia whitfieldii* fruit is called *uri* by the Igbos in the Eastern part of Nigeria where its juice was used for body decoration by women.

The seed and pulp of the fresh fruit is crushed and the fluid turns black when rubbed on the body and left for some time. This is an old art that is no more in vogue. The dye is said to be permanent (Jansen, 2005). Apart from its use for body decoration, it is used by the Igbos for the cure of *akpata* (measles). In some other African countries the fruit juice is applied to sores and wounds to promote healing, and to leprosy areas of the skin (Jansen, 2005).

Baphia nitida is a plant of red or orange colour wood that also has pharmacology value. The source of the dye which is soluble in alkali is the bark and heart of the tree (Gilles, et al. 2011). The locally prepared cakes called *uhie* by the Igbos can be mixed with other materials and rubbed on the skin of babies to smoothen their body.

1.2 Problem Statement

Natural dyes were used for dyeing of cloths before the advent of synthetic dyes. The commercial production of synthetic dyes of various shades made the use of natural dyes obsolete. However, it has been reported in several literature of the environmental hazard and toxic effect of synthetic dyes on the skin hence the renewed interest in natural dyes (Cardon, et al. 2006; Kasiri & Safapour, 2014).

Again, synthetic dyes are not readily available to the local colourist and home dye user since most of them have to be imported into the country. This also makes it costly and difficult for even some small scale textile industries to remain in business. Similarly, institutions of higher learning are not able to carry out some research work requiring dyes due to either unavailability of the original dye needed or the high cost of getting them.

Fresh *Uri* fruit and *Uhie* powder as earlier stated have been used mostly in Nigeria for body decoration and medicinal purpose with little interest in their cloth dyeing ability. Dry *uri* fruit has not been considered to be useful. Also with the advent of well researched pharmaceutical drugs and synthetic body decoration colourants, both plants have been neglected and are gradually becoming extinct especially in Nigeria. Similarly, the chemical composition and structure of the *Uri* dye is not known since little or no research work has been done in this area. Again the *Uri* and *Uhie* dye interaction with cotton fabric is not well known particularly in Nigeria. Similarly, there is limited knowledge on the right extraction method and application of the dye extracts on cotton fabric. All these affect the use of these dyes for the purpose of cloth dyeing.

Our local colourists in most cases do not fully understand the written instructions concerning the handling and application of synthetic dyes. This leads to wrong application and poor dyeing. This usually affects the quality of product and cost as

customers will either not buy the product or price it below its actual cost prize. In the same vein, wrong application of synthetic dyes leads to wastage of dye, especially due to poor dye exhaustion which puts the environment at a greater risk when such dye effluent is discharged into fresh drinkable water.

1.3 Objectives of the Study

The major objective of this research is to extract dyes from *Rothmannia whitfieldii* fruit (*Uri*) and *Baphia nitida* plant cakes (*Uhie*) and use them in the dyeing of a natural cotton fibre. The specific objectives of this research are as follows:

- i. To analyse and identify *uri* and *uhie* dye extracts scientifically.
- ii. To determine the effect of dye extraction method and temperature on extraction of dyes from *uri* and *uhie*.
- iii. To determine the effect of temperature in the dyeing of cotton fabric with *Uri* and *Uhie* dyes and the effects of washing and rubbing on the colour fastness of the cotton fabrics dyed with *uhie* and *uri* dyes.

1.4 Justification of Study

Uri and *Uhie* natural dyes can serve as good replacement to imported synthetic dyes. Understanding their dyeing behaviour will help to achieve this replacement.

Our environment will be safer when the operations of these dyes are well known. Unfortunately they are grossly neglected when it comes to cloth dyeing. The *uri* plant in particular may be at the verge of extinction in Nigeria, since many have taken to cutting the trees down since the use of *uri* dye for body decoration by women is no longer in vogue. Therefore, proper study of the *uri* dye and its application on fabric will awaken interest in the plant and save it from extinction. Such awakening can equally be achieved for the *uhie* as a good alternative for red/orange colour dye.

Also analyzing the *Uri* dye will properly show the class of dye and provide the much needed reason behind its colour and interaction with fabrics. These plants can be cultivated and the dyes easily extracted, thus making them readily available and cost effective. Local or home dye users who find it difficult to understand the dyeing instructions of synthetic dyes will find the use of such natural dyes simple and efficient to work with.

With the renewed interest around the globe on natural dyes, this research will be a great contribution to such global interest. Nigeria has in abundance the *uhie* cakes which have export value that can be harnessed. This research will provide a document on the *uri* and *uhie* dyes which can be consulted for academic and practical purposes.

1.5 Scope of the Study

Natural dyes could be extracted from various sources using different methods. However in this research, efforts will be made in extracting natural dyes from *Baphia nitida* plant cakes (*uhie*) and sun-dried mature *Rothmannia whitfieldii* fruit (*uri*). The extraction methods will be limited to aqueous extraction, solvent extraction, acid and alkali extraction using beakers for 45 minutes at room temperature and at 65°C in each case

Dye extract with the most intense colour will be characterized in three areas of exhaustion dyeing, colour fastness and Fourier Transform Infra-red (FTIR) spectroscopy. The wavelength of maximum absorption will also be ascertained using a spectrophotometer. Fabrics to be dyed will be limited to plain weave cotton fabrics.

All tests will be carried out in the Polymer and Textile Engineering Laboratory, Federal University of Technology, Owerri except for the FTIR spectroscopy which will be performed at the Chemical Engineering Laboratory, Ahmadu Bello University, Zaria and spectrophotometer tests at Zion Medical Laboratories, Owerri.

CHAPTER TWO

LITERATURE REVIEW

2.1 Previous Research on Plant Natural Dyes

The use of natural dyes in textile colouration is an age long practice especially by those who have little or no scientific knowledge of the constituents and behaviour of dyes. Dyes are coloured compounds capable of being introduced into/unto a fibre and fixed inside the fibre (Khatri et al., 2011). Dyes are also defined as organic chemicals that can selectively absorb and reflect light wavelengths within the visible light spectrum (Hatch, 1993). They attach to fibre either by absorption, adsorption or chemical reaction and are held in/on the fibre by ionic forces, hydrogen bonding, Van-der Waals forces or covalent chemical linkages (Whewell, 2011).

A compound has to possess the following properties in order to function as a dye (Christie, 2001):

(A) Intense colour: Two main parts of dyes responsible for colour are:

- I. The chromophore: This is the unsaturated part of the dye molecule. Usually, in textile dyes they are aromatic rings and azo groups.
- II. The auxochromes: These are the electron-donor or electron acceptor groups or atoms e.g. carbonyl (-CO) groups (as in anthraquinone), nitro (-NO₂) groups

- (i.e. electron acceptors) or phenol (-OH) groups, OMe, amine (-NH₂) groups, dimethylamino (-NMe₂) groups (i.e. electron donors)
- (B) Solubility in almost all cases, in an aqueous solution (either permanently or only during dyeing operations)
 - (C) Ability to be absorbed and retained by the fibre (substantivity) or to be chemically combined with it (reactivity)
 - (D) Fastness, that is, ability to withstand the treatment the fibre undergoes in manufacturing process and in normal use.

Natural dyes from different sources all possess these properties however, the difficulty in getting natural dyes in commercial quantity and wide variety of colours also contributed to its replacement by synthetic dyes. Nevertheless, the use of natural dyes is gradually regaining its lost glory especially due to its environmental friendliness. Many have undertaken to carry out research work on natural dyes from plant sources and reported the result of such research in various books and journals.

Investigations have shown the dyeing properties and functionality of non-aqueous dye extracted from *juniperus chinensis* heartwood (Nam & Lee, 2013). The red colour dye was extracted with methanol and showed relatively good affinity for silk and cotton fabric. It was observed that the dye uptake of both fabrics increased with increase in dye concentration and was highest at pH values of 8 and 6 for

cotton and silk respectively. However, only the dye uptake of silk increased with increase in temperature and time. Moreover, dyed fabrics showed various colours depending on mordant types and mordant concentration. Light, wash and perspiration fastness were not good. However, rubbing and dry cleaning fastness showed relatively good grade. In addition, dyed fabrics of ultraviolet-cut ability and deodorant ability were improved and also showed very good antimicrobial abilities of 99.9%.

Mordants are metal salts usually applied in dyeing with natural dyes either to improve colour fastness or to change colour shade of a natural dye. Some researchers have also studied the use of metal salts to produce different colours in fabrics dyed with tea leaves or marigold flowers (Mihalick & Donnelly, 2006). Some others delved into the comparison of aluminium mordants on the colour fastness of natural dye on cotton fabric (Haar et al., 2013). Aluminium potassium sulfate and Aluminium acetate, in three concentrations 5%, 10%, and 20% on-the-weight-of-fabric (owf) were evaluated for colour fastness to laundering and light of natural dye extracts (madder, weld, and coreopsis) on cotton print cloth. The outcome of the investigation showed that the type of aluminium mordant used had much effect on colour fastness to washing while the type of dye used had much effect on colour fastness to light.

The extraction of dye from Dapap tree (*Erythrina*) particularly *Erythrina Fusca* L and its application on cotton and silk have been studied (Mahmudi et al., 2014). Variables studied include dye fixation time (60, 90 and 150 minutes) using fixer solutions of FeSO_4 and CaCO_3 . Result obtained indicates dye to be red colour with FeSO_4 as a better fixer solution than CaCO_3 . Examination, characterization and chemical/biochemical analysis of natural dyes have been embarked upon by Samanta and Agarwal (2009). Extraction of dye from different plant sources, effect of different mordants and mordanting processes were all investigated, including the effect of conventional and non-conventional dyeing processes and colour yield. They further investigated the modification of textile substrate and improvement of fastness property of natural dyes. Their result showed that a lot of natural dye plant sources have remained untouched. Again that the colour of substrate dyed with natural dye does not depend only on natural dye colour but on mordant used and mordanting procedure followed. Evaluations of the efficiency of eight different procedures used for the extraction of natural dyes were embarked on by Manhita, et al. (2011). Contemporary wool samples dyed with cochineal, madder, woad, weld, brazilwood and logwood were used for the study. Among the tested methods, an extraction procedure with Na_2EDTA in water/DMF (1:1, v/v) proved to be the most suitable for the extraction of the studied dyes, which presented a wide range of chemical structures. They also went further to state that the identification of the

natural dyes used in the making of an eighteenth century Arraiolos carpet was possible using the Na₂EDTA/DMF extraction of the wool embroidery samples and an LC-DAD-MS methodology. The effectiveness of the Na₂EDTA/DMF extraction method was observed in the extraction of weld dye component. Hence, the identification of nine flavone derivatives in a single historical sample has proved that natural dyes can be used in the manufacture of arraiolos carpet.

The colour fastness properties of the flowers of *Erythrina Suberosa* dye used on wool have been studied (Singh & Purohit, 2012). This was done using mordants such as, lemon juice: copper sulphate, lemon juice: potassium dichromate, lemon juice: ferrous sulphate, lemon juice: stannous chloride in the ratio of 1:3, 1:2 and 3:1. Dyeing was done along with pre-mordanting, simultaneous mordanting and post-mordanting techniques. Due to different ratio of mordant and combinations various shades of colour were obtained. Colour fastness results gave fair to excellent fastness grades. The photofading behaviour of gardenia blue on cellulose has been examined (Oda, 2012). He examined the inhibiting effect of phenyl ester ultraviolet absorbers towards the photofading of gardenia blue on cellulose and reported that the presence of a simple ultraviolet absorber is not of particular value in improving the light fastness of natural dye, rather the introduction of a singlet oxygen quenching group (e.g. the nickel complex of 1- benzoyloxynaphthalene-3-sulphonic acid) into an ultraviolet absorber can have an important effect. Similarly,

the fading rates of some selected natural dyes have been studied (Crews, 1987). The fading rate curves of the selected natural dyes were constructed from colour difference measurements made using a tristimulus colourimeter. The result indicates that most natural dyes fade rapidly initially followed by a slower rate of fading. Also only the most lightfast natural dyes fade at a constant rate over time. The implications of this study for museum textiles were also discussed.

The need for a practical alternative to the common immersion method for natural dyeing propelled the investigation of contact dyeing (Kadolph & Casselman, 2004). Contact dyeing is a very low liquor ratio method of dyeing where the actual natural dyestuff is placed around and between the goods to be dyed. The dyestuff and goods are then compressed into a bundle that is placed in a plastic bag and heated by using steam, or microwave oven, or solar energy. The focus in contact dyeing is the use of innovative materials such as organic waste, found objects, and pantry or kitchen items. Appropriate dyestuffs, materials, and equipment are described, but specific results are unpredictable. This chance factor is the primary goal in contact natural dyeing which is to create complex, random patterns and colours easily and inexpensively, without the use of chemical mordants that are used during immersion methods using natural dyes (Kadolph & Casselman, 2004). Investigation of the ultra-violet (UV) protection properties of natural dyes; antibacterial and deodorizing properties of natural dyes; application of natural dyes

for textile printing; effect of different mordants and mordanting method and ultrasonic method of natural dyeing have been done (Rungruangkitkrai & Mongkholrattanasit, 2012). Dyeing with natural dyes using padding techniques; thermodynamics and kinetics of dyeing with natural dyes were also studied. Their result showed that application of natural dye through pad-dry and pad-batch techniques are excellent eco-option. Also that natural dye can give antibacterial/UV protection and a deodorizing effect. The use of natural dyes in printing on wool materials have been examined (Pragati, 2013). The natural dye imparted an eco-friendly and antibacterial quality on the wool. An eco-friendly dyeing of wool using a natural dye from weld together with a synthetic dye has also been reported (Mirjalili et al., 2011).

So much interest shown in the extraction and application of natural dyes has been reported (Grover & Patni, 2011). Studies were undertaken in the extraction and application of natural dye from the floral part of *woodfordia fruticosa*. Different extraction techniques were evaluated to determine the best extraction method. The dye colour obtained was dark yellowish-brown but gave different colour shades with varied mordant, fabric and yarn used. Investigation has also been done on the extraction of natural dye from green chili (*Capsicum annum*) plant (Kulkarni et al., 2011). Green chili main colouring agent is oleoresin. The dye was extracted using the solvent extraction method while the dyeing was done with two different

mordants; copper sulphate and ferrous sulphate. The mordants were used in the ratio 1:1, 1:3, and 3:1 with three mordanting techniques- pre-mordanting, simultaneous mordanting and post mordanting. The mordants produced different yellow shades of the chili dye, and gave good light fastness, good rub fastness and moderate wash fastness when the dye was applied on a 100% scoured cotton material. Calorimetric study on polyamide dyeing with weld and pomegranate peel natural dye has been carried out (Shams-Nateri et al., 2014). Nylon, a polyamide was dyed in four different ways termed: non-mordanting, pre-mordanting, meta-mordanting and after-mordanting. Aluminium potassium sulphate salt was used as mordant and the dyeing behaviour of the dye was assessed using calorimetric evaluations and colour fastness properties. They also studied the spectrophotometric properties by Principal Component Analysis (PCA). Their result shows that weld in comparison with pomegranate peel resulted in lighter and yellower colours. Again rubbing fastness in all dyed samples was excellent, while samples dyed with pomegranate peel showed better wash fastness properties. Also after-mordanting dyeing produced the best light fastness and overall fastness property. Cotton cloth was also dyed with natural dye extracted from pomegranate peel and its fastness evaluated (Satyanarayana & Ramesh, 2013). The extraction was achieved using ethanol/water mixture as a solvent in soxhlet apparatus.

Different tests were also conducted to observe the strength of dyeing and the results presented.

It is important to know the optimum condition for the extraction of natural dyes. A research on methods of finding the optimum condition for the extraction of indigo from leaves of *Indigofera tinctoria* and *Baphicacanthus cusia* Brem plants have been carried out (Chanayath et al., 2002). They also investigated the chemical constituent and chemical structure of the dye extract from both plants. This was done in order to develop an extraction method for preparation of ready-to-use dyes.

The preparation of dye bath and the use or non-use of mordant to provide a variation of colours has been investigated (Katz, 2011). He came up with a simple recipe on how it can be achieved by home craft dyers. Some other dyers have also investigated the use of some plants that naturally accumulate mordanting substances such as aluminium (Ellis, 2013). Different mordants can also be combined with a single dye bath to achieve different colour shades. The physical and chemical properties of some natural dyes produced by traditional means have been studied (Acquaviva et al., 2010). Four selected dyes, namely red (Madder), yellow (Weld and Turmeric) and blue (Woad) colours, produced by means of traditional techniques at the Museo dei Colori Naturali (Lamoli, Italy), were used for the investigation. The use of goldenrod dye to give a golden yellow colour on textile materials particularly yarns has been discussed by McKahan (2000). She

also discussed the harvesting techniques and the dye recipe. Review of the recent advancement in the application of natural dyes has been undertaken by Shahid et al., (2013). The review covers a period of fifteen years (1998-2013) with specific reference to technological development in natural textile dyeing and use of natural dyes in functional finishing of textiles, food colouration and dye-sensitized solar cells. Methods for the preparation of natural dye for use in the laboratory have also been presented (Wilson, 1999).

Natural dyes and their derivatives have been used as ecologically pure new generation dyes safer than synthetic arene based dyes (Zvezdina et al., 2010). New dyes obtained from chlorophyll and protoporphyrin derivatives include pheophorbide (a+b), chlorin e_6 , 6-N-(2-aminoethylamido) chlorin e_6 dimethyl ester, and 6-N-(2-aminoethylamido) deuteroporphyrin methyl ester. The dyes were tested in colouration of wool, cotton, and acetate fibres. The nonlinear properties of natural dyes: chlorophyll a and b have been examined (Kouissa et al., 2013). There has also been a report of the investigation of the oxidation of luteolin, a natural flavonoid dye (Ramea-Ova et al., 2013). As earlier stated in this work, natural dyes come from several sources and have different structures.

In a review of the sources and structures of colours used in Western historical textiles it was reported that most blue and purple colours were derived from indigo obtained either from woad or from the indigo plant (though some from other

sources e.g. shellfish and lichens were used) (Ferreira, et al. 2004). Reds were often anthraquinone derivatives obtained from plants or insects. Yellows were almost always flavonoid derivatives obtained from a variety of plant species. They further stated that most other colours were produced by what they called “over-dyeing” e.g. greens were obtained by over-dyeing a blue with a yellow dye. They concluded that direct analysis of dyes isolated from artifacts allows comparison with the historical record.

An attempt has been made to optimize the process of dyeing polyester (PET) fabric with natural dyes (Shahin & Ahmed, 2014). In order to check the dyeability of polyester to natural dye, it was first treated with NaOH solution for natural dyes extracted from Rhubarb; *Rheum officinale* plant was used to dye the fabric. From their result, they noticed that the colour strength of the PET fabric increased as a result of the alkali treatment which may be attributed to the alteration in the hydrophobicity of polyester fibre. They also observed that the natural dyes displayed the characteristics of disperse dyes. Furthermore, addition of salicylic acid to the dye bath accelerated the rate of dyeing and subsequently higher colour strength was attained. Non- ionic dispersing agent was also used to ensure better dyeing uniformity and higher dispersion stability of dye liquor. The most effective parameters that may affect the dye uptake of the natural dye on alkali-treated PET fabric and the final dyeing properties including dye bath pH, dyeing temperature

and time were investigated. The dyeability of PLA fabric with natural dye emodin has also been investigated by Wu & Ke (2011)

Natural dyes have been extracted from the leaves and stems of *Alpinia blepharocalyx* K. Schum and used for dyeing of silk material (Wang et al., 2013). The reported analysis of the designed experiment revealed that extraction at a plant/water ratio of 1:20 could reach an optimal production of natural dyes when extraction was performed at 80°C, for 4 hours, under 20 minutes ultrasound, in the presence of 10g/l sodium hydroxide, and with two extractions. The extracted natural dyes were applied to the dyeing of silk fabrics using different methods, with or without a mordant. The result indicated that mordants have a significant effect on the colour of dyed silk fabrics. The silk fabric dyed with the pre-mordant method using potassium aluminium sulphate as a mordant showed a bright yellow with a higher colour strength and the optimal dyeing conditions reached when the extracted natural dyes were pre-mordanted with 10g/l potassium aluminium sulphate at pH 6, and for a 20 min dyeing time.

The natural staining berries of *Phytolacca americana* L. plant have been analyzed and used for dyeing (Park and Jung, 2014). Five different mordants including copper acetate, aluminium potassium sulfate, sodium tartrate plus citric acid, Iron II sulfate and potassium dichromate were combined during dyeing. The results show that extracted dye from the berries stained silk fabrics with ivory implying

that the original purple colour from the berries disappeared and transformed into ivory. But the silk fabric dyed in a combination with mordants of aluminium potassium sulfate, sodium tartrate plus citric acid and potassium dichromate were stained differently. In addition, only differences in lightness and darkness were observed. Remarkably, the combination of the dye from the berries with a mordant of copper acetate and Iron II sulfate induced the staining of the silk fabrics into khaki and dark khaki, respectively. Park & Jung (2014) stated that this study is the first systemic report on staining silk fabrics with *Phytolacca americana* L.-berries and chemical mordants and suggest application of natural products to the fibre industry.

A research work has been carried out on the chemical modification of natural dyes and their application on textiles (Drivas, 2008). This was done in order to come up with ways of reducing the use of synthetic dyes. Alizarin and purpurin plant dyes were used for dyeing and the dyed samples subjected to two colour fastness tests: laundering, and artificial light: Xenon arc fading lamp test. The dyes were used on PET and PLA fabrics and the bonding forces operating between the dyes and the substrate were examined. Extracts of two forest trees *Bixa orellana* and *Caesalpinia sappan* have been evaluated and their application on cotton fabric examined (Divya et al., 2013). In this study dyes were extracted from the bark of *C. sappan*, seeds of *B. orellana* and a combination of both plant parts. The photochemical compounds

present in the dyes were analyzed using thin layer chromatography (TLC). From the result it was observed that carotenoids were in Bixa Orellana while Caesalpinia Sappan contains anthocyanin, phenolic acids and flavonoids. The extracts were applied on cotton fabric using various natural and synthetic mordants and the colour fastness to rubbing and washing tested. According to the report, this study is to help improve the natural dye resources and to proffer environmental safe replacement for synthetic dyes.

In another development, rare earth was used as mordant for the dyeing of ramie fabrics with four different natural dyes (Zheng et al., 2011). The effect of pre-mordanting, simultaneous mordanting and post mordanting dyeing methods were studied. The result indicated that highest dye uptake by the fabrics was obtained with the post mordanting method. In addition the effects of dyeing conditions such as dyeing temperature and time, dye bath pH and the concentration of rare earth on the dye uptake were investigated systematically. The result proved that fabrics dyed with natural dyes in presence of rare earth as mordant exhibited high colour shade stability in the dye baths with pH varying from acidic to neutral and alkaline. It was also observed that use of rare earth as mordant improved the colour fastness to washing, rubbing and light of the ramie fabrics dyed with the natural dyes. A comparison of rare earth mordant to the commonly used metallic mordants showed that the use of rare earth chloride as mordant can greatly reduce the ionic

concentration used in natural dyeing. According to Zheng et al., (2011) this study proved that rare earth can be an environmentally friendly mordant in natural dyeing.

The application by padding of cotton fabric with 10 g/l of two natural dyes derived from the Acacia plant family has been researched (Ratnapandian et al., 2012). Of the three mordanting techniques used post-mordanting gave the most even shade. Also among the two mordants employed, copper sulfate produced a level light brown shade at 15 g/l concentration while ferrous sulfate performed best at 5 g/l yielding a yellow-grey shade. In addition the result indicate an optimum process-sequence for the copper sulfate mordant as "pad (dye) → dry → steam followed by pad (mordant) → steam → dry", and for ferrous sulfate it was "pad(dye) → steam → dry followed by pad (mordant) → steam → dry". As expected, a change in mordant resulted to a change in shade by same dye. The team concluded that padding is a readily adaptable process for the dyeing of cotton using natural dyes and acceptable fastness in shades can be obtained.

2.2 Natural Dye Extraction Methods

Extraction refers to the separation of the desired colour component by physical or chemical means with the aid of a solvent (Samanta & Konar, 2011). The colour component of plants must be extracted before it can be properly applied as a dye

on a textile material. The roots, bark, leaf, fruits, stem and flower of plants contain in addition to colouring matter compounds other components such as water-insoluble fibres, carbohydrates, proteins, chlorophyll, and tannins hence the need for extraction (Saxena & Raja, 2014). Reducing the size of dry plant material either by grinding, pounding or cutting aids better release of the colour component from the plant material. This is due to a more intimate contact of the plant particles with the extracting solvent/solution (Osabohien, 2009).

Some of the natural dye extraction methods include (Saxena & Raja, 2014):

- i. Aqueous extraction
- ii. Alkali or acid extraction
- iii. Microwave and ultrasonic assisted extraction
- iv. Fermentation
- v. Solvent extraction
- vi. Super critical fluid extraction.

2.2.1 Aqueous extraction

This involves the soaking of the plant material with water in a vessel. The extraction is done under varying conditions such as time of extraction, material to

liquor ratio, temperature of extraction bath, particle size of plant material etc. (Samanta & Konar, 2011)

2.2.2 Alkali or Acid extraction method

Extraction in this case is done under dilute acidic or alkaline condition under various conditions. This is achieved by adding acid or alkali in aqueous medium and using such prepared solution at a known pH for extraction.

2.2.3 Super critical fluid extraction

In this extraction method, a gas functions as a supercritical fluid above its critical values of temperature and pressure. The physical properties of such fluids are somewhere between those of a liquid and a gas. They are able to spread out along a surface more easily than a true liquid because they have much lower surface tension than liquids. Again their viscosity is low hence they have very good diffusivity and thus better interaction with the substrate (Saxena & Raja, 2014).

Supercritical fluid with carbon dioxide (CO₂) as a solvent is an alternative to chemical solvent extraction method (Saxena & Raja, 2014; Samanta & Konar, 2011). It is nontoxic, cheap, easily available, and does not leave residues. Supercritical extractions using CO₂ is operated at temperatures between 32 and 49°C and pressures between 1,070 and 3,500 psi. CO₂ is a nonpolar molecule and

behaves as a nonpolar organic solvent. A co-solvent or a modifier may be added to improve the solubility of slightly polar solutes (Saxena & Raja, 2014).

2.2.4 Microwave and Ultrasonic assisted extraction

This involves the use of ultrasound or microwave to improve the extraction of natural dye in a reduced aqueous or solvent medium. Time and temperature requirements are also reduced resulting to low energy usage (Saxena & Raja, 2014).

2.2.5 Fermentation

In this method enzymes produced by microorganisms in the atmosphere or those present in the natural dye source are used to ferment the dye source when soaked in water for extraction for long period of time. The most common example of this type of extraction is indigo extraction. Fresh or semi-dry natural dye source is used in this case. The enzymes disintegrate and release the colouring matter from the natural source (Saxena & Raja, 2014).

2.2.6 Solvent extraction method

Organic solvents such as acetone, methanol, ethanol, ethyl ether are used in soaking the natural dye source for extraction. It is also possible to use mixture of solvents, solvent and water or solvent and acid/alkali at a certain ratio. Such

mixtures can extract both solvent soluble and solvent insoluble substances from the plant/natural dye source. This method mostly does not require heating (Saxena & Raja, 2014).

2.3 Natural Dye Application Techniques

Natural dyes are applied to textiles usually by dyeing since they are majorly extracted in aqueous media and used immediately. Indigo may be the only exception to this. If natural dyes will be used at a later time it is converted to powder form or concentrated solid for easy storage and also to maintain the same dye hue in dyeing (Saxena & Raja, 2014).

Basically there are three methods of dyeing textiles (Leube, 2003)

- i) Mass dyeing: dyeing of a synthetic polymer before fibre formation.
- ii) Pigment dyeing: affixing an insoluble colourant on the fibre surface with a binder.
- iii) Exhaustion dyeing: from an aqueous bath with dyes that have affinity for the fibre.

In exhaustion dyeing, the material to be dyed is in contact with the dye liquor throughout the dyeing process. The dye which is soluble or slightly soluble in the

dyebath is selected and progressively absorbed by the material until equilibrium is reached (Schonberger & Schafer, 2003). Dye first moves to the surface of the fibre before diffusing into the fibre and depending on the dye-fibre interaction it is fixed chemically or physically.

Two methods of dye application to textile in exhaustion dyeing are the continuous and the discontinuous process. In both cases dyeing is achieved by immersing the textile in a concentrated dyebath for a particular time interval with or without heating and squeezing off excess liquid (padding) after which separate procedures for diffusion and fixation in the fibre are applied. The liquid phase which transports the dye in textile dyeing is water (Leube, 2003).

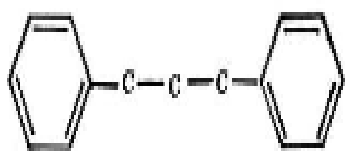
Under the exhaustion dyeing method, natural dyes depending on their class can be dyed with or without the aid of a mordant. Fibres can be pre-mordanted that is, applying mordant before dyeing; post-mordanted that is, applying mordant after dyeing or simultaneous mordanting that is, applying mordant during dyeing. The metal ions of mordants form complexes between the fibre and the natural dye. The process therefore enhances dye uptake, improves colour fastness and in most cases creates different hue from the original dye hue (Sequin-Frey, 1981).

In vat dyeing, a reducing agent is required to make them soluble in water. After dyeing the fabric is left in the open to oxidize or sometimes an oxidizing agent is

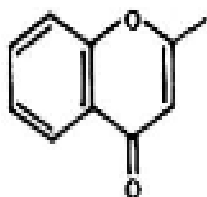
used to convert the dye into its water-insoluble form inside the fibre (Vat Dyes, retrieved 2014).

2.4 Structure of Natural Dyes

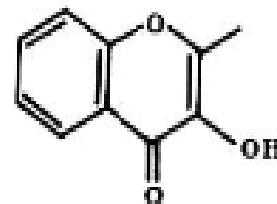
Flavonoid (yellow): All flavonoids contain $C_6-C_3-C_6$ however, the sub-groups providing plant colour are the flavones, flavonols, isoflavones, chalcones and the catechins; below are some structures (Sequin-Frey, 1981).



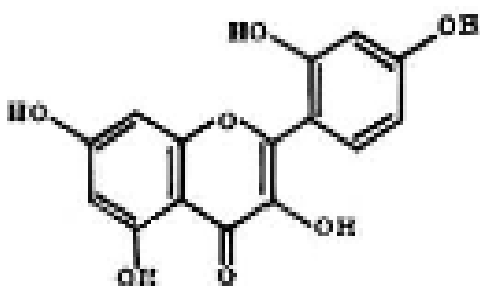
Flavonoid skeleton



Flavones



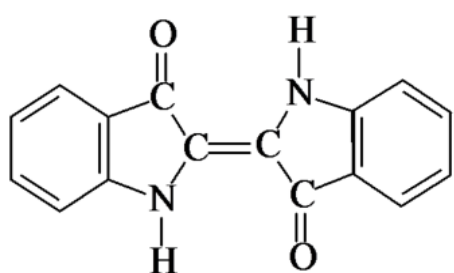
Flavonols



Morin, the yellow dye from fustic (*chlorophora tinctoria*)

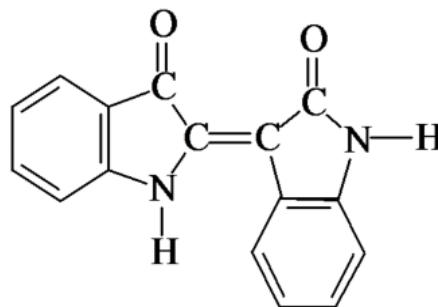
Fig. 2.1: Flavonoid (yellow) constituents

Indigo dye (blue): the main constituents are indigotin and indirubin as shown below (www.nptel.ac.in 2014). Indigo is an example of a natural vat dye used in textile dyeing years before synthetic dyes were first manufactured (Sequin-Frey, 1981).



(I)

Indigotin

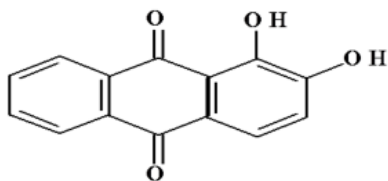


(II)

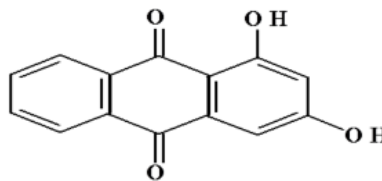
Indirubin

Fig. 2.2: Indigo dye constituents

Red dye: the major constituents of madder a red dye are anthraquinone, alizarin, purpuroxanthin, rubiadin, manjistin, purpurin, pseudopurpurin (www.nptel.ac.in 2014)



Anthraquinone



Alizarin

Fig. 2.3: Madder dye constituents

Brazilin (C.I. Natural Red 24): this is the major colour constituent of ceasalpinia echinata (Brazil wood) and ceasalpinia sapan. L (sappan wood); the structure is shown below (www.nptel.ac.in 2014)

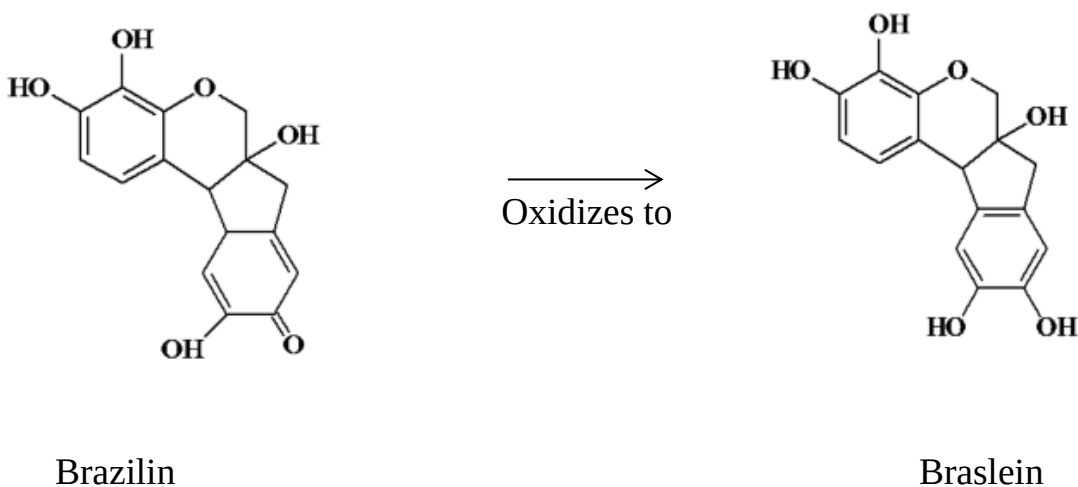


Fig. 2.4: Brazil wood constituents

Carotenoids: the colour is due to long conjugated double bonds. Annatto and Saffron are examples (www.nptel.ac.in 2014).

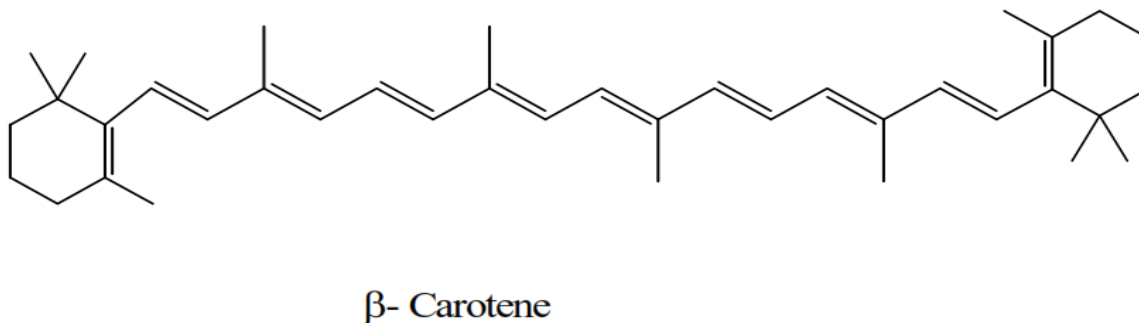


Fig. 2.5: Carotenoids constituent

2.5 Advantages and Disadvantages of Natural Dyes

Natural dyes have several advantages some of which were highlighted by dye researchers as follows (Samanta & Konar 2011):

- a) Natural dyes produce colour shades that are usually soft, lustrous and soothing to the human eye.
- b) A small variation in the dyeing technique or the use of different mordants with the same dye can give several colour ranges or create totally new colours, which are not easily possible with synthetic dyestuffs. Hence natural dyes can give a wide range of colours
- c) Natural dyes are usually renewable, being agro-renewable/vegetable based and at the same time biodegradable. This is unlike the raw materials for synthetic dyes.
- d) The waste in the dye process in some cases can be used as agricultural manure thus solving the problem of waste disposal.
- e) Natural dye industry is labour intensive, thereby providing job opportunities for all those engaged in cultivation, extraction and application of these dyes on textile/food/leather etc.
- f) Application of natural dyes has potential to earn carbon credit by reducing consumption of fossil fuel (petroleum) based synthetic dyes.

- g) Natural dyes are not toxic to the skin and mostly non-hazardous to human health.
- h) Some of the natural dyes are enhanced with age, while synthetic dyes fade with time.
- i) Natural dyes do not stain other fabrics when they bleed, turmeric being an exception.
- j) They are usually not attacked by moth and can replace synthetic dyes in kid's garments and food-stuffs for safety.

Disadvantages associated with natural dyes include, use of toxic mordants and poor wash colour fastness (Burch, 2005). Some other problems include the difficulty in reproducing exactly the same colour shade from the same natural dye, lack of enough scientific information on most natural dyes, difficulty in standardizing a recipe for the use of natural dye, difficulty in producing in commercial quantity for most natural dyes. However, these disadvantages have become the reason for most research work on natural dyes. There are also literature reports on breakthroughs in some of these areas of disadvantage (Samanta & Konar, 2011).

2.6 Some Plant Sources of Natural Dyes in Nigeria

Some of the plant sources of natural dyes in Nigeria have been documented as non-wood forest products of Nigeria and they include (Osemeobo & Ujor, 1999):

Pterocarpus Soyauxii (osisi uhie),

Pterocarpus erinaceus,

Baphia nitida (osisi uhie),

Rothmania whitfieldii (osisi uri),

Lawsonia inermis (lalle),

Anonidium mannii,

Bixa orellana,

Hurungana madascariensis,

Pterocarpus Osum,

Cyanastrum cordifolium,

Lonchocarpus cyanedeens,

Rothmanis hispida.

2.7 Uri Plant and Previous Research on Uri Dye

Rothmannia whitfieldii (synonym: *Randia malleifera*) known as *Uri* in the eastern part of Nigeria is a plant of the Rubiaceae family. The plant is found within tropical Africa from Senegal to Sudan and in the southern part of Africa: Angola and Zimbabwe (Jansen, 2005). Descriptively, it is a shrub or small tree of up to 15 m tall. The fruit juice and fresh seeds contain a blue-black dye, which is widely used in tropical Africa as a cosmetic for body decoration, to mark an outline for tattooing and to rub into tribal markings in the skin to make them more conspicuous. Jansen reported that no chemical study of the colourants or dye-precursors present in the flowers and fruits is available for *Rothmannia whitfieldii*, however he presumed that the fruit pulp contains alkaloids with dyeing properties like several other *Rothmannia* species with similar uses. He also reported the medicinal properties of the plant in several countries where it occurs.

Uri fruit is a globose berry of 3–7 cm in diameter, with smooth to strongly 10-ribbed, velvety brown pubescent when young but glabrescent. It has many-seeds crowned by the persistent calyx. The seeds are lens-shaped with a dimension of 7–11 mm × 3–4 mm.

There are about thirty different species of *rothmannia* which include (Jansen, 2005):

Rothmannia engleriana: small tree with fruits 2–5 cm long, found in Angola, DR Congo, Zambia, Malawi, Mozambique, Tanzania and Burundi. The ripe fruit is edible; it is juicy, sweet and aromatic. An infusion of the roots is used against stomach ache and snake bite. The wood is used as firewood and to make tool handles and spoons.

Rothmannia fischeri: shrub or small tree up to 8 m tall, fruits 3–6 cm long, found in Kenya, Tanzania, DR Congo, Malawi, Zambia, Zimbabwe and South Africa.

Rothmannia hispida (synonym: *Randia hispida*.): shrub or small tree up to 10 m tall, fruits 6–11 cm long, occurring from Guinea to DR Congo. The wood on cutting and exposure to the air takes on a blue colour. In Nigeria, leaf sap and fruit juice are used to draw black designs on the body and to blacken tattoos. When mixed with palm oil, they are applied on the skin against fungal infections.

Rothmannia lateriflora: shrub or small tree up to 8 m tall, fruits cylindrical, 5-ribbed, up to about 6 cm × 4 cm, occurring in Cameroon, Gabon and DR

Congo; among the Mongo of DR Congo, the juice of the fruit is used to blacken tattoos.

Rothmannia lujae (synonym: *Randia coriacea*): tree up to 30 m tall, fruits 15–20 cm long, occurring from Nigeria to DR Congo; seeds are used in Nigeria to make a dye used by women for painting patterns on the skin; a bark decoction is drunk against abdominal troubles; the bark, leaf and root contain some tannin.

Rothmannia macrosiphon: shrub or small tree up to 7 m tall, fruits 2–3 cm long, occurring in Kenya and Tanzania; the fruit yields a blue-black dye.

Rothmannia manganjae: shrub or small tree up to 15 m tall, fruits 2–4 cm long, occurring in Kenya, Tanzania, Mozambique, Malawi and Zimbabwe. This species closely resembles *Rothmannia longiflora* but has a much shorter corolla; sterile or young flowering specimens of both species are particularly hard to distinguish.

Rothmannia munsae (synonym: *Randia megalostigma*, *Randia lane-poolei*): shrub or tree up to 17 m tall, fruits up to 7 cm long, occurring from Sierra Leone to Cameroon and DR Congo.

Rothmannia octomera: shrub or small tree up to 2 m tall, flowers 7–8-merous, fruits sub-cylindrical, up to 14 cm long, occurring from Nigeria to

DR Congo; in DR Congo and Nigeria, the fruit juice is used to draw black designs on the body and to blacken tattoos; pulped roots are applied against pneumo-bronchial troubles in Congo.

Rothmannia urcelliformis: shrub or small tree, up to 15 m tall, fruit up to 10 cm long, widespread all over tropical Africa; in Ethiopia, in the province of Illubabor. The fruits are crushed and boiled in water to obtain a blue dye for cloth; they contain the iridoid alkaloid gardenamide A. Its fruits are said to be poisonous and have some molluscicidal property. The powdered dry fruits are used alone or mixed into a hunting poison in Central African Republic.

Rothmannia longiflora: Shrub or small tree up to 9 m tall, often with climbing stems. From the fruits, branches and leaves however, 4-oxonicotinamide-1-(1'- β -D-ribofuranoside) has been isolated. This N-glycoside is only known from human urine and has never been isolated from other higher plants.

2.8 *Baphia nitida* Plant and Previous Research on *Uhie* Dye

Uhie is actually an Igbo name for red colour and is the name given to the locally made *Baphia nitida* plant cakes (due to its colour) sold in Nigerian local markets.

Incidentally, red colour dye can be extracted from different trees with particular names. Some of such trees in Africa include:

- i. *Pterocarpus soyauxii*: This tree is found in the South-Eastern Nigeria, Eastern DR Congo, and Northern Angola and belongs to the family of the Papilionaceae (Fabaceae) (Jansen, 2005). Some of its vernacular names as reported by Jansen are, African padauk, and barwood. While its English names include redwood, large fruited camwood, Gabon padouk, barwood, African padouk, African coralwood (Orwa, et al., 2009). Further report stated that *Pterocarpus soyauxii* is a hard wood and the source of its dye is from the heartwood. The dye is still used today to colour red fabrics, fibres and cloth. Dye extracted from the roots and heartwood is lumbered. Dye can also be extracted by pounding bark in a mortar or in natural holes in rock, the pulverized material is then water moistened and molded for sale as cakes (Orwa et al., 2009). The tree is however listed as “endangered” by Rainforest Alliance (Bowman, 1992).
- ii. Others are Benin camwood (*Baphia pubescens*) and *Pterocarpus erinaceus*, *Baphia massaiensis* (used as source of red dye for leather hides) (Jansen, 2005).
- iii. *Baphia nitida* is another important tree that yields a red colour dye. Nigerian local names for it include Aboshi (Igbo), Irosun (Yoruba), and Ubara (Efik)

(Okoro, 2012). Giles and Okoro reported that *Baphia nitida* is also known as camwood belonging to the family of Papilionaceae (Fabaceae) (Gilles et al., 2011; Okoro, 2012). Insoluble red colour dyes can be extracted mainly from the heartwood and roots but soaking the bark in water also yields red dye (Jansen, 2005). According to Jansen, between the 17th and 18th century *Baphia nitida* was exported in large quantity in the shape of logs to Europe and North America where it was used for wood work and as a major source of redwood dye for wool, cotton and silk. While in Africa, it was used majorly as body paint believed to have magical and medicinal powers. He also stated that the principal dyeing substances are the isoflavonoid-flavonoid dimers, santalins A and B and santarubins A, B and C, but several other compounds such as baphic acid, baphiin, deoxysantarubin, homopterocarpin, maackiain, pterocarpin and santal possibly also contribute to the colouring properties. In addition, the Colour Index (C.I) number of the dye is 75560 and classified as Natural Red 22, together with other redwoods. The tree is about 9m tall however most of the previous research work on *Baphia nitida* is in the area of its pharmacological importance.

However, there has been an identification of some redwood species of historical importance in textile dyeing using high performance liquid chromatography and UV/Vis spectrometry detection analytical approach (Surowiec et al., 2004). The

result of the investigation shows that the group of extracted dyestuffs considered as "insoluble" because of their non-aqueous or alkaline extraction conditions were present in the wood of the *Pterocarpus* family and *Baphia nitida* species. Also, the crude extracts of tinctorial and related species and their chromatographic fingerprints were studied and the result indicates that some species not yet mentioned in literature have potential dyeing properties. Subsequent investigation on the redwood cargo of a 200-year-old archaeological shipwreck allowed identification of the water-logged wood species. Furthermore, the different methods of dyestuff extraction used for dyeing according to traditional recipes and their impact on analytical results were studied. From the outcome it was observed that standard recovery obtained by acid hydrolysis of dyestuff from dyed yarns is inadequate hence, alternative solvent-based procedures were proposed. This made it possible for identification of species in textile threads. The applied approach was validated by analysis of dyed reference yarns with some indications of crude material extraction mode. They concluded that the employed method of analysis was useful for "insoluble" wood species identification in cultural heritage artifacts as well as for phytochemical purposes, notwithstanding that very few detected colour compounds were chemically identified.

Recent research on the chemical nature of the red dyes isolated from *Pterocarpus santalinus* and certain West African plants, such as *Baphia nitida*, *Pterocarpus*

osun and *Pterocarpus soyauxii*, have been reviewed (Banerjee & Mukherjee, 1981). They reported that *P. santalinus* contains santalins A, B and C, but no santarubin. Also that santalins and santarubins were found in *P. osun*, *P. soyauxii* and *B. nitida*. The structural formulae of the santalins were presented and their differences from santarubins indicated. Furthermore, the report showed that santalins A and B have some similarities in structure with hematein which is probably responsible for their staining properties; the possible mechanism of staining was examined. The use of *Baphia nitida* extract as a Histological Stain for Interglobular Dentine, Striated Muscle, and Counter staining have been examined (Fasan, 1972). For the investigation, shavings of the dried heartwood of the tree *Baphia nitida* were ground to a fine powder, and 6g of the powder extracted in 100 ml absolute ethanol at 27–30°C for 6–24 hr. The extract was filtered with Whatman no. 1 paper and stored in a screw-capped bottle. In order to stain the interglobular dentine of nondecalcified sections of formalin-fixed teeth, sawed cross sections 20–30 µ thick were dehydrated in ethanol and stained in the undiluted extract for 6–12 hr. at room temperature. From the result, the interglobular dentine was stained a bright golden brown on a pale brown background. Also for staining striated muscle, the extract was diluted 1:1 with distill water and filtered. A mordant was used for the formalin-fixed paraffin sections with 0.25% KMnO₄ for 5 min, and bleaching was done with 5% oxalic acid for 10 min., after which they

were washed in water and stained for 2–24 hr. at room temperature. The result shows that the striations were stained light to deep golden brown. In addition, for use as a counter stain, a 1:6 dilution of the original extract was required. When applied after haematoxylin for 15–30 min, it stained tissue components in varying shades of golden brown with distribution comparable to that produced by 1% eosin.

Dyes have been extracted from *pterocarpus santalinus* using response surface methodology (Hemanthraj et al., 2014). This method was used in order to investigate the optimal conditions for dye extraction. Factors such as extraction temperature, extraction time, and solid to liquid ratio were identified to be significantly affecting natural dye extraction efficiency. They optimized conditions for dye extraction by different techniques such as Solvent, Ultrasonic and Microwave extraction by using three-level three-factor box-behnken design. From the result, microwave assisted extraction method showed the highest natural dye yield percentage which is 50.0 for ethyl acetate solvent and 50.2 for methanol solvent.

2.9 Chemistry of Cotton Fibre

Cotton is composed of about 90 percent of cellulose and serves as one of the main sources for cellulose with its fibres containing polymer chains of cellulose both in amorphous and crystalline forms (Bittar, 2015). Cellulose is a polysaccharide consisting of a linear chain of several hundred or over ten thousand $\beta(1-4)$ (that is, beta-glucose monomers) linked D-glucose units. It has the formula $(C_6H_{10}O_5)_n$ where n is a very large number. Its molecular and chain structure shows that cellulose is derived from D-glucose units, which condense through $\beta(1-4)$ glycosidic bonds (Bittar, 2015).

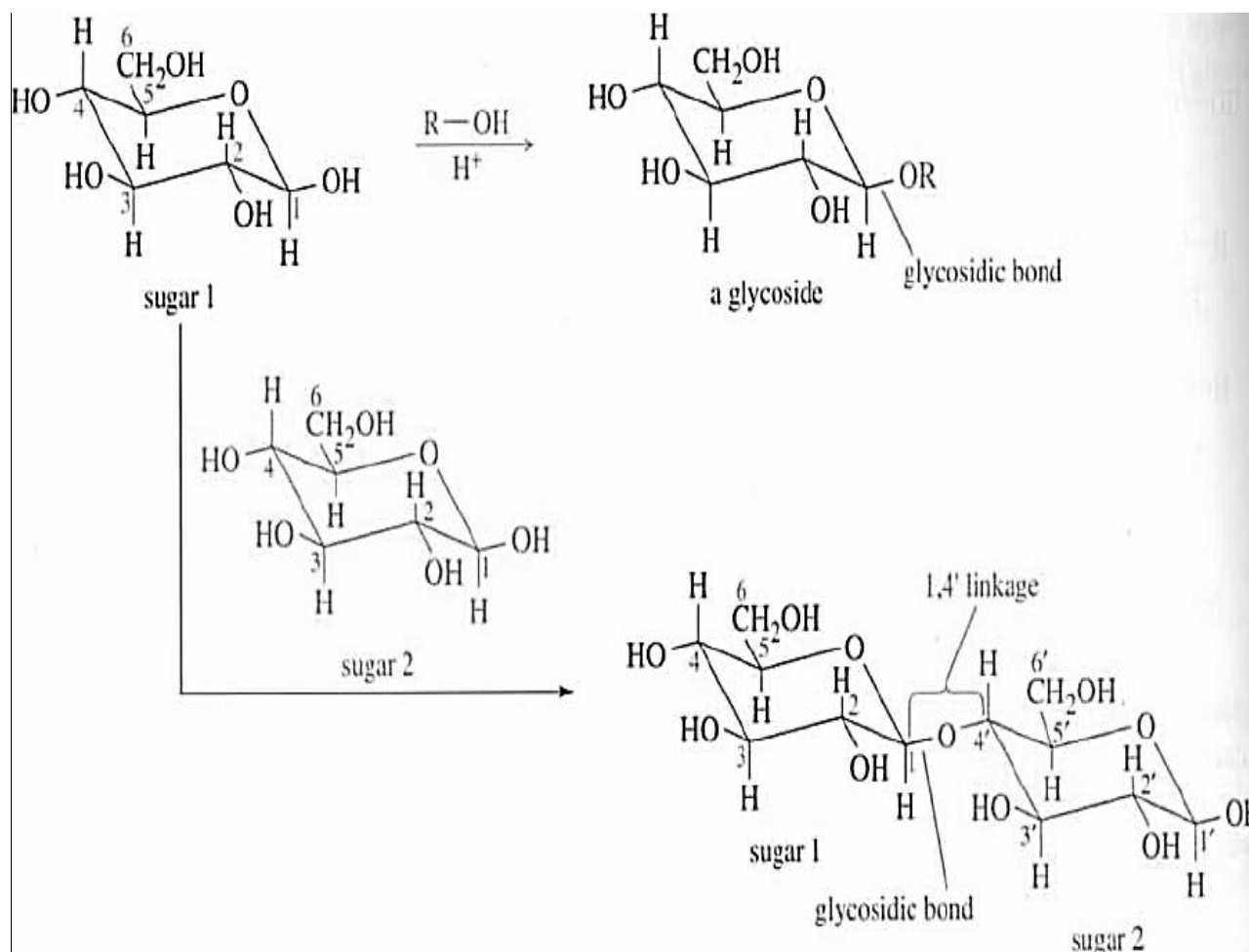


Fig. 2.6: Condensation of D-glucose unit

Cellulose can also be said to be a polydisperse linear homopolymer, consisting of regio- and enantio selectively β -1,4-glycosidic linked d-glucopyranose units (anhydroglucose units[AGU]). H-NMR spectroscopy has shown that the β -D-glucopyranose adopts the C_1 chain conformation, the lowest free energy conformation of the molecule. As a result, the hydroxyl groups are positioned in the ring plane (equatorial), while the hydrogen atoms are in the vertical position

(axial). The polymer contains free hydroxyl groups at the C-2, C-3, and C-6 atoms (Klemm et al., 2015).

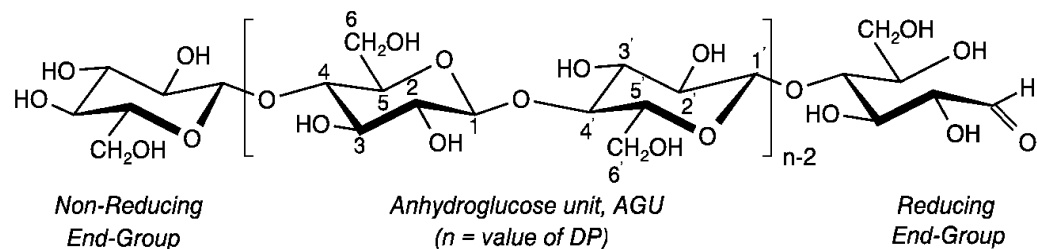


Fig. 2.7: Cellulose polymer unit

Cotton fabrics are therefore fabrics produced with cellulose fibres from cotton plant and taken through the process of cleaning, spinning, weaving, wet-treatment, dyeing and finishing.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The following materials were used for this research:

- Cotton fabric (88 ± 1 warp and 80 ± 1 weft per inch)
- Distill water
- *Uri* plant fruit
- *Uhie* (cakes, wood and powder)
- Sodium chloride (NaCl)
- Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$)
- Potassium aluminium sulphate [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$]
- Sodium hydroxide (NaOH) pellets
- Citric acid ($\text{C}_6\text{H}_8\text{O}_7$)
- Iso-propanol [$(\text{CH}_3)_2\text{CHOH}$]
- Bar soap

The materials were sourced from different markets and shops within Nigeria. About 1.8m length of plain weave desized and bleached cotton fabric was bought from the Owerri main market. The *Uhie* (cakes) and the *Uri* fruit pod were sourced from Owerri main market, Relief market Owerri, and Upper Iweka market Onistha. *Baphia nitida* wood and powder not fully processed were sourced from Ogbomoso, Oyo State. The chemicals were bought from Pac Besh Scientific Co (Nig.) located in Owerri while the distill water was sourced from Chemisciences Nigeria Ltd. along Wetheral Road Owerri.

The apparatus used for this research include the following:

- ✚ Thermometer (110⁰C maximum)
- ✚ Water bath: Thermostatic water cabinet. Model: HH size 64x35x31cm
- ✚ Spectrophotometer: Visible Spectrophotometer 728; wavelength range 320nm to 1020nm (from Zion Medical Laboratories, Owerri)
- ✚ Beakers (100ml, 250ml and 1000ml)
- ✚ Electronic weighing balance: Setra BL-410S (from PTE dept. Laboratory, FUTO)
- ✚ Measuring cylinder (100ml, 250ml)
- ✚ Stop watch (from PTE department Laboratory, FUTO)
- ✚ Grey scales for change (from PTE department Laboratory, FUTO)
- ✚ Grey scales for staining (from PTE department Laboratory, FUTO)

- ✚ Crockmeter (from PTE department Laboratory, FUT0)
- ✚ pH paper
- ✚ Sample test bottles
- ✚ Stirrer
- ✚ Kitchen knife
- ✚ Automatic pipette (from Zion Medical Laboratories, Owerri)
- ✚ Rotadyer Machine (from PTE department Laboratory, FUT0)
- ✚ Yarn counting magnifying glass (from PTE department Laboratory, FUT0)
- ✚ Colour matching chamber (from PTE department Laboratory, FUT0)
- ✚ FTIR machine (from Chemical Engineering department ABU, Zaria)
- ✚ White synthetic fabric (160 ± 1 warp and 86 ± 1 weft per inch)
- ✚ Manual sieve ($600 \mu\text{m}$) (from Soil and Erosion Laboratory, FUT0)
- ✚ Centrifuge (from Zion Medical Laboratories, Owerri)

3.2 Methods

The objectives of the research were achieved as shown below:

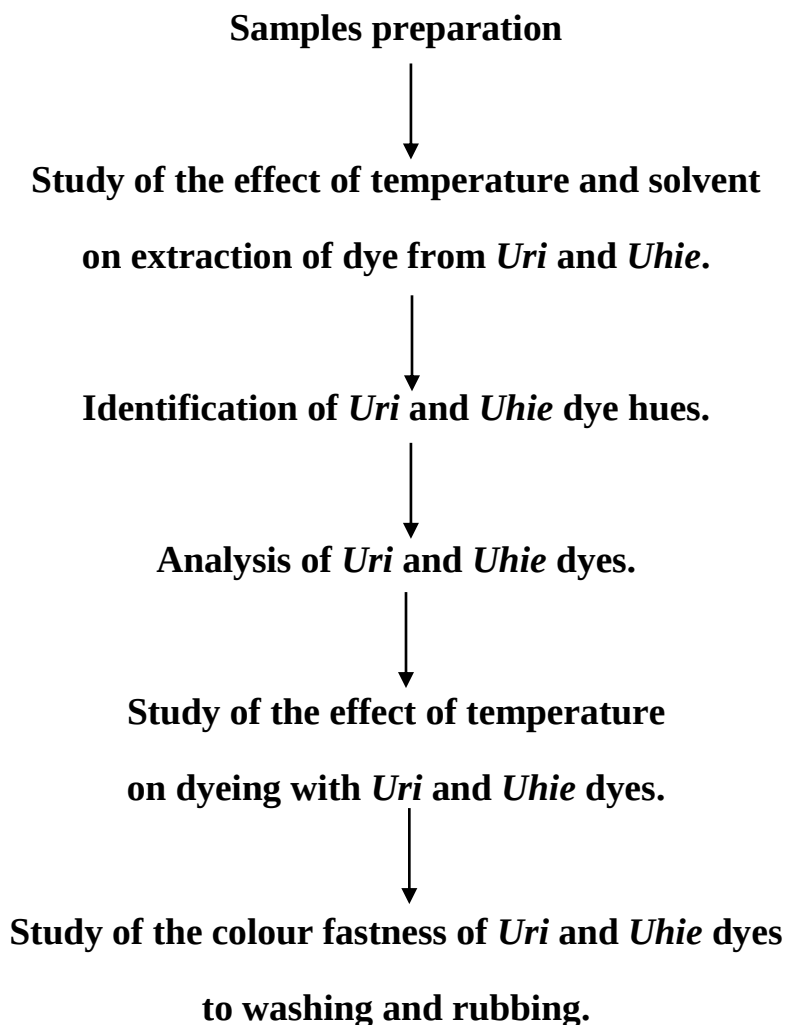


Fig. 3.1 Research work flow chart

Most of the works in this research were carried out in the Polymer and Textile Engineering department Laboratory FUTO with some done outside FUTO where the equipment required was readily available.

3.2.1 Samples Preparation

The cotton fabrics were cut with scissors and weighed with an electronic weighing balance. The cut fabrics were carefully trimmed and weighed again to obtain the required weight of fabric.

Ground pulp and seed of dry *Uri* fruit pod was used for the dye extraction. The pod is about 3-7cm in diameter with about ten distinct ridges and several seeds inside. The seeds and pulp of fresh *Uri* fruit were dried under the sun before grinding them. The required weight of the *uri* fruit powder for each test was weighed out using the electronic weighing balance. The *uri* powder was first sieved manually at the Soil and Erosion Laboratory in FUTO with a sieve of 600 μ m aperture size before weighing out the required powder weight for the test.

The *Uhie* cakes were produced using a grinding stone to grind the *Baphia nitida* plant wood (with bark removed) which was mixed with water and molded with hand into cakes. The cakes were later crushed to powder and sieved manually at the Soil and Erosion laboratory in FUTO with a sieve of 600 μ m aperture size before weighing out the required powder weight for the test.

For the alkali and acid solution preparation the equation 3.1 (www.chem.ccu.edu) was used:

$$\text{Mass percent} = \frac{\text{weight of solute (g)} \times 100}{\text{weight of solute} + \text{weight of solvent (g)}} \quad 3.1$$

1% alkali solution was prepared by dissolving 1g of sodium hydroxide pellets in 99ml of distill water. While 1g of citric acid pellets were dissolved in 99ml of distill water for preparation of 1% acid solution. The pH of both the alkali and acid solutions were checked with a pH paper.



Fig. 3.2 *uhie* cakes



Fig. 3.3 Dry *uri* fruits

3.2.2 Study of the effect of Solvent and Temperature in the Extraction of dye from *Uri* and *Uhie*

The test was carried out with a solid to liquor ratio of 1:50 (g:ml) using water, alkali solution, acid solution and iso-propanol. The tests were carried out at room temperature and at 65°C. The absorbance of each of the extracts with significant colouration was also ascertained.

i. At Room Temperature ($27 \pm 2^{\circ}\text{C}$)

1g of *uhie* plant powder was put in a 100ml beaker after which 50ml of distill water was added and the solution stirred. Extraction was done for 45minutes before carefully draining the supernatant liquid using a white synthetic fabric as sieve. The liquid drained was stored in a sample test bottle.

The above procedure was followed while using 1% alkali solution, 1% acid solution and iso-propanol as solvents. The same procedure was also followed while extracting from *uri* plant powder.

ii. At 65°C

50ml of distill water was poured into 100ml beaker. The beaker with the water was put in a water bath with temperature set at 65°C . The beaker was left in the water bath until the distill water temperature got to 65°C when measured with a thermometer. 1g of the *uhie* powder was then added to the beaker and stirred. After 45 minutes of extraction the supernatant liquid was drained using a white synthetic fabric as sieve and stored in a sample test bottle.

The above procedure was followed while using 1% alkali solution, 1% acid solution and iso-propanol as solvents. The same procedure was also followed while using *uri* plant powder.

iii. Absorbance of Extracts

Absorbance of extracts was taken using the spectrophotometer and the procedure used was as follows:

The spectrophotometer was first blanked with the particular solvent or solution used for extracting any of the dyes before taking their absorbance readings. Three 1cm² cuvettes that could contain about 2.5ml of fluid were used; one to contain the blank, another to contain dye extracted at room temperature and the last to contain the dye extracted at 65°C.

An automatic pipette was used to put the blank and the dye extracts in their respective cuvettes. The spectrophotometer was then set to a particular wavelength between 400nm to 800nm at which absorbance readings can be taken for a particular extract. It is then blanked before the absorbance readings of the dye extracts at that particular wavelength was taken and recorded.

For *uri* dye extracted with distill water, distill water was used as blank and pipetted into the first cuvette. The *uri* dye extracted with distill water at room temperature was also pipetted into the second cuvette while the *uri* dye extracted at 65° C was pipetted into the third cuvette.

The spectrophotometer was then set to a particular wavelength at which the absorbance readings were taken. Absorbance readings at different wavelengths

with interval difference of 10nm were taken and recorded. The above procedure was used only for dye extracts with significant visible colour.

3.2.3 *Uri* dye extraction using Fermentation and Traditional method

i. Traditional Method

Fresh or semi dry *uri* fruit pod was used for this. The seed and pulp were brought out from *uri* fruit, cut open with a kitchen knife. The seed and pulp were crushed manually with a little quantity of water added after crushing. The thick paste was drained using a white synthetic fabric. Water was added to the plant materials held by the fabric and drained again.

ii. Fermentation Method

The seed and pulp of semi dry *uri* fruit pod were cut into small pieces put in a small bowl and covered with water. The bowl was then covered with a black polyethylene bag and kept for four days to ferment.

The fluid of the fermented *uri* was drained after the four days and centrifuged for 20 minutes at a speed of 3000 rpm. The centrifuged fluid was allowed to stand for a day without any agitation.

3.2.4 Identification of *Uri* and *Uhie* dye Colours.

The colour of *uri* and *uhie* dye extracts to be used for dyeing at different temperatures (see 3.2.6) was identified visually and with a spectrophotometer. The colour of the dye extracts on cotton fabric was also considered in the visual identification of hue. The hue of the *uri* dye extracted with water was also scientifically identified using the spectrophotometer. This test was carried out a day after dye extraction with centrifuged extract samples and non-centrifuged samples.

Spectrophotometric Identification

The spectrophotometer was first blanked with the 1% alkali solution used for extracting the dyes before taking their absorbance reading. For the *uri* dye extracted with water, distill water was used for blank. Two of 1cm² cuvette was used; one to contain the blank and the other to contain the dye extract.

An automatic pipette was used to put the blank and the dyes in their respective cuvettes. The spectrophotometer was then set to particular wavelengths at which absorbance readings can be taken for a particular extract. Different wavelengths with interval difference of 10nm were used. The spectrophotometer was blanked at each wavelength before absorbance readings were taken.

For the centrifuged samples, the dye extract samples were centrifuged at 2000 rpm for 15 minutes before using the procedure above to check their absorbance.

3.2.5 Analysis of *Uri* and *Uhie* dyes.

For this analysis, three tests on dyeing of cotton fabric with and without certain dye additives at two different temperatures were carried out. The *Uri* plant and *Uhie* plant dyes used were extracted with 1% alkali solution for the test. Dyeing was done at a material to liquor ratio of 0.5:40 for 30 minutes. The tests were recorded in sections A, B, C, D and E.

A. Dyeing of Cotton Fabric without a Reducing agent or Mordant

i. At Room Temperature ($27 \pm 2^{\circ}\text{C}$):

40ml of *Uri* dye extract was poured into a 100ml beaker. 1g of pure sodium chloride (NaCl) was added and stirred. 0.5g of already wetted cotton fabric was then entered into the dye bath and stirred. The dye bath was stirred again after 15min of dyeing and the fabric was removed after 30minutes of dyeing.

The fabric was rinsed in cold distill water and dried under a shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles.

ii. At 60°C

40ml of *Uri* dye extract was poured into 100ml beaker (dye bath) and put inside a water bath with temperature set at 60°C. When the temperature of the dye bath equaled that of the water bath, 1g of NaCl was added and stirred and 0.5g of already wetted fabric was then entered into the dye bath and dyeing done for 30 minutes. The dye bath was also stirred at 15 minutes interval during dyeing.

The fabric was removed after the dyeing time, rinsed with cold distill water and dried under a shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles.

B. Dyeing of Cotton Fabric with a Mordant

Fabric Preparation for Dyeing With Mordant

25% of mordant on the weight of the fabric (owf) and a material to liquor ratio (MLR) of 0.5:40 were used. The weight of mordant used was calculated using equation 3.2 (Wet processing Calculations, 2001) and 3.3 (Textile Calculations and Equations, 2014);

$$1. \quad g/l = \frac{w \times 10}{\text{Liquor ratio (liquid only)}} \quad 3.2$$

where w = mordant percentage owf required

$$2. \quad g = \frac{\text{required quantity in g/l} \times \text{liquor ratio} \times \text{fabric weight}}{1000} \quad 3.3$$

Therefore for 25% mordant owf, the weight of mordant used was

Step 1 using equation 3.2

$$\frac{25 \times 10}{40} = 6.25g/l$$

Step 2 using equation 3.3

$$\frac{6.25 \times 40 \times 0.5}{1000} = 0.125g \sim 0.1g$$

0.1g of alum ($KAl(SO_4)_2 \cdot 12H_2O$) mordant was dissolved with 40ml of distill water in a 100ml beaker. The solution was put in a water bath with temperature set at 70°C . When the temperature of the solution got to 70°C as measured with a thermometer, 0.5g of cotton fabric was entered into the solution and stirred. After 30min, the fabric was removed and excess water squeezed out. Fabric was then ready for dyeing.

i. Dyeing At Room Temperature ($27 \pm 2^{\circ}\text{C}$):

40ml of *Uri* dye extract was poured into 100ml beaker and 1g of NaCl added and stirred. 0.5g of the mordant prepared fabric was entered into the dye bath and stirred. After 15 min of dyeing the dye bath was stirred and after 30 min the fabric was removed and rinsed in cold distill water before drying under shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles.

ii. Dyeing at 60°C

40ml of *Uri* dye extract was poured into 100ml beaker (dye bath) and put inside a water bath with temperature set at 60°C . When the temperature of the dye bath equaled that of the water bath, 1g of sodium chloride (NaCl) was added and stirred. 0.5g of mordant prepared cotton fabric was then entered into the dye bath and dyeing carried out for 30 minutes. Dye bath was also stirred at 15 min interval during dyeing.

Fabric was removed after dyeing time and rinsed with cold distill water. It was dried under shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles.

C. Dyeing of Cotton Fabric with a Reducing agent

i. At Room Temperature ($27 \pm 2^{\circ}\text{C}$):

40ml of *Uri* dye extract was poured into 100ml beaker. 1g of NaCl and 0.8g of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) was added and stirred. 0.5g of already wetted-out cotton fabric was then entered into the dye bath and stirred. The dye bath was stirred again after 15 minutes of dyeing and the fabric was removed after 30 minutes of dyeing.

The fabric was left in the open for 10 min. before rinsing in cold distill water and dried under a shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles.

ii. At 60°C

40ml of *Uri* dye extract was poured into 100ml beaker (dye bath) and put inside a water bath with temperature set at 60°C . When the temperature of the dye bath equaled that of the water bath 1g of NaCl and 0.8g of $\text{Na}_2\text{S}_2\text{O}_4$ were added and stirred. 0.5g of already wetted-out fabric was then entered into the dye bath and dyeing carried out for 30 minutes. Dye bath was also stirred at 15 minutes interval during dyeing.

Fabric was removed after dyeing time and left for 10min in the open before rinsing with cold distill water. It was dried under shade. 10ml of the dye liquor before and after dyeing was stored in a sample test bottle.

The procedures used above for the three dyeing tests A-C for the *uri* dye were also followed for the *uhie* dye and the absorbance of all dye liquor stored before and after dyeing checked with the spectrophotometer following the procedure in 3.2.4. Designation of fabrics dyed at room temperature using both *uri* and *uhie* dyes were as follows:

Test A designated as A₁

Test B designated as B₁

Test C designated as C₁

Fabrics dyed at 60⁰C using both *uri* and *uhie* dyes are:

Test A designated as A₂

Test B designated as B₂

Test C designated as C₂

D. Colour fastness Tests

Colour fastness tests to rubbing, washing and staining for each of the fabrics dyed in A-C of 3.2.5 above were ascertained.

a. Colour Fastness to Rubbing

This test was carried out with a crockmeter having a rubbing finger diameter of 16mm. The ISO 105-X12:2001(see appendix A) method was followed for both wet and dry rubbing test. 10 rubbing cycles (10 times to and 10 times fro) was done for each of the fabrics dyed at the different temperatures. Assessment of fabric staining was done with the cards of grey scale for staining following ISO 105-A03.

Dry Rubbing

Test fabric was placed on the base board of the crockmeter parallel to the track of rubbing. The dry rubbing cloth was mounted on the rubbing finger of the crockmeter and held tight with a clip. The finger was then rested on the test fabric and rubbing done back and forth over a straight track for ten complete cycles. After the ten cycles, the rubbing cloth was removed from the finger and checked with the grey scales for staining.

Wet Rubbing

Distill water was used to wet the rubbing cloth before mounting it on the rubbing finger. Same procedure for the dry rubbing was then followed.

b. Colour fastness to Washing and staining

For the colour fastness to washing tests, ISO 105-C10:2006 (E) (see appendix B) was followed using a Rotadyer machine in the Polymer and Textile Engineering department Laboratory of FUTO. The test number followed was the A (1) which involves washing for 30 minutes at a temperature of 40⁰C without any stainless steel balls. The liquor ratio was 50:1 (ml:g).

Soap solution was prepared by dissolving 5g of bar soap in 1litre of distill water. The fabric samples were prepared by sewing the dyed cotton fabric of size 100±2mm × 40±2mm and weight 0.5g together with a plain weave bleached cotton fabric of same size and weight at their shorter ends.

Stainless steel pots used for washing are of dimension: height 200mm, diameter 25mm and capacity 110ml.

After washing, rinsing and drying the grey scales for change in colour were used to check the change in colour of the washed fabric in relation to the unwashed fabric following ISO 105-A02 while the grey scales for staining were used to check the level of staining (if any) of the adjacent fabric. The grey scale assessment was done

in a colour matching chamber using artificial day light (D-65) in a dark room at the Polymer and Textile Engineering (PTE) department FUTO Laboratory.

E. Fourier Transform infra-red spectroscopy (FTIR) Analysis

This test was run at the Chemical Engineering Department Laboratory of Ahmadu Bello University (ABU), Zaria. The dye extracts and the dry powders of the *uri* and *uhie* plants were analysed. The samples analyzed by the FTIR are:

Sample A---- *Uhie* plant dry powder

Sample B---- *Uri* fruit dry powder

Sample C---- *Uhie* dye extracted with 1% alkali at 65⁰C

Sample D---- *Uri* dye extracted with 1% alkali at 65⁰C

Sample E---- *Uri* dye extracted with distill water at 65⁰C

3.2.6 Study of the effect of Temperature on Dyeing with *Uri* and *Uhie* dyes

Dye Extraction before Dyeing

Dye stock of 2% dye concentration is to be used for the dyeing of cotton fabric to a 2% shade. MLR of 1:50 will be used for dye extraction hence; to dye fourteen different fabrics with each dye extract using a liquor ratio of 0.5:40 about 800ml of

1% alkali solution will be needed. The weight of plant powder to be used was calculated below from equation 3.1

$$\begin{aligned} \text{Weight of solute} &= \frac{\text{mass percent} \times \text{weight of solvent}}{100 - \text{mass percent}} \\ &= \frac{2 \times 800}{100 - 2} \\ &= 16.3g \end{aligned}$$

The dyes were extracted at 65°C.

800ml of 1% alkali solution was put in 1000ml beaker. The beaker was then placed in a water bath with temperature set to 65°C. When the temperature of the alkali solution equaled the water bath temperature, 16.3g of *uhie* powder was added and stirred. Extraction was done for 45minutes after which the extract was drained to serve as the *uhie* dye liquor of 2% concentration stock solution.

This procedure was also followed in extracting dye from the *uri* plant powder. 10ml of the dye liquor before dyeing was collected with sample test tubes.

Dyeing of Cotton Fabric

Dyeing was done with MLR of 0.5:40 at different temperatures, starting with room temperature, 40°C, 50°C, 60°C, 70°C, 80°C and 90°C. The cotton fabric was dyed

to a 2% shade using 30% of salt (NaCl) owf. Equations 3.1 and 3.2 were used to calculate weight of salt in grams as shown below,

Equation 3.2

$$\frac{30 \times 10}{40} = 7.5g/l$$

Equation 3.3

$$\frac{7.5 \times 40 \times 0.5}{1000} = 0.15g$$

The dyeing was done using the following procedure;

i. At Room Temperature ($27 \pm 2^{\circ}\text{C}$):

40ml of *Uri* dye was poured into 100ml beaker. 0.15g of pure sodium chloride (NaCl) was added and stirred. 0.5g of wetted-out cotton fabric was then entered into the dye bath and stirred. The dye bath was stirred again after 15 minutes of dyeing and the fabric was removed after 40 minutes of dyeing.

The fabric was rinsed immediately in cold distill water and dried under a shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles.

ii. At 40°C

40ml of *Uri* dye was poured into 100ml beaker (dye bath) and put inside a water bath with temperature set at 40°C. When the temperature of the dye bath equaled that of the water bath 0.15g of NaCl was added and stirred. 0.5g of already wetted-out fabric was then entered into the dye bath and dyeing done for 40 minutes. Dye bath was also stirred at 15 minutes interval during dyeing.

Fabric was removed after the dyeing time, rinsed with cold distill water and dried under shade. 10ml of the dye liquor before and after dyeing was stored in sample test bottles. This procedure was followed for dyeing at other temperature ranges of 50°C, 60°C, 70°C, 80°C, and 90°C.

The procedure above was also used for dyeing with the *uhie* dye except that *uhie* dyeing was done for 30 minutes. Designation of fabrics dyed at different temperatures using both *uri* and *uhie* dyes were as follows:

Uri dyed fabrics:

Room temperature dyeing, designated as A₁

40°C dyeing designated as B₁

50°C dyeing designated as C₁

60°C dyeing designated as D₁

70°C dyeing designated as E₁

80°C dyeing designated as F₁

90°C dyeing designated as G₁

Uhie dyed fabrics:

Room temperature dyeing, designated as A₂

40°C dyeing designated as B₂

50°C dyeing designated as C₂

60°C dyeing designated as D₂

70°C dyeing designated as E₂

80°C dyeing designated as F₂

90°C dyeing designated as G₂

3.2.7 Calculation of Percentage Dye Uptake

The percentage dye uptake or dye absorption during each of the dyeing test above can be calculated with the equation (Divya et al., 2013):

$$\% \text{ dye absorption} = \frac{\text{absorbance } b \text{ } d - \text{absorbance } a \text{ } d \times 100}{\text{Absorbance before dyeing}} \quad 3.4$$

where

a d = after dyeing

b d = before dyeing

With the aid of a spectrophotometer the absorbance of the dye liquor for both the *uri* and *uhie* dyes before and after dyeing were checked using the procedure in 3.2.4.

A blank of 1% NaOH was used to zero the spectrophotometer. *Uri* dye (before dyeing) was pipetted into a second cuvette and the absorbance readings at different wavelengths were taken. The wavelength that gave the highest absorbance was used as the wavelength of maximum absorbance to measure the absorbance of the *uri* dye after each of the dyeing test carried out in 3.2.5.

The same procedure was used for measuring the *uhie* dye absorbance before and after dyeing.

3.2.8 Colour Fastness Tests

a. Colour Fastness to Rubbing

This test was carried out with a crockmeter having a rubbing finger diameter of 16mm. The ISO 105-X12:2001(see appendix A) method was followed for both wet and dry rubbing test. 10 rubbing cycles (10 times to and 10 times fro) was done for each of the fabrics dyed at the different temperatures. Assessment of fabric staining was done with the cards of grey scale for staining following ISO 105-A03.

Dry Rubbing

Test fabric was placed on the base board of the crockmeter parallel to the track of rubbing. The dry rubbing cloth was mounted on the rubbing finger of the crockmeter and held tight with a clip. The finger was then rested on the test fabric and rubbing done back and forth over a straight track for ten complete cycles. After the ten cycles, the rubbing cloth was removed from the finger and checked with the grey scales for staining.

Wet Rubbing

Distill water was used to wet the rubbing cloth before mounting it on the rubbing finger. Same procedure for the dry rubbing was then followed.

b. Colour fastness to Washing and staining

For the colour fastness to washing tests, ISO 105-C10:2006 (E) (see appendix B) was followed using a Rotadyer machine in the Polymer and Textile Engineering department Laboratory of FUT0. The test number followed was the A (1) which involves washing for 30 minutes at a temperature of 40⁰C without any stainless steel balls. The liquor ratio was 50:1 (ml:g).

Soap solution was prepared by dissolving 5g of bar soap in 1litre of distill water. The fabric samples were prepared by sewing the dyed cotton fabric of size 100±2mm × 40±2mm and weight 0.5g together with a plain weave bleached cotton fabric of same size and weight at their shorter ends.

Stainless steel pots used for washing are of dimension: height 200mm, diameter 25mm and capacity 110ml.

After washing, rinsing and drying the grey scales for change in colour were used to check the change in colour of the washed fabric in relation to the unwashed fabric following ISO 105-A02 while the grey scales for staining were used to check the level of staining (if any) of the adjacent fabric. The grey scale assessment was done in a colour matching chamber using artificial day light (D-65) in a dark room at the Polymer and Textile Engineering (PTE) department FUT0 Laboratory.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

i. Dye Extraction

The results of the study in sections 3.2.2 and 3.2.3 on the effect of solvent and temperature in the extraction of dye from *uri* and *uhie* and the use of fermentation and traditional methods for *uri* dye extraction are presented in Tables 4.1- 4.6

Table 4.1: Visual effect of solvent and temperature on the colour of *uri* dye extract

Plant	Temperature	Water	Alkali	Acid	Iso-propanol
<i>Uri</i>	Room temperature	Light ash	Deep brown	Colourless	Colourless
	65°C	Black	Deep brown	Colourless	Colourless
	Fermentation	Murky yellow	-	-	-
	Traditional method	Black	-	-	-

Table 4.2: Visual effect of solvent and temperature on the colour of *uhie* dye extract

Plant	Temperature	Water	Alkali	Acid	Iso-propanol
<i>Uhie</i>	Room temperature	Colourless	Very deep red	Colourless	Orange
	65°C	Pale pink	Very deep red	Slight evidence of colour change	Deep orange

Table 4.3: Effect of temperature on the colour yield (absorbance) of *Uhie* dye extracted with Iso-Propanol at different wavelengths

Wavelength (λ) (nm)	Absorbance at 65°C	Absorbance at Room Temperature
580	0.453	0.235
590	0.342	0.176
600	0.256	0.132
610	0.192	0.100
620	0.145	0.076
630	0.113	0.058

**Table 4.4: Effect of Temperature on the colour yield (absorbance) of *Uhie* Dye
Extracted with Alkali Solution at different wavelengths**

Wavelength (λ) (nm)	Absorbance at 65°C	Absorbance at Room temperature
620	2.473	1.825
630	2.080	1.458
640	1.691	1.162
650	1.377	0.937
660	1.139	0.771
670	0.946	0.639
680	0.788	0.530
690	0.674	0.452
700	0.579	0.388
710	0.493	0.329
720	0.429	0.286
730	0.379	0.252
740	0.332	0.220

Table 4.5: Effect of Temperature on the colour yield (absorbance) of *Uri* dye extracted with Alkali Solution at different wavelengths

Wavelength (λ) (nm)	Absorbance at 65°C	Absorbance at Room Temperature
660	2.810	0.949
670	2.553	0.839
680	2.314	0.747
690	2.059	0.657
700	1.845	0.587
710	1.662	0.528
720	1.475	0.466
730	1.339	0.422
740	1.200	0.378
750	1.079	0.341
760	0.975	0.309
770	0.877	0.278
780	0.795	0.252
790	0.712	0.227

**Table 4.6: Effect of Temperature on the colour yield (absorbance) of *Uri* dye
Extracted with Distill Water at different wavelengths**

Wavelength (λ) (nm)	Absorbance at 65°C	Absorbance at Room Temperature
620	2.036	0.601
630	1.832	0.531
640	1.524	0.470
650	1.238	0.388
660	1.008	0.334
670	0.865	0.290
680	0.757	0.260
690	0.674	0.238
700	0.616	0.220
710	0.583	0.206
720	0.511	0.198

ii. Dye Colour Identification

The spectrophotometer absorbance results for *uri* and *uhie* dye colour identification as studied in section 3.2.4 are recorded in Tables 4.7 – 4.9.

Table 4.7: Spectrophotometric colour Identification of *Uri* dye extracted with alkali

A. One day after dye extraction

Wavelength (λ) (nm)	Absorbance
760	1.046
770	0.960
780	0.824
790	0.738
800	0.667

B. After 2000rpm centrifuge

Wavelength (λ) (nm)	Absorbance
660	1.148
670	0.981
680	0.867
690	0.749
700	0.635

Table 4.8: Spectrophotometric colour Identification of *Uhie* dye extracted with alkali

A. One day after dye extraction

Wavelength (λ) (nm)	Absorbance
720	1.050
730	0.947
740	0.844
750	0.742
760	0.662

B. After 2000rpm centrifuge

Wavelength (λ) (nm)	Absorbance
610	1.140
620	0.953
630	0.797
640	0.679

Table 4.9: Spectrophotometric colour Identification of *Uri* dye extracted with distill water at 65°C

A. One day after dye extraction

Wavelength (λ) (nm)	Absorbance
660	1.008
670	0.865
680	0.757
690	0.674

B. After 2000rpm centrifuge

Wavelength (λ) (nm)	Absorbance
640	1.156
650	0.974
660	0.833
670	0.735
680	0.673

iii. Effect of Temperature and dyeing additives on dyeing of cotton fabric

Results of studies in section 3.2.5 and 3.2.6 as observed with a spectrophotometer on dyeing of cotton fabric with *uri* and *uhie* dyes are presented in Tables 4.10 – 4.15

Table 4.10: Dye analysis; absorbance of *uri* dye before and after dyeing test

Before dyeing		Absorbance After dyeing					
$\lambda_{(\max)}$ nm	Abs	No M, no RA	No M, no RA	M	M	RA	RA
656	0.997	Hot	Cold	Hot	Cold	Hot	Cold
		1.290	0.916	0.929	0.862	1.004	0.977

Table 4.11: Dye analysis; absorbance of *uhie* dye before and after dyeing

Before dyeing		Absorbance After dyeing					
$\lambda_{(\max)}$ nm	Abs	No M, no RA	No M, no RA	M	M	RA	RA
702	0.986	Hot	Cold	Hot	Cold	Hot	Cold
		0.857	0.833	0.897	0.637	0.730	0.580

Table 4.12: Absorbance of *Uhie* dye before dyeing

Wavelength (λ) (nm)	Absorbance
720	1.050
730	0.947
740	0.844
750	0.742

Table 4.13: Absorbance of *Uhie* dye after dyeing at different temperatures measured at 730nm

Temperature ($^{\circ}\text{C}$)	Absorbance
A ₂ . Room Temperature (27)	0.771
B ₂ . 40	0.830
C ₂ . 50	0.854
D ₂ . 60	0.801
E ₂ . 70	0.864
F ₂ . 80	0.878
G ₂ . 90	1.017

Table 4.14: Absorbance of *Uri* dye before dyeing

Wavelength (λ) (nm)	Absorbance
760	1.046
770	0.960
780	0.824
790	0.738

Table 4.15: Absorbance of *Uri* dye after dyeing at different temperatures measured at 770nm

Temperature ($^{\circ}\text{C}$)	Absorbance
A ₁ . Room Temperature (27)	0.957
B ₁ . 40	1.479
C ₁ . 50	1.001
D ₁ . 60	1.040
E ₁ . 70	1.104
F ₁ . 80	1.114
G ₁ . 90	1.877

iv. Colour Fastness

Colour fastness results of fabrics used for dye analysis and fabrics dyed at different temperatures studied in section 3.2.8 are detailed in Tables 4.16 – 4.19

Table 4.16: Dye analysis; Colour fastness to Rubbing

A. Fabric Dyed with *Uri* dye

Dyed fabric sample	Dry rubbing	Wet rubbing
A ₁	4/5	4/5
B ₁	4/5	4/5
C ₁	4/5	4
A ₂	4/5	4
B ₂	4	4/5
C ₂	4/5	4

B. Fabric Dyed with *Uhie* dye

Dyed fabric sample	Dry rubbing	Wet rubbing
A ₁	3/4	3/4
B ₁	4	4/5
C ₁	3	4/5
A ₂	3/4	3
B ₂	4	4/5
C ₂	3/4	4

Table 4.17: Colour fastness to Rubbing of fabrics dyed at different temperatures

A. Fabrics dyed with *Uri* dye

Dyed fabric sample	Temperature °C	Dry rubbing	Wet rubbing
A ₁	Room temperature	4/5	4
B ₁	40	5	4/5
C ₁	50	4/5	4
D ₁	60	4/5	4
E ₁	70	4/5	4
F ₁	80	4	4
G ₁	90	4/5	3/4

B. Fabrics dyed with *Uhie* dye

Dyed fabric sample	Temperature °C	Dry rubbing	Wet rubbing
A ₂	Room temperature	4/5	3/4
B ₂	40	4/5	3/4
C ₂	50	4/5	3/4
D ₂	60	4/5	3/4
E ₂	70	4/5	3/4
F ₂	80	4/5	3/4
G ₂	90	4/5	3/4

Table 4.18: Dye analysis; Colour fastness to washing

A. Fabric Dyed with *Uri* dye

Dyed fabric sample	Colour change (CC)	Colour Staining (CS)
A ₁	4/5	5
B ₁	4/5	5
C ₁	4	5
A ₂	4	5
B ₂	5	5
C ₂	4	5

B. Fabric Dyed with *Uhie* dye

Dyed fabric sample	Colour change (CC)	Colour Staining (CS)
A ₁	3/4	5
B ₁	4/5	5
C ₁	3/4	5
A ₂	3/4	5
B ₂	4	5
C ₂	3/4	5

Table 4.19: Colour fastness to washing of fabrics dyed at different temperatures

A. Fabrics dyed with *Uri* dye

Dyed fabric sample	Temperature °C	Colour change (CC)	Colour Staining (CS)
A ₁	Room temperature	4	5
B ₁	40	3/4	5
C ₁	50	3/4	5
D ₁	60	3/4	5
E ₁	70	3/4	5
F ₁	80	3	5
G ₁	90	3	5

B. Fabrics dyed with *Uhie* dye

Dyed fabric sample	Temperature °C	Colour change	Colour Staining (CS)
A ₂	Room temperature	3/4	5
B ₂	40	3/4	5
C ₂	50	3	5
D ₂	60	3	5
E ₂	70	3	5
F ₂	80	3	5
G ₂	90	3	5

4.2 Discussion

4.2.1 Effect of Solvent and Temperature on dye extraction from *Uhie* and *Uri* plant materials.

The use of different solvents for the extraction of dye from the both the *uri* and *uhie* powder was done in a bid to ascertain the best solvent that extracts dye from both plant materials. The pH of the 1% acid and alkali solution were 3 and 11. Room temperature of $27 \pm 2^{\circ}\text{C}$ was determined by measuring the temperature of water stored in a container in the laboratory before starting any experiment. Similarly, grinding the plant materials to powder increased the plant surface area in contact with the extracting liquor and hence improved and/or quickened dye extraction. After the extraction time the dye extracts were drained using a synthetic fabric as sieve. From Tables 4.1 and 4.2 it could be seen that not all the solvents extracted colour from the plant materials. This is also seen in Figs. 4.1-4.18 below.

UHIE DYE EXTRACTS



Fig.4.1: with 1% acid, at room temperature



Fig.4.2: with 1% acid, at 65°C



Fig.4.3: with 1% alkali, at room temperature



Fig.4.4: with 1% alkali at 65°C



Fig.4.5: with water at room temperature



Fig.4.6: with water at 65°C



Fig.4.7: with iso-propanol at room temperature



Fig.4.8: with iso-propanol at 65°C

URI DYE EXTRACTS



Fig.4.9: with iso-propanol at 65°C



Fig.4.10: with iso-propanol at room temperature



Fig.4.11: with 1% acid at 65°C



Fig.4.12: with 1% acid
at room temperature



Fig.4.13: with 1%
alkali at 65°C



Fig.4.14: with 1% alkali
at room temperature



Fig.4.15: with water
at room temperature



Fig.4.16: with water
at 65°C



Fig.4.17: traditional
method



Fig.4.18: fermentation
method

For the *uri* plant in Table 4.1 and Figs. 4.9-4.12 it could be observed that both acid and iso-propanol solution remained colourless after the extraction time. The reason behind this could be that the dye molecule in the *uri* plant does not have similar or closely related total solubility parameter with both solvents hence not soluble in them even at a raised temperature. According to Hansen (2000) solute will not dissolve in a solvent with solubility parameters too different from its own. They will not also dissolve if their total solubility parameters are close or similar but have different affinities. However, with alkali solution the *uri* plant gave a very deep brown colour extract as seen in Figs. 4.13 and 4.14 indicating that the dye molecule in *uri* dissolved and was therefore able to separate from the other *uri* fruit plant particles.

Using the spectrophotometer for quantitative analysis in Table 4.5 and Fig. 4.19, it could be observed that the absorbance of the dye extracted at 65°C is higher than that of the dye extracted at room temperature. This could be due to the rapid movement of the solvent molecules striking the solid surfaces harder and more often leading to increase in the rate at which dye molecules were dissolved. This agrees with the fact that solids dissolve faster at increased temperature (www.chem.ccu.edu, 2016). According to Beer's law, absorbance is directly proportional to concentration at all wavelengths; hence the higher absorbance result at 65°C means that the extracted dye at that temperature is more

concentrated than at room temperature. Since the dye extracted at both temperatures went through same procedure with the exception of heat, it can be concluded that the higher absorbance readings at 65°C is not due to impurities but an indication of higher dye yield at the higher temperature.

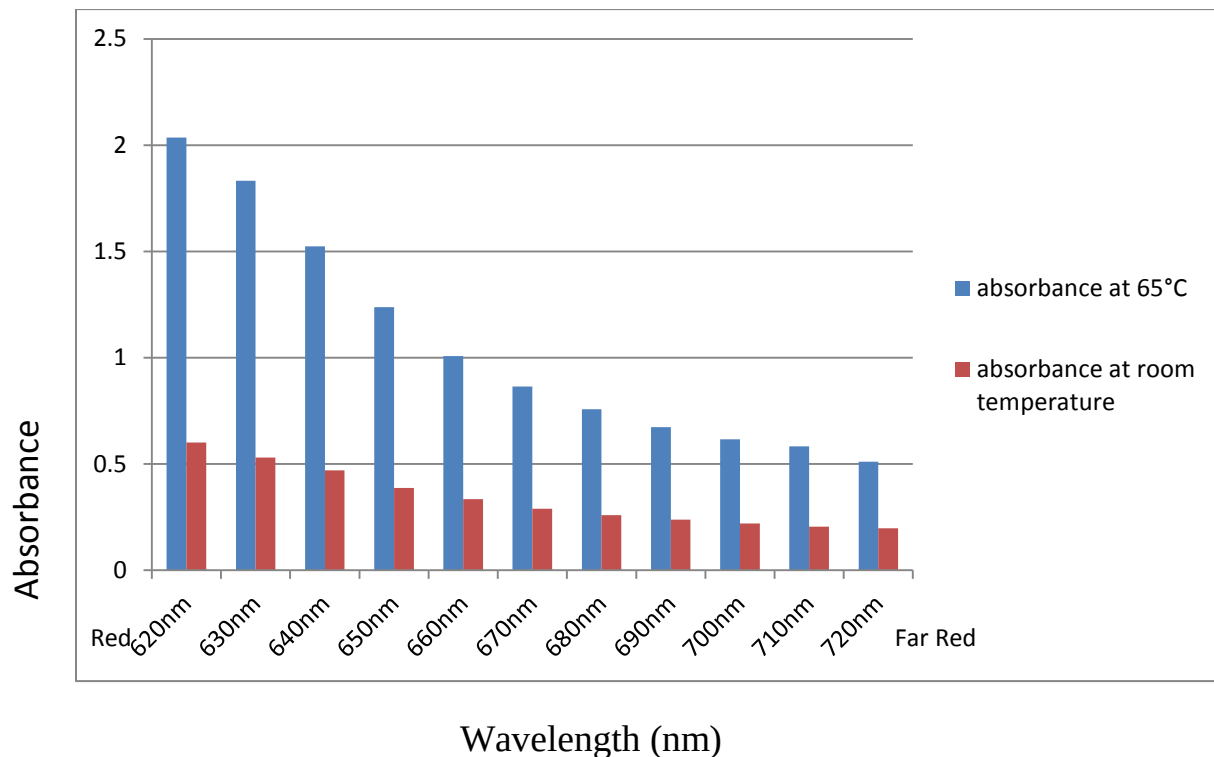


Fig. 4.19: Effect of Temperature on the colour yield (absorbance) of *Uri* dye extracted with Alkali Solution at different wavelengths

Similarly, *uri* dye extraction with water, Figs. 4.15 and 4.16 also showed significant colouration of the solution. Again the extraction at 65°C gave a black coloured extract similar to the extract through the traditional method in Fig. 4.17.

Equally, the absorbance result of the dye extracted at 65°C with water in Table 4.6 and represented in Fig.4.20 is higher than the extract at room temperature.

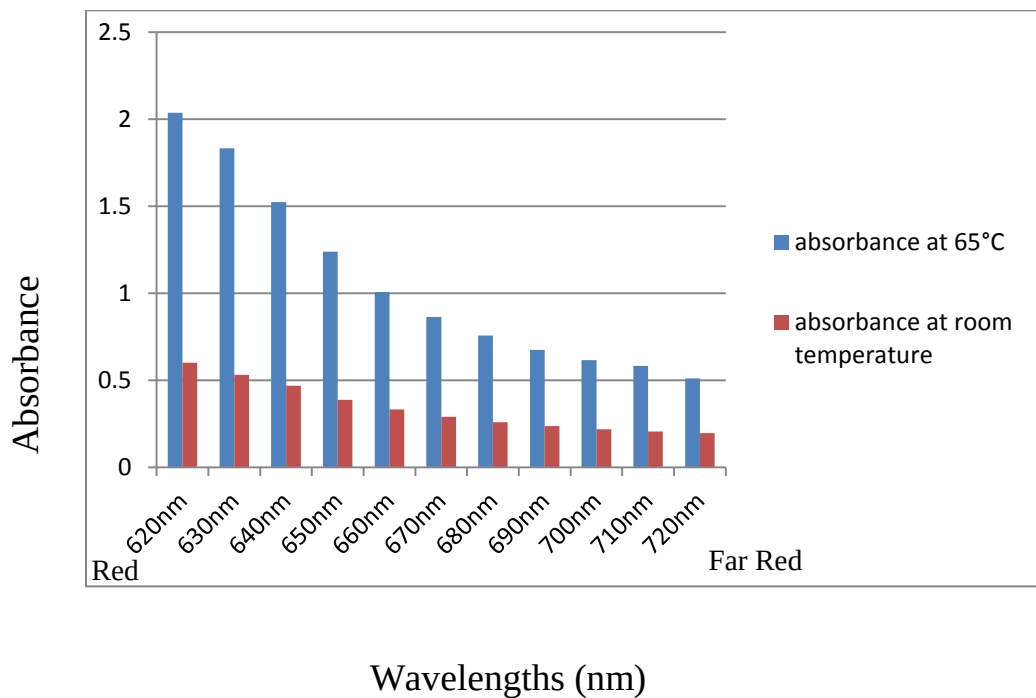


Fig. 4.20: Effect of Temperature on the colour yield (absorbance) of *Uri* dye Extracted with Distill Water at different wavelengths

It should be noted that the *uri* dye extract using water and the traditional method when mixed with drops of alkali changed colour to deep brown. This perhaps indicates that the natural dye molecule in *uri* plant does not dissolve in water but dissolves in alkali solution. It could also be said that hot water causes the plant particles to swell releasing the smaller particles where the dye molecules are attached but does not dissolve the dye molecules contained in them hence the black colour of the extract which is also the colour of the dry *uri* plant powder. Alkali

solution however dissolves the dye molecules giving the deep brown colour which may also be an indication of the presence of tannin. Tannins have been reported to be the most important ingredients which are necessary for brown colour shades when dyeing with natural dyes (Janani et al., 2014).

Fermentation method of *uri* dye extraction was done to check if *uri* fruit will yield an indigo dye since this method is majorly used for the extraction of indigo from natural source. However, murky yellow liquid (Fig. 4.18) drained out after fermentation of *uri* seed and pulp gave no further colour change or any residue after being centrifuged and allowed to stand for a day. Hence fermentation of semi dry *uri* plant fruit pulp and seed yielded no significant dye extract. This could be an indication that *uri* dye is not an indigo dye. Alkali solution is thus recommended as the solvent for dye extraction from dry *uri* fruit as observed in the higher absorbance value seen in Table 4.5.

In Table 4.2 it was observed that *uhie* plant dye was not extracted by all extraction liquor. At room temperature extraction, water (Fig. 4.5) and acid (Fig.4.1) solutions remained colourless after the extraction time. The reason for this could be related to that of *uri* above. Iso-propanol solution (Fig. 4.7) however turned to orange colour while the alkali solution (Fig. 4.3) turned deep red after the extraction time. At 65°C extraction both water (Fig. 4.6) and acid (Fig. 4.2) solutions gave slight evidence of colour change. Iso-propanol solution yielded a

deeper orange colour (Fig. 4.8) extract while alkali solution still gave a deep red solution (Fig. 4.4). Similar to *uri* dye extract, the absorbance result of iso-propanol and alkali solution extract of *uhie* dye in Tables 4.3 and 4.4 at 65°C is higher than at room temperature. This can also be seen in Figs 4.21 and 4.22. It can therefore be said that *uhie* plant dye is soluble in both iso-propanol and alkali solution but more in alkali solution due to its intense dye extract which is also confirmed by the higher absorbance values in Table 4.4. Hence alkali solution is said to be a better solvent for the extraction of dye from *uhie*.

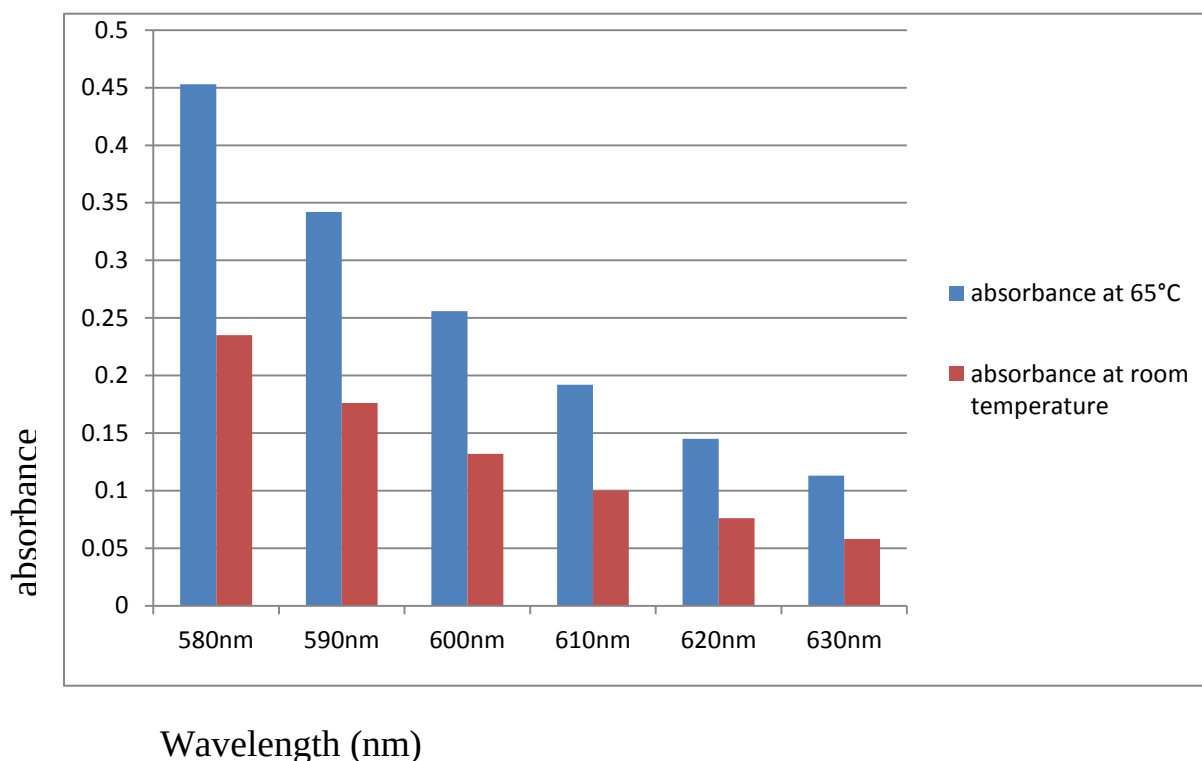


Fig. 4.21: Effect of Temperature on the colour yield (absorbance) of *Uhie* dye Extracted with Iso-Propanol at different wavelengths.

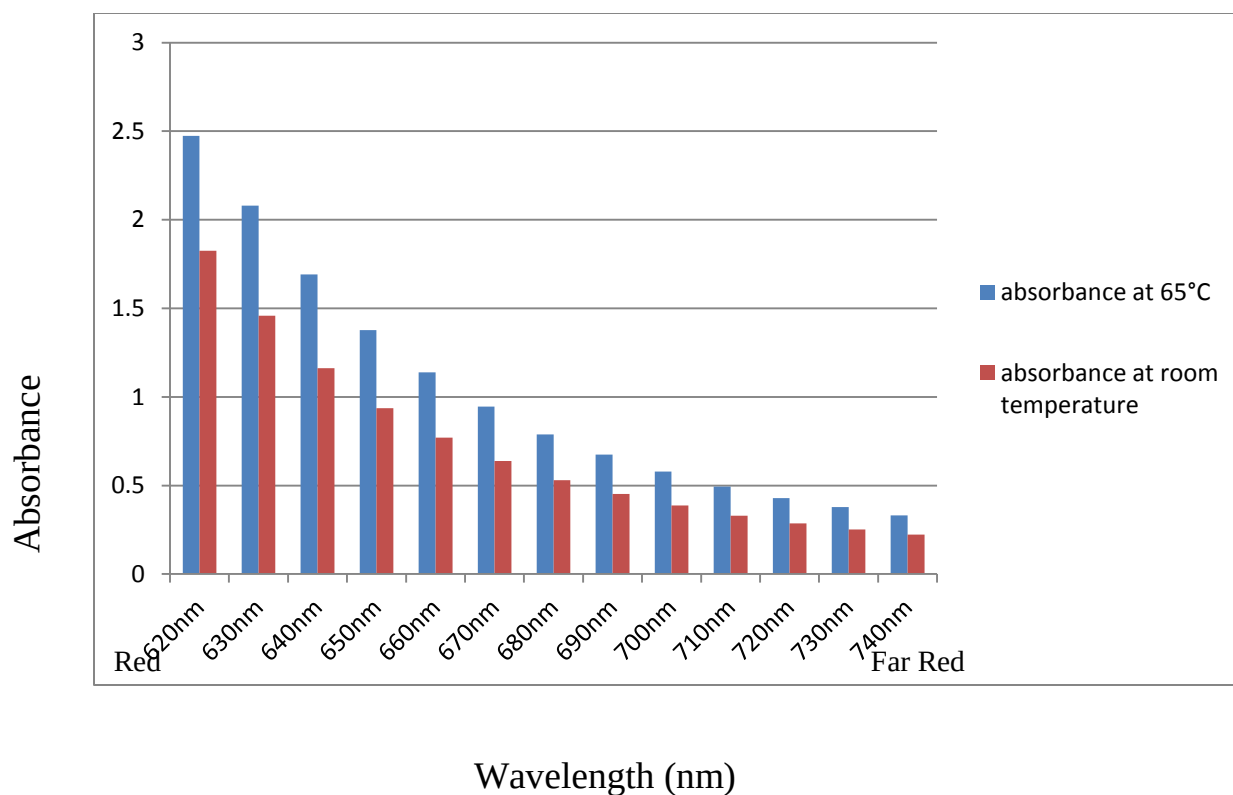


Fig. 4.22: Effect of Temperature on the colour yield (absorbance) of *Uhie* Dye Extracted with Alkali Solution at different wavelengths

4.2.2 Identification of *Uhie* and *Uri* plant dye hues

Visually both *uri* and *uhie* plants had dye extracts with two different colours depending on the extraction solvent used. For the *uri* plant it can be seen that a very deep brownish colour can be achieved with alkali extraction and a black colour with water extraction. Also for the *uhie* plant, a very deep red colour with alkali extraction and an orange colour with iso-propanol extraction were obtained.

Using the spectrophotometer, the *uhie* and *uri* dye hues examined were the extracts used for fabric dyeing that is, dye extracted with alkali. The wavelength with the absorbance reading not more than 1.0 was considered. This is because absorbance readings above 1.0 falls within the nonlinear absorbance range and cannot be trusted (www.chem.uky.edu, 2015). The wavelength of maximum absorbance reading for each of the dye extracts was checked with the colour spectrum of visible light to determine the colour or range of colour the wavelength matches. Visible light ranges between the wavelengths of 400nm to 800nm meaning that any colour visible to the eye is seen within this range. Wavelengths below or above this range are the ultra violet (UV) and the infra-red (IR) which are colourless and cannot be seen with the human eye (see Appendix C).

Absorbance readings were taken a day after extraction to allow tiny impurities which may have passed through during draining of dye extract to settle at the bottom of the sample bottle. Also automatic pipette was used in order not to disturb the already settled particles. Similarly, samples were centrifuged to settle more unsettled impurities at the bottom of the centrifuge test tube in order to have a clearer solution with fewer impurities.

For the *uri* dye in Table 4.7, before centrifuging, the wavelength of maximum absorbance was 770nm which is a wavelength for very deep or far red colour. However, after centrifuging, the wavelength of maximum absorbance dropped to

670nm which is also for red colour (See Appendix C). The change in wavelength after centrifuging is an indication that the extracted dye is not a pure solution. The presence of tiny particles in a solution leads to light scattering and even absorption by the particles when light is passed through the solution. Since different colour absorb particular light wavelengths, the presence of other light absorbing/scattering particles will affect the absorbance of such coloured solution as observed between the centrifuged and non- centrifuged dye extracts. Therefore, it can be said that centrifuging helps to reduce the impurity level of such extracted dye. It will therefore be more appropriate to use 670nm as the wavelength of *uri* dye hue.

In Table 4.8 centrifuged and non-centrifuged *uhie* dye samples also gave two different wavelengths of maximum absorbance; 730nm for the non-centrifuged and 620nm for the centrifuged. The reason for this is also same with that of the *uri* dye above. Hence 620nm will be taken as the wavelength for *uhie* dye hue which is still within the range for red but not as deep as *uri*. A close look at the fabric dyed with *uri* and *uhie* dyes at 90^oC confirms the difference in the colour of both *uhie* and *uri* dyes. For the *uri* dye extracted with water in Table 4.9, 650nm after centrifuging will be taken as the wavelength of the dye hue.

4.2.3 Analysis of *Uhie* and *Uri* dyes

The analysis of *uhie* and *uri* dye extracts with the most intense colour was done so as to ascertain if actually the extracts will be able to colour textile materials such as cotton fabric with some degree of fastness. Again it was done in order to be able to classify them if indeed the extracts succeed in dyeing a cotton fabric.

A. Effect of mordant and reducing agent

The ability of both extracts to dye cotton fibre was considered in three different areas; first is the ability to dye without a mordant and reducing agent, second is the ability to dye with a reducing agent only and third is the ability to dye with mordant only. Dyeing was done in these three areas at room temperature and at 60°C. The implication of dyeing without a mordant and a reducing agent is to check if the dye is a direct (substantive) dye. Direct dyes have moderate affinity for the fibre without mordant or reducing agent. Dyeing with a reducing agent is to check if the dye is a vat or indigo dye. Vat or indigo dyes will only dye a fabric when they are first reduced to a leuco form thus making them soluble and able to enter the fibre pores where when the fabric is out of dye bath they oxidize back to the insoluble fast dye. Dyeing with mordant is to check if the dye is a mordant dye. Mordant dyes have no direct affinity for the fibre except in the presence of a

mordant. Mordants can be applied to the fibre before dyeing, after dyeing or during the dyeing period.

Furthermore, 1g of sodium chloride (NaCl) was used as an electrolyte in the dyeing analysis which is about 200% owf. As an electrolyte sodium chloride (NaCl) in an aqueous medium dissociates into Na^+ ion and Cl^- ion providing the optimum condition for a quick movement of dye molecules towards the fibre (Hubbe et. al., 2012). 200% NaCl (owf) was used at this stage of dye extract analysis to ensure that dye exhaustion was greatly enhanced and the effect of other factors such as temperature, mordant and reducing agent will be easily noted. Similarly, the quantity of the reducing agent and mordant used based on the weight of fabric (owf) was high for the singular reason of their effect to be well noticed. Also, the percent shade of dyeing was not actually stated as it was not yet certain if the extracts will dye a cotton fabric with some degree of fastness and some conditions under which it can happen.

In Fig. 4.23 below one can see that the cotton fabric was dyed by both dyes at the two different temperatures in all the three areas considered.

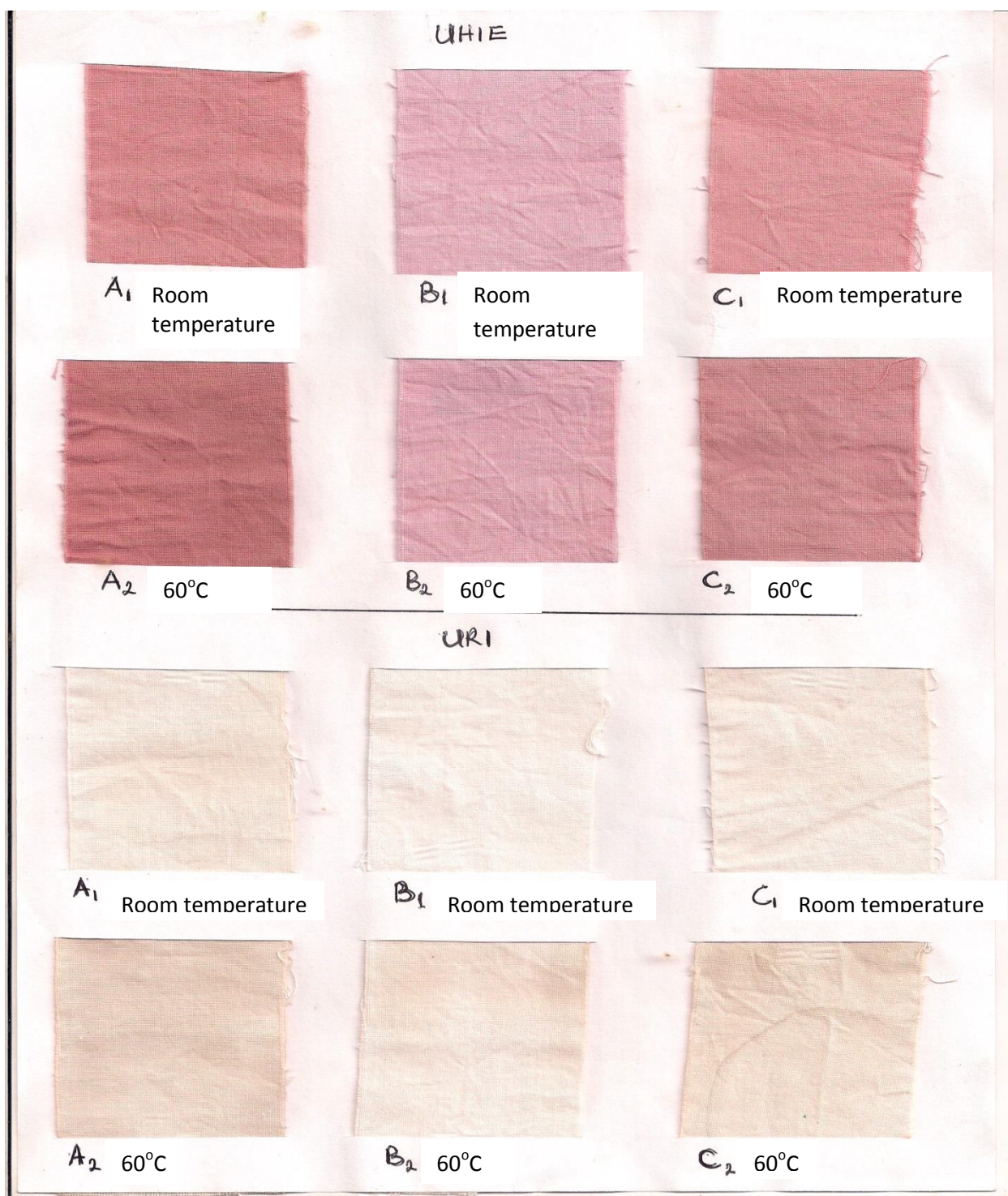


Fig. 4.23: Dye analysis; cotton fabrics dyed with *uhie* and *uri* dyes at room temperature and 60°C

However, the colour depth on the fabrics differed based on temperature and additive used. The dye extract colour depth on fabrics dyed at room temperature is in this order from highest to lowest;

$$A_1 \rightarrow C_1 \rightarrow B_1.$$

Where:

A_1 fabric dyed without mordant and reducing agent

B_1 fabric dyed with mordant only

C_1 fabric dyed with reducing agent

Colour strength on fabrics dyed at 60°C is same as when dyed at room temperature and at room temperature $A_2 \rightarrow C_2 \rightarrow B_2$.

Where:

A_2 fabric dyed without mordant and reducing agent

B_2 fabric dyed with mordant only

C_2 fabric dyed with reducing agent

Comparing the colour strength on fabrics dyed at both temperatures it was observed that fabrics dyed at 60°C had a deeper/stronger colour shade than fabrics dyed at room temperature with the exception of fabric dyed with mordant.

It is very likely that the lighter shade of the dyed pre-mordanted fabric at both temperatures is due to the presence of the mordant. Technically, mordants are chemicals used in some textile fibres to provide affinity for dyes (Celanese Acetate, 2001). When used on cellulose they are capable of forming highly adhesive basic metal compounds on the fibre. Such compounds are able to produce insoluble colour complexes with certain azo and anthraquinone dye derivatives (Leube, 2003). The use of mordant in dyeing also leads to bathochromic shift in colour, notwithstanding the duller hue and improved washing and light colour fastness (Mennicke, 2003).

Mordant can be metal salts of iron, copper, tin, chrome and aluminium that help in binding dye to fabric by forming a chemical bridge from dye to fibre thereby improving the colouring ability of a dye and increasing its fastness properties. Shade of colour on fabric depends on the type of metal mordant used (Janani et al., 2014). However, mordants of chrome, tin and copper pose a health hazard both to man and the environment hence are not recommended to be used again in textile dyeing. Alum and iron are safer to use and can produce several different colours when used with the appropriate dye. Tannins and oils classified as mordant are also safe (Maiwa Handprints, 2015).

For this research alum (potassium aluminium sulphate $[KAl(SO_4)_2 \cdot 12H_2O]$) was used as a mordant and its presence made the colour shade of dyed fabric B₁ and B₂

less deep/strong as A_1 , C_1 and A_2 , C_2 . Visually, B_1 and B_2 fabric hue tilted towards pink. This may be due to the bathochromic shift effect of the metal mordant. On the other hand there was no remarkable difference in the colour shade of B_1 and B_2 as observed between A_1A_2 and C_1C_2 probably because the amount of mordant in both pre-mordanted fabrics dyed at the different temperatures is the same hence could not attach to more dye molecules even at increased temperature.

The effect of temperature was however more pronounced in A_1A_2 and C_1C_2 dyed fabrics. Fabrics dyed at 60°C had stronger shades than those dyed at room temperature. Possibly it could be that the dye extracts which are impure yielded more dye at high temperature and thus became more concentrated with dye molecules which mean more dye molecules available for attachment to the fabric. This is supported by the high absorbance readings of the dye extracts after dyeing at 60°C in Tables 4.10 and 4.11 where RA= reducing agent and M= mordant. Furthermore, diffusion of dye molecule in the fibre determines the rate of dyeing, therefore, following Fick's first law, diffusion coefficient D which is between 10^{-10} to $10^{-12}\text{cm}^2/\text{s}$ can only be increased by increasing temperature (Leube, 2003). It then means that more dye molecules diffused into the cellulose fibre at increased temperature hence making the fabric absorb more dye molecules and have deeper colour shade than at room temperature.

The effect of the reducing agent (sodium dithionite $[\text{Na}_2\text{S}_2\text{O}_4]$) was not so pronounced. The colour strength of fabrics C_1C_2 and A_1A_2 are almost similar. The dye extract liquor with the reducing agent did not change colour when the $\text{Na}_2\text{S}_2\text{O}_4$ was added meaning that there was no reduction reaction. Again the dyed fabric colour did not change when it was left in the open for oxidation before washing. All this is an indication that the dye extract used is not a vat.

The fact that both the *uri* and *uhie* dye extracts dyed the cotton fabric well without mordant or reducing agent indicates that the dye extracts are neither mordant nor vat dyes. The dyes extracts are also not acid dyes since they were applied under alkali medium. They are not also basic (cationic) dyes because basic dyes have no affinity for cellulose. We therefore note that the dye extracts are substantive dyes that is, direct dyes having strong affinity for cellulose fibre (the dyes could also be reactive dyes). *Uri* dye extract however will require high temperature in order for its colour shade on cellulose fabric to be conspicuous. Direct dyes are bound to the cellulose fibre by hydrogen bonding or Van der Waals forces and the strength of these bonds is low (Leube, 2003). An example of hydrogen bonding (H-bonding) between a direct dye and cellulose is shown below (www.monographs.iarc.fr, 2015):

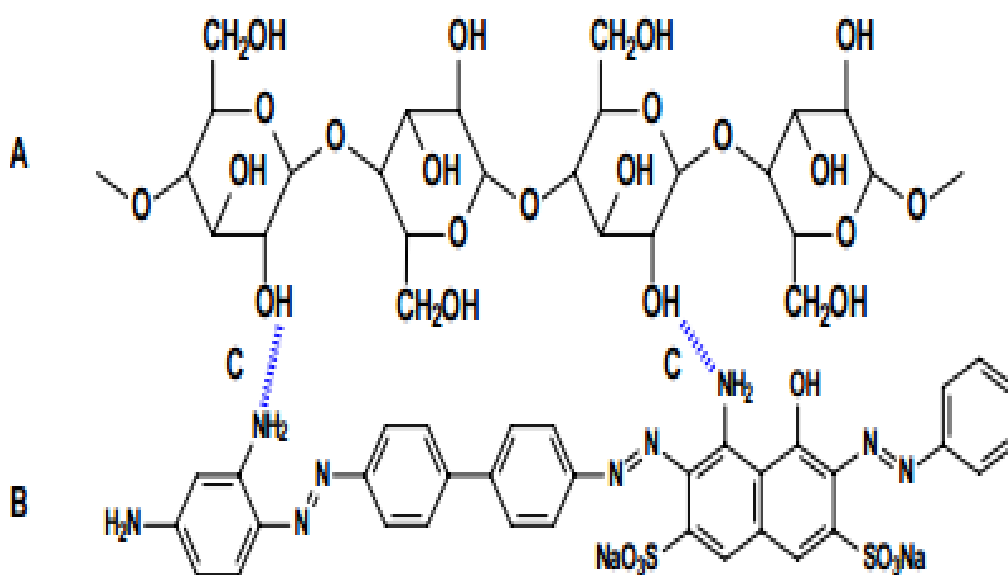


Fig. 4.24 Representation of H-bonding (C) between cellulose (A) and a direct dye (B)

According to Leube, direct dyes in an aqueous medium are anionic which will naturally be repelled by the negative charge on the cellulose fibre surface when placed in water. For this reason an electrolyte (in this case NaCl) is required so that its cations will neutralize the cellulose negative charges and thus enhance the movement of the dye molecules towards the fibre. Dye molecules are first adsorbed to the fibre surface before they diffuse into the cellulose fibre amorphous regions and are absorbed (Leube, 2003).

B. Colour Fastness Tests

Colour fastness is the resistance of the colour of dyed textiles to the conditions they may endure when in use (Leube, 2003). Colour fastness to two of such conditions was considered in this research, rubbing and washing. Colour fastness to rubbing is used to evaluate the amount of colour transferred from a coloured textile material to other surfaces by rubbing (Texanlab, 2015), while colour fastness to washing is used in assessing the change or loss of colour during washing of a coloured textile and the possibility of staining other garments or lighter portions washed with it (Texanlab, 2015). Grey scales to colour change and grey scales to staining were used in the assessment of the fabrics after each test. The grey scale to colour change is a pair of five standards used to evaluate the level of contrast between the treated (washed) and untreated (unwashed) fabrics. The contrast is related to the one of the standard pairs to give the grey scale rating, whereas the grey scale to staining uses a different five pair standard to evaluate the transfer of colour from a test specimen to an adjacent fabric (Hunterlab, 2008).

Result of colour fastness test to rubbing and washing for both *uri* and *uhie* dyed fabrics are reported in Tables 4.16 and 4.18. In Table 4.16 the colour fastness to dry and wet rubbing for the *uri* dyed fabric was excellent as none was below grade 4 on the grey scale for the three areas of dye analysis and at both 60°C and room temperature. This however is not the case for the *uhie* dyed fabrics. The *uhie* dyed

fabric with mordant B₂ had excellent fastness which was not less than grade 4 both for wet and dry rubbing at both temperature range. The fabric A₁ fastness to wet and dry rubbing was good with grade 3/4 for both. Fabric A₂ had a slightly good wet rubbing fastness of 3 but a good dry fastness of 3/4. Fabric C₁ had a slightly good dry rubbing fastness of 3 but an excellent wet rubbing fastness of 4/5 while C₂ had good dry and wet rubbing fastness of 3/4 and 4 respectively.

Fabrics B₁ and B₂ therefore gave the best colour fastness to rubbing for both wet and dry rubbing for *uhie* dyed fabric, while all *uri* dyed fabric gave excellent wet and dry fastness to rubbing

Fastness to washing with soap as seen in Table 4.18 shows grey scale result of change in colour of dyed fabric and staining of adjacent cotton fabric. The fabric dyed with *uri* showed excellent fastness to colour change with the least grade being 4 especially for C₁, A₂, and C₂ fabrics. B₂ fabric with rating of 5 implies no colour change and B₁ having 4/5 very slight colour change.

The colour staining assessment for all the fabrics at the three areas checked and both temperatures gave a grade of 5 meaning that the adjacent cotton fabric was not stained by the dye. This is also true for the *uhie* dyed fabrics.

Fastness to colour change for the *uhie* dyed was excellent for fabrics B₁ and B₂. A₁A₂ and C₁C₂ fabrics have good fastness to colour change of 3/4.

On the overall, B₁ B₂ fabrics for both *uri* and *uhie* have the best colour fastness property to washing and rubbing. It can thus be concluded that the use of alum as mordant in dyeing of cotton fabric with *uri* or *uhie* dye extracts will improve colour fastness to washing and rubbing but will not improve colour depth or change the dye hue on the fabric. Similarly, fabrics dyed with *uri* or *uhie* dye extracts will not stain an adjacent white cotton fabric washed together with it. The washed fabrics are shown in Fig. 4.25 and Fig. 4.26

UHIE

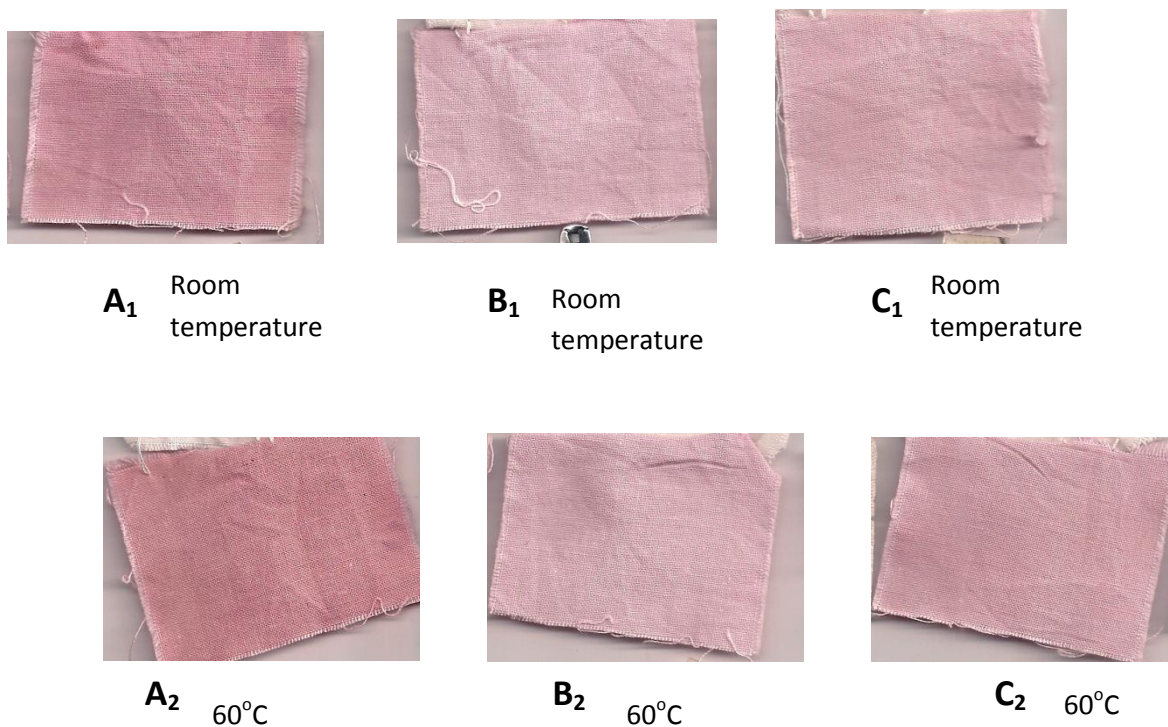


Fig. 4.25: Dye analysis: cotton fabrics dyed with *uhie* dye at room temperature and 60°C after washing with soap

URI

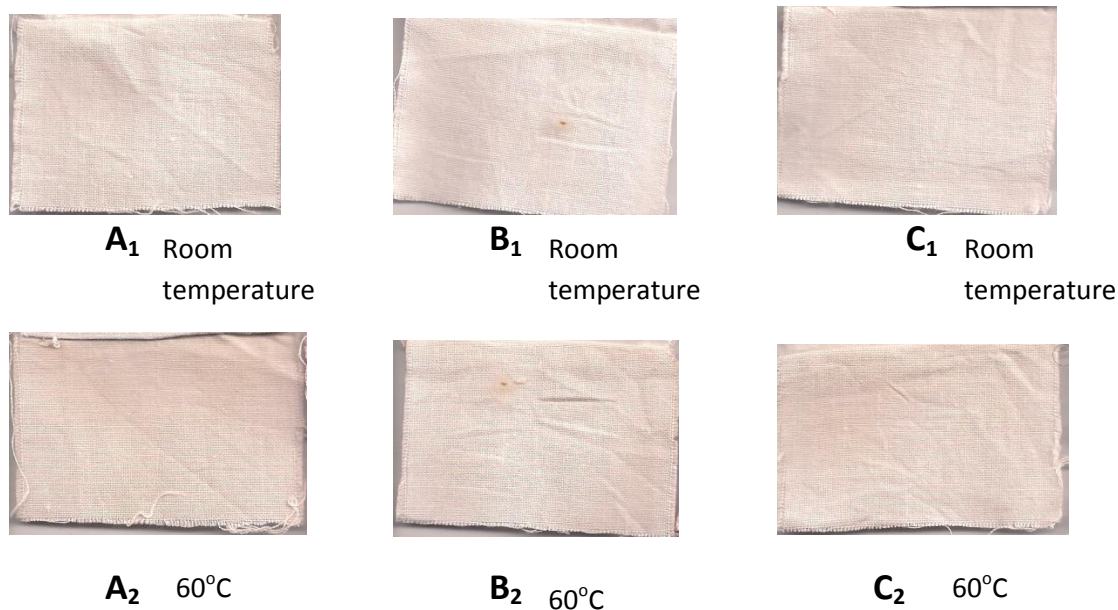


Fig. 4.26: Dye analysis: cotton fabrics dyed with *uri* dye at room temperature and 60°C after washing with soap

C. Fourier Transform Infra-red Spectroscopy (FTIR) Analysis

This test was done using the transmittance method with the following parameters:

Wavenumber range: 4000 – 650 cm⁻¹

Sample scans: 16

Background scans: 16

Resolution: 8

System status: Good

Apodization: Happ-Genzel

Infra-red (IR) spectroscopy of five samples were taken and their absorption spectra with peaks corresponding to certain frequencies (cm^{-1}) are shown in Figs. 4.27 – 4.31. Peaks appearing in IR spectrum occur where the frequency of the electromagnetic waves corresponds with the natural frequency of vibration between two atoms in the test material (Morton & Hearle, 1975).

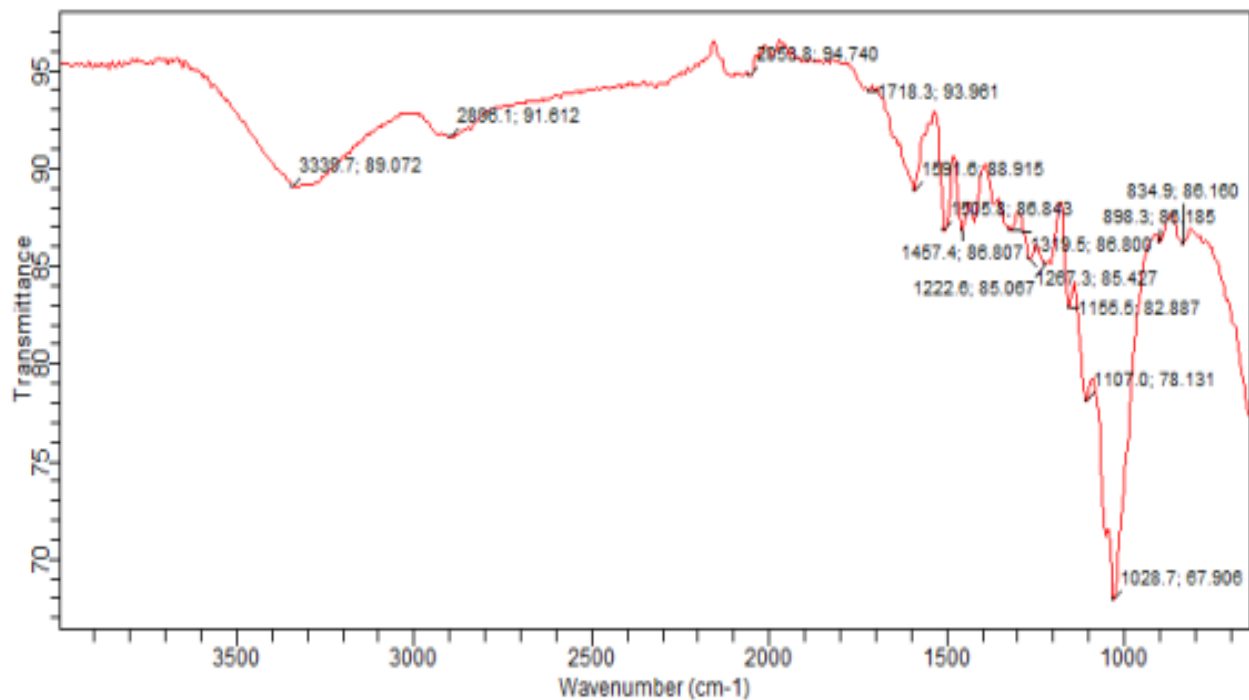


Fig. 4.27: Infra-Red Spectrum of Sample A (*Uhie* dry powder)

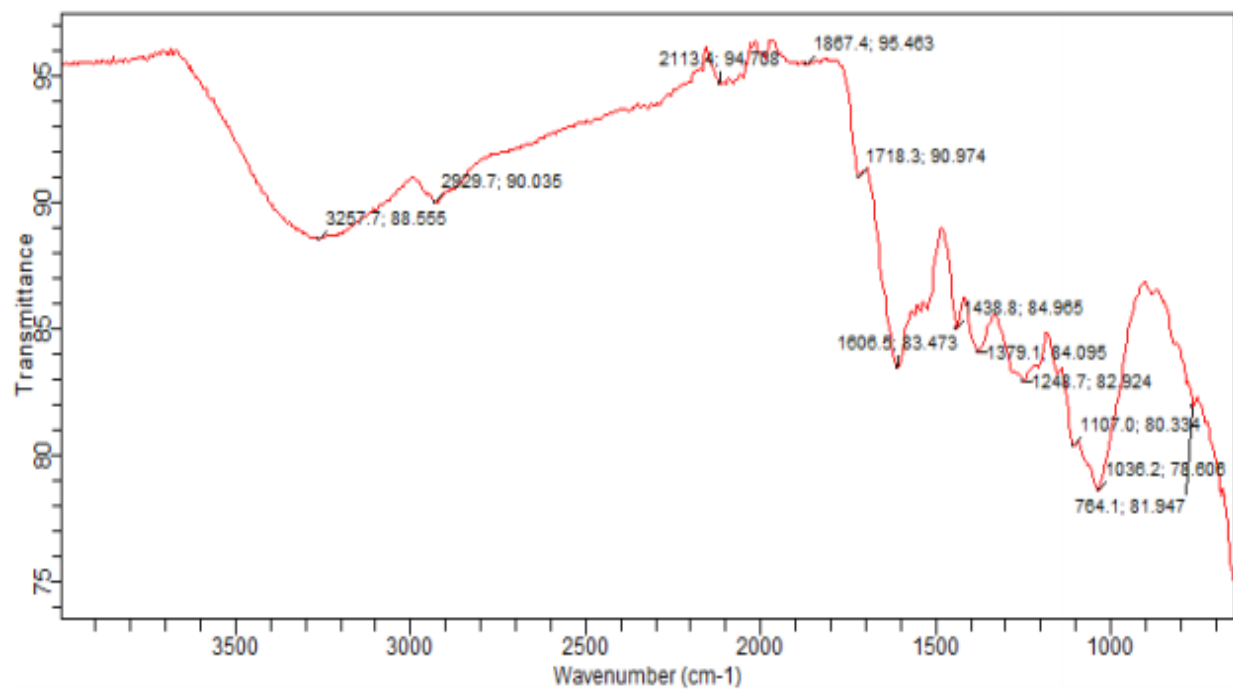


Fig. 4.28: Infra-Red Spectrum of Sample B (*Uri* fruit dry powder)

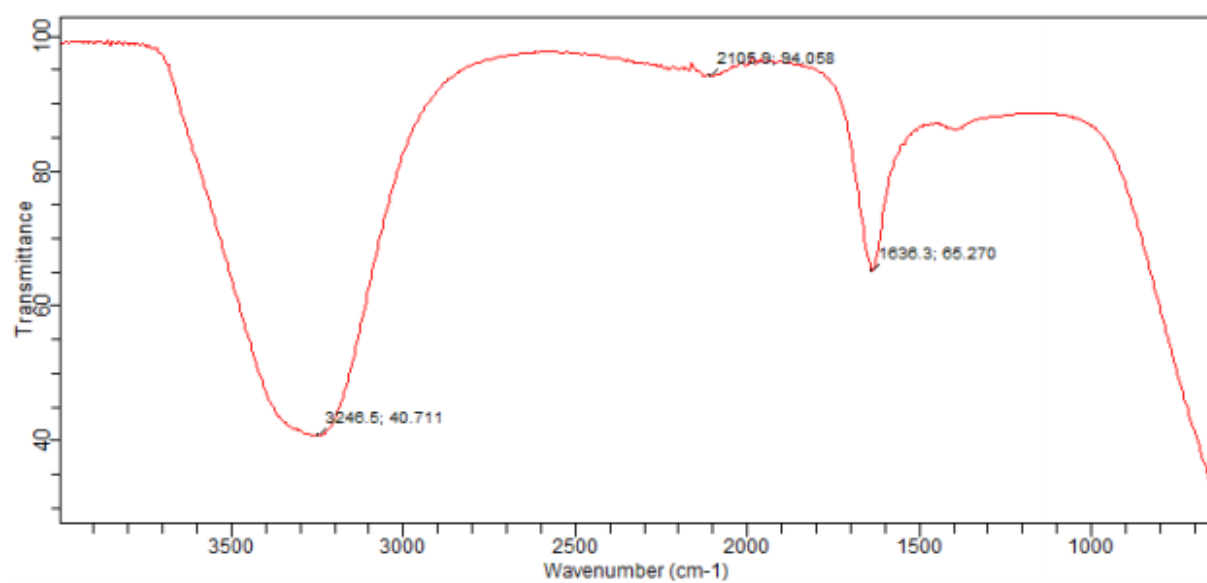


Fig. 4.29: Infra-Red Spectrum of Sample C (*Uhie* dye extracted with 1% alkali at 65°C)

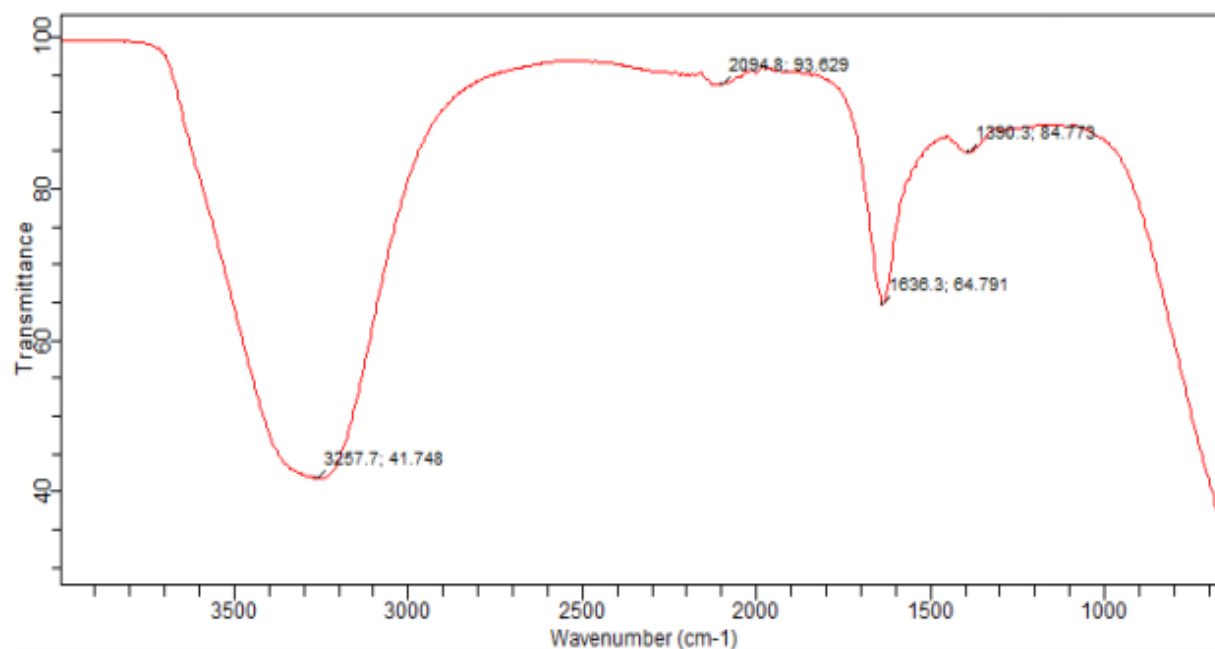


Fig. 4.30: Infra-Red Spectrum of Sample D (*Uri* dye extracted with 1% alkali at 65°C)

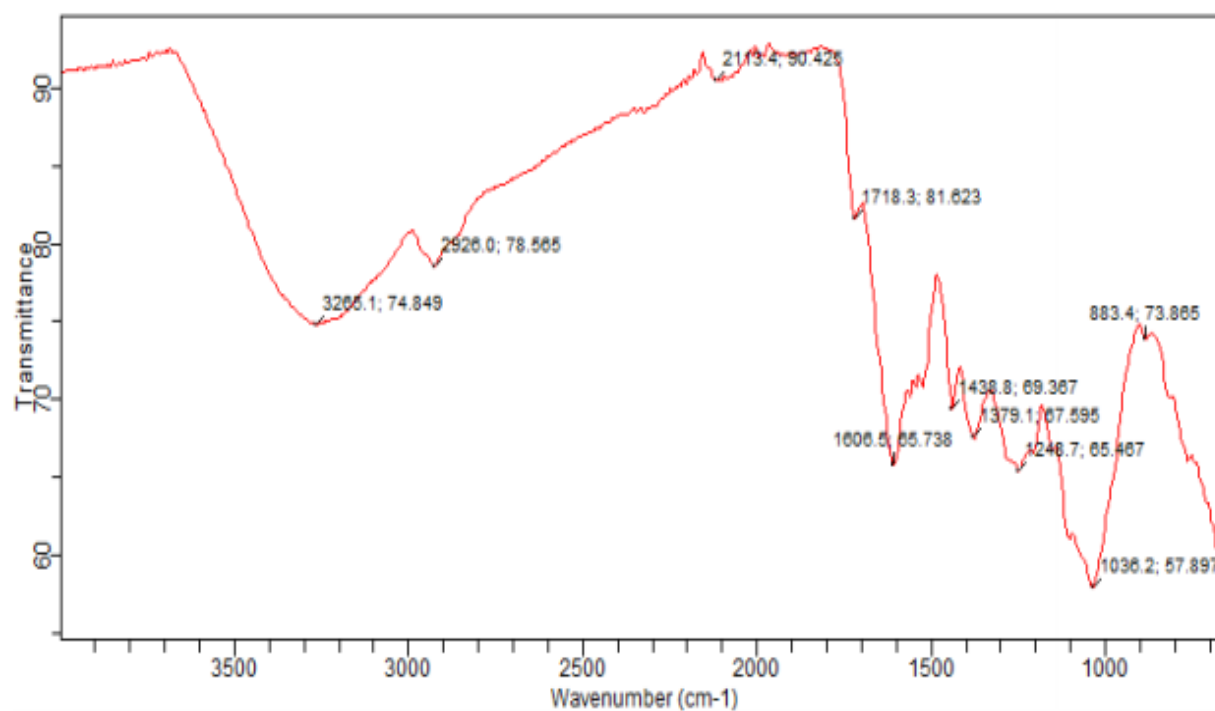


Fig. 4.31: Infra-Red Spectrum of Sample E (*Uri* dye extracted with distill water at 65°C)

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. The fact that materials are a unique combination of atoms, no two compounds produces exactly the same infrared spectrum. Therefore, infrared spectroscopy can be used to positively identify (qualitative analysis) different kinds of materials. Also, the size of the peaks in the spectrum is a direct indication of the amount of material present (Thermo Nicolet, 2001).

For the purpose of interpretation infrared spectrum can be split into four distinct regions (MCT3, 2016):

- A. $4000\text{--}2500\text{ cm}^{-1}$: absorption of single bonds to hydrogen – eg C–H, O–H, N–H
- B. $2500\text{--}2000\text{ cm}^{-1}$: absorption of triple bonds – eg $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$
- C. $2000\text{--}1500\text{ cm}^{-1}$: absorption of double bonds – eg $\text{C}=\text{C}$, $\text{C}=\text{O}$
- D. $1500\text{--}400\text{ cm}^{-1}$: absorption owing to other bond deformations – eg. rotating, scissoring and some bending.

There are some exceptions – eg. N–H bending is observed at $1550\text{--}1620\text{ cm}^{-1}$.

The region between $1500\text{--}400\text{ cm}^{-1}$ is the fingerprint region because it is unique to each compound. This region helps to identify particular molecules because no other compound will have the same pattern of absorptions. However, interpretation

of peaks in this region is sometimes complicated due to large number of vibrations at the region. It should be noted that infrared spectroscopy is used majorly to confirm the presence of functional groups in a compound and not for determination of the structure of a compound (MCT3, 2016).

The resources in Appendix D were used to interpret the IR spectrum of each of the samples stating the possible bond and the functional groups at each peak as presented in Tables 4.20 – 4.24

Table 4.20: Functional groups in Sample A

Wavenumber (cm ⁻¹)	Bond	Functional group
3339.7	O–H stretch, H–bonded	alcohols, phenols
2896.1	C–H stretch	Alkanes
2053.8	–C(triple bond)C– stretch or N=C=S stretching	Alkynes or isothiocyanate
1718.3	C–H bending or C=O stretch	Aromatic compound
1591.6	N–H bending or C=C stretching	Amines or Cyclic alkene
1505.8	N–O asymmetric stretch	Nitro compound
1457.4	C – H bend	Alkanes
1319.5	N–O symmetric stretch or C–O stretch	Nitro compound or Acyl
1267.3- 1222.6	C – N stretch	Aromatic
1155.5-1028.7	C–N stretch or C–O stretch	Aliphatic amines or Ethers
898.3-834.9	=C–H bend	Alkenes

Table 4.21: Functional groups in Sample B

Wavenumber (cm⁻¹)	Bond	Functional group
3257.7	O–H stretch, H–bonded	alcohols, phenols
2927.7	C–H stretch	Alkanes
2113.4	–C(triple bond)C– stretch	Alkynes
1867.3	C–H bending or C=O stretch	Aromatic compound
1718.3	C=O stretching	Cyclo or aliphatic ketone
1606.5	N–H bending or C=C stretching	Amines or Cyclic alkene
1438.8	C–H bend or C=C stretch (in-ring)	Alkanes or Aromatics
1379.1	C–H bending	Alkanes
1248.7 – 1036.2	C–N stretching	Aromatic amines
764.1	C–H bend	Aromatics

Table 4.22: Functional groups in Sample C

Wavenumber (cm⁻¹)	Bond	Functional group
3246.5	O–H stretch, H–bonded	alcohols, phenols
2105.9	–C(triple bond)C– stretch	Alkynes
1636.3	C=C stretching or N – H bending or C=C stretching	Conjugated alkene or Amines or Cyclic alkene

Table 4.23: Functional groups in Sample D

Wavenumber (cm⁻¹)	Bond	Functional group
3257.7	O–H stretch, H–bonded	alcohols, phenols
2094.8	–C(triple bond)C– stretch or N=C=S stretching	Alkynes or Isothiocyanate
1636.3	C=C stretching or N – H bending or C=C stretching	Conjugated alkene or Amines or Cyclic alkene
1390.3	C – H bending or O – H bending or N – O symmetric stretch	Alkane or Phenol, alcohol or Nitro

Table 4.24: Functional groups in Sample E

Wavenumber (cm ⁻¹)	Bond	Functional group
3265.1	O–H stretch, H–bonded	alcohols, phenols
2926	C–H stretch	Alkanes
2113.4	–C(triple bond)C– stretch	Alkynes
1718.3	C=O stretching	Cyclo or aliphatic ketone
1606.5	N–H bending or C=C stretching	Amines or Cyclic alkene
1438.8	C–H bend or C=C stretch (in-ring)	Alkanes or Aromatics
1379.1	C–H bending	Alkanes
1248.7 – 1036.2	C–N stretching	Aromatic amines
883.4	=C–H bend Or C – H bend	Alkenes Or Aromatics

One of the objectives of this research is to analyse *uri* and *uhie* plant dye extracts. Hence interest was centred on samples C and D which are the dye extracts of *uhie* and *uri* plants using 1% alkali solution at 65°C which were also used for dyeing of cotton fabric. Samples A and B are the *uhie* plant dry powder and the *uri* fruit dry powder while sample E is the *uri* plant extract with distill water.

The dyeing and the colour fastness test helped us to identify both dye extracts as direct dyes. The FTIR test is to help us know the chemical constituents of the dye extracts. The fact that samples C and D spectra in Figs. 4.29 and 4.30 are simple, that is, with less than five absorption bands is an indication that they are low molecular weight compounds (Coates, 2000). IR spectra of samples C and D are also similar except at the fingerprint region. From Tables 4.22 and 4.23 we observe that the broad peak at 3246.5 cm^{-1} for sample C and 3257.7 cm^{-1} for sample D indicates the presence of alcohols or phenols which is part of the parent plant as seen in Tables 4.20 and 4.21; perhaps a little of the plant particle impurities in the extract gave rise to it. This however has little or nothing to do with the dye extract hue and behaviour.

The peak at 2105.9 cm^{-1} for sample C and 2094.8 cm^{-1} for sample D, is an indication of the presence of $\text{--C(triple bond)C--}$ stretch that is an alkyne. This is most likely because the intensity of the peak is weak which is also why it may be symmetrically substituted. In addition to this the $\text{--C(triple bond)C--}$ stretch may be conjugated since the peak is a little lower than 2150 cm^{-1} (www.researchgate.net, 2016). This may have contributed to the colour of the both dyes.

1636.3 cm^{-1} peak is exactly the same for both dye extracts. This medium peak falls within the three suggested functional groups (www.ochemonline.com, 2016). If the bond is the C=C conjugated alkene it means that the dye extract colour is actually

from it because the presence of long conjugated double bonds have been known to be the cause of red colour in some natural dye extracts; example is Bixin found in some plants. Bixin is one of the few red colour direct dyes of plant origin; its structure is shown below (Sequin-Frey, 1981):



Fig.4. 32: Conjugated double bond of Bixin dye

Since the visible light wavelength of maximum absorption of both dyes falls within red colour spectrum, we may conclude that the conjugated double bond is the actual functional group that gave especially the *uhie* dye extract (sample C) its red colour. Sample D will have an additional effect due to the medium peak at 1390.3 cm⁻¹. If this peak represents phenol, it will mean that sample D may also have tannins like catechin (Fig.4.33) or just be a direct dye having structures like carthamin, Fig.4.34 (Sequin-Frey, 1981).

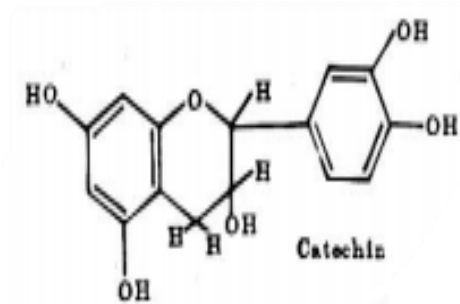


Fig. 4.33: Catechin structure

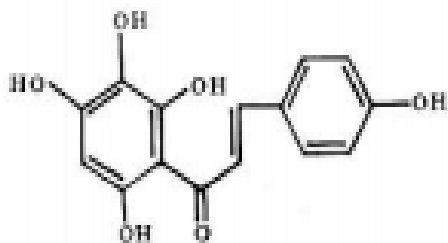


Fig. 4.34: Carthamin structure

The deep brown colour of *uri* dye extract has earlier in this research been attributed to possible presence of tannins which now appears to be confirmed by the IR spectrum, if peak 1390.3 cm^{-1} represents phenol. It should be noted that the peak could also be a C–H (alkane) or N–O (nitro) bond in which case it will give a structure not related to the examples in Figs. 4.33 and 4.34. The peak irrespective of the bond, could be responsible for the high temperature requirement for effective dyeing with *uri* dye extract.

The very different fingerprint region of the IR spectrum of samples A and B is a clear indication that the two are different compounds; *uhie* and *uri*. This also is seen in Tables 4.20 and 4.21. But in the case of samples B and E (Figs. 4.28 and 4.31) their full IR spectrum showed very close similarity. Similarly, both have the same functional groups as observed in Tables 4.21 and 4.24. This implies that both samples have similar chemical constituents. Sample B is *uri* fruit dry powder while sample E is *uri* dye extract using distill water at 65°C . The two samples being the same is an indication that *uri* plant fruit powder was not dissolved by water hence

no dye was actually extracted confirming an earlier statement in section 4.2.1. With this it is now evident that alkali solution is the solvent for dry *uri* fruit powder which could be why the *uri* extract with water and traditional method will turn to deep brown colour when mixed with drops of NaOH solution.

4.2.4 Effect of Temperature on Dyeing of Cotton Fabric with *uhie* and *uri* dye Extracts.

Dyeing at different temperatures was done with a liquor ratio of 0.5:40.

40ml of the 2% dye stock was used directly after extraction in order to achieve a 2% shade on the fabric. This is slightly different when powdered pure natural or synthetic dyes are used for dyeing. Also quantity of NaCl used (0.15g) was calculated on the weight of fabric (owf).

The effect of temperature could be visibly seen on the fabrics dyed with both the *uhie* and *uri* dye extracts. As temperature increases the colour shade on the fabrics increases or becomes deeper; A $\longrightarrow$ G as seen in Figs. 4.35 and 4.36 below.

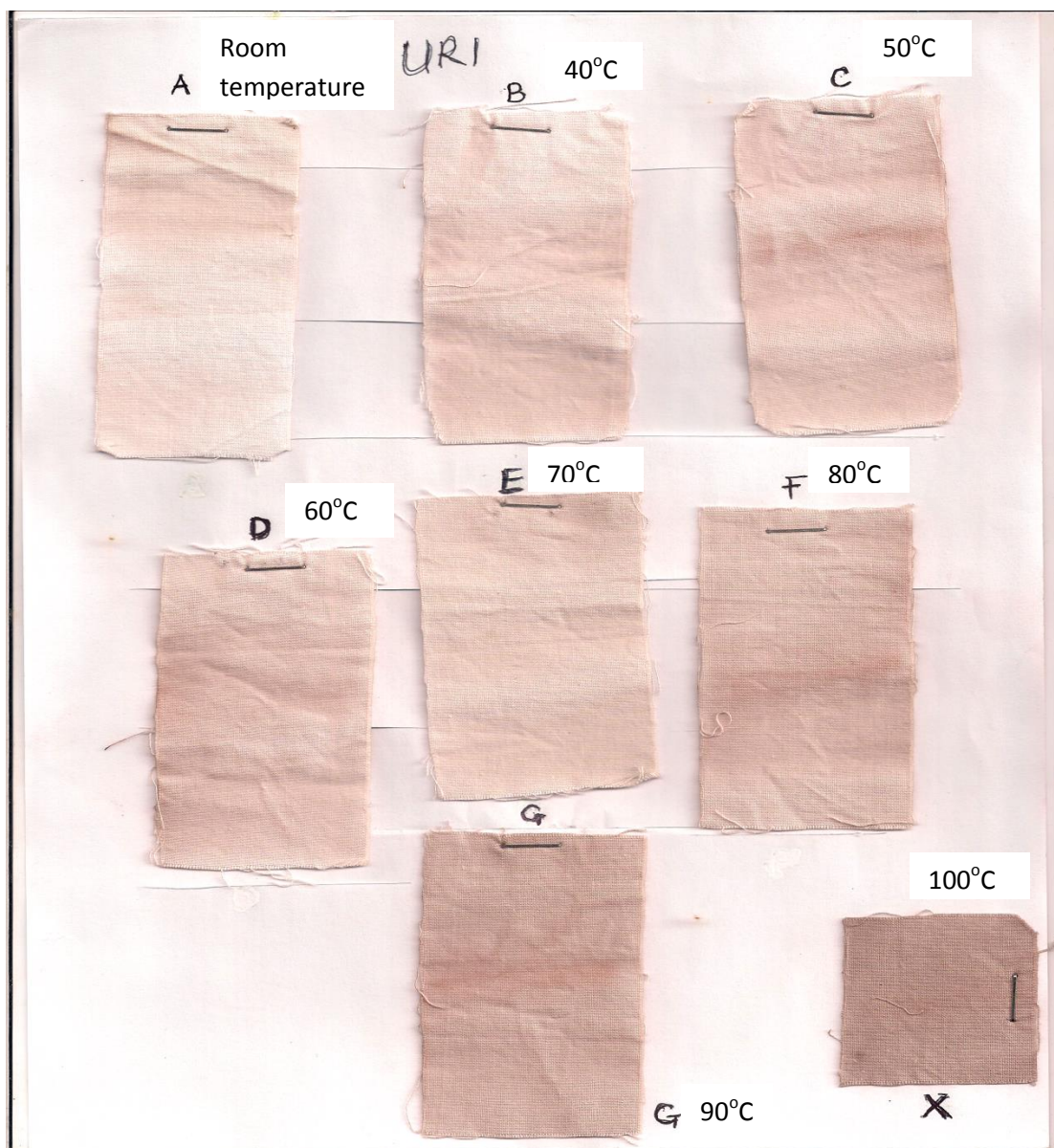


Fig. 4.35: Cotton fabrics dyed with *uri* dye at different temperatures

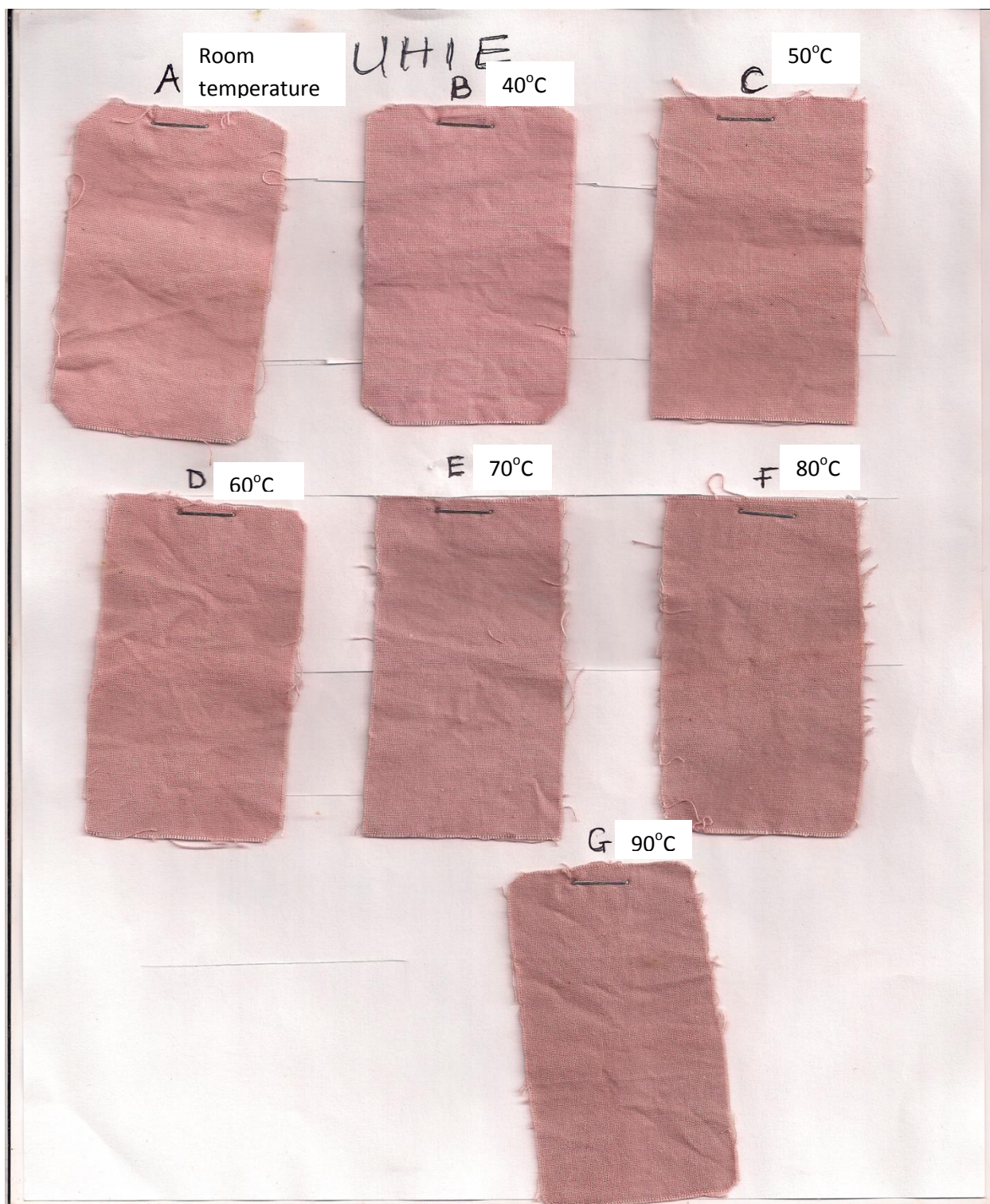


Fig. 4.36: Cotton fabrics dyed with *uhie* dye at different temperatures.

Temperature thus has a great effect on the dyeing of cotton fabric with direct natural dye. However, this effect can also be attributed to the presence of impurities which were also observed during the dye extract analysis in Tables 4.10 and 4.11. From Tables 4.14-4.15 it is observed that the absorbance of *uri* dye after dyeing was higher than the absorbance before dyeing except for effluent at room temperature (Fig.4.37). The wavelength used to check absorbance after dyeing is the wavelength of maximum absorbance of the dye extract before dyeing.

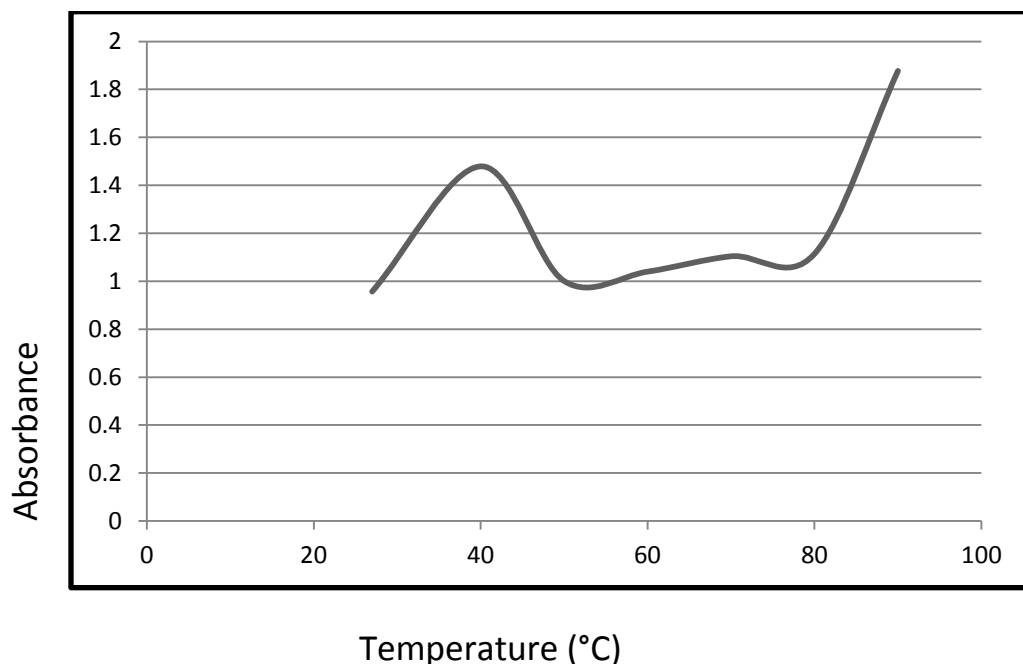


Fig. 4.37: Effect of temperature on the absorbance of *Uri* dye after dyeing (measured at 770nm).

The absorbance of *uhie* dye after dyeing at temperatures above room temperature is higher than the absorbance at room temperature as seen in Tables 4.12-4.13 and Fig 4.38. This should not be the case as the deeper colour shade of fabrics dyed with the *uhie* dye above room temperature should imply more dye absorption which would have reduced the dye concentration after dyeing and resulted to a lower absorbance.

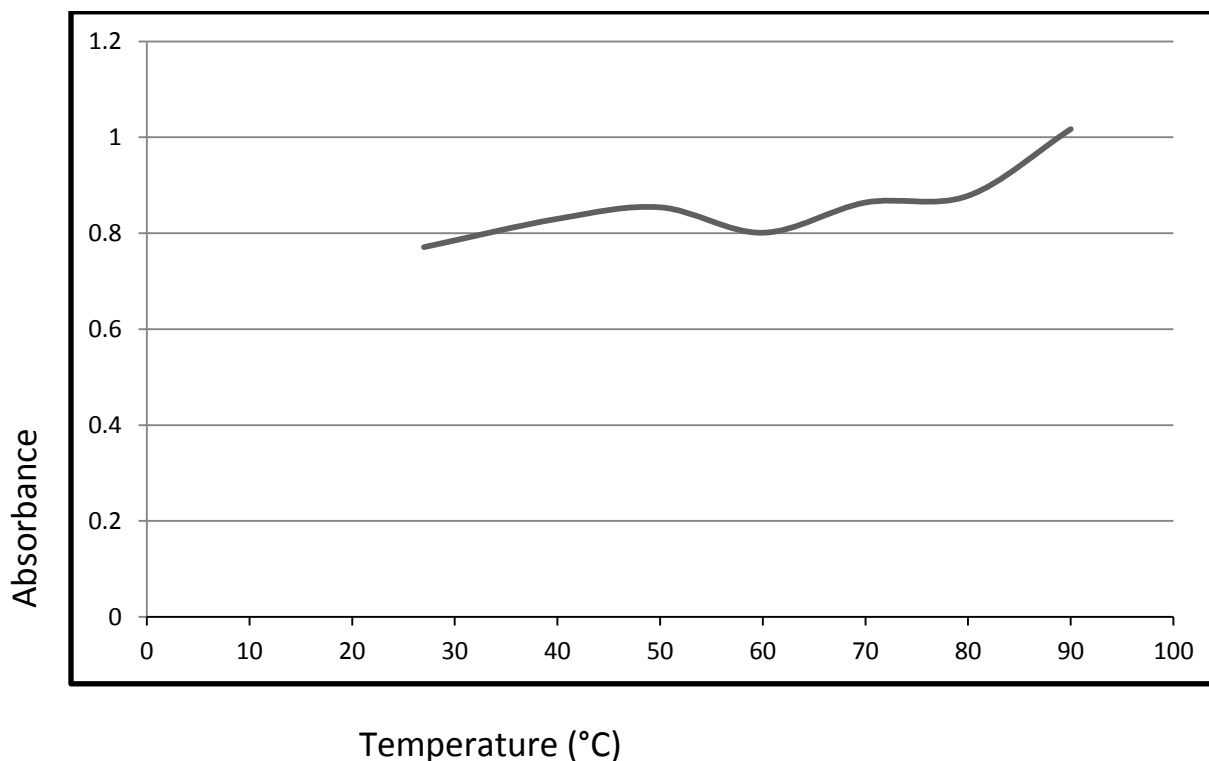


Fig.4.38: Effect of temperature on the absorbance of *Uhie* dye after dyeing (measured at 730nm).

Such after dyeing absorbance results can be due to the fact that impurities yielded more dye at temperatures above room temperature both for the *uri* and *uhie* dyes, thus making it impossible to have a positive percent dye uptake for temperatures above room temperature using equation 3.4 for *uri* dye and gives a percent dye uptake that should not be trusted for the *uhie* dye. This also means that one may only attribute the shade of fabric dyed at room temperature with *uhie* dye as the required 2% shade or that at each of the different temperatures the depth of fabric colour is 2% shade at that temperature making the percent colour shade temperature dependent.

The fabric dyed with *uri* dye at room temperature may not be taken to be the 2% shade since *uri* dye requires high temperature for effective dyeing of cotton fabric. It is also for the purpose of improving the *uri* dye colour yield that the dyeing time was extended to 40min. and it can be seen that the colour depth on the cotton fabric increased as dyeing temperature increased; A→G. This phenomenon can still be attributed to the presence of colour releasing impurities and also to the increased diffusion of more dye molecules into the cellulose fibre giving rise to more dye absorption. Fabric X in Fig. 4.35 is cotton fabric dyed with *uri* dye at a boiling temperature for 55min. This still confirms the effect of temperature and time on dyeing with *uri* dye and informed the use of 40min for dyeing with *uri* dye.

The colour fastness to rubbing and washing of the dyes were carried out and reported in Tables 4.17 and 4.19. *Uri* and *uhie* dyed fabrics had excellent dry rubbing fastness. *Uri* dyed fabrics also had excellent wet rubbing fastness of not less than 4 except for fabric G with 3/4 while *uhie* dyed fabrics had a good wet rubbing fastness of 3/4.

Colour fastness to washing with soap showed a remarkable colour change especially for fabrics dyed at temperature above room temperature with the *uri* dye as seen in Fig. 4.39. B to E fabrics dyed with *uri* dye have 3/4 grey scale rating while fabric F and G had a rating of 3 perhaps due to their deeper colour shade. For fabrics dyed with *uhie* dye, colour change was obvious for all fabrics- A to G as shown in Fig. 4.40. While fabrics A and B had fastness rating of 3/4 fabric C – G had fastness rating of 3 probably due to their deeper colour shade. The deeper colour shade of fabrics F and G dyed with *uri* and fabrics C – G dyed with *uhie* is an indication of having more dye molecules in the cellulose fibre hence these fabrics lost more dye molecules during washing leading to their lower colour change on the grey scale rating. This conforms to the statement that for direct dyes wet fastness decreases as colour depth increases (Leube, 2003).

The grey scale to staining rating of 5 for all fabric dyed with both *uri* and *uhie* dyes is an indication that the adjacent fabrics were not stained. It then implies that both *uri* and *uhie* natural dyes will not stain adjacent cotton fabric washed with them.

This agrees with one of the advantages of natural dyes stated in chapter one of this research work that natural dyes do not stain other fabrics when they bleed.

URI



A Room temperature



B 40°C



C 50°C



D 60°C



E 70°C



F 80°C



G 90°C

Fig. 4.39: Cotton fabrics dyed with *uri* dye at different temperatures after washing with soap.

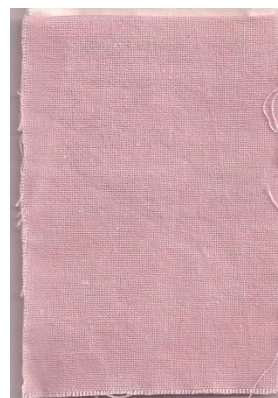
UHIE



A Room temperature



B 40°C



C 50°C



D 60°C



E 70°C



F 80°C



G 90°C

Fig. 4.40: Cotton fabrics dyed with *uhie* dye at different temperatures after washing with soap.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Within the scope of this research work, the objectives were all met. The extraction of *uri* and *uhie* dyes were achieved with 1% sodium hydroxide solution at both room temperature and 65°C. Organic solvent like iso-propanol can also be used to extract colour from *uhie* plant but not from *uri* fruit. Temperature of extraction also plays an important role in both dye extractions; increase in temperature helps to extract more dye. The coloured extracts with 1% alkali solution dyed cotton fabric with reasonable degree of fastness.

The hue of *uhie* dye has a wavelength of maximum absorbance of 620nm while that of *uri* is 670nm. Both are within the red colour wavelength of the visible light spectrum. However, *uri* dye is of deeper and different shade than the *uhie* dye. *Uri* dye by visual observation has a deep brown or dark tan colour which in the visible light spectrum falls within the far red region. The colour shade of the fabrics dyed with both dye extracts also show the difference in *uhie* and *uri* dye hues. Similarly, FTIR spectroscopy confirmed their differences with an indication that *uri* dye may contain tannins and that both dyes have a conjugated double bond.

Uri and *uhie* dyes extracted with the procedure used in this research are impure because of the presence of undissolved particles in the dye extracts. However, it should be noted that the presence of these impurities in both the *uhie* and *uri* dye liquor did not affect dye levelness on the fabrics. Unnecessary patches were not also noticed on the dyed fabrics due to their presence. Again these impurities did not hinder fabric dyeing rather their presence improved dye shade especially at temperatures above room temperature. For the local colourist the presence of these impurities may be an advantage as they will not need so much dye extract to achieve deep shades.

But on the contrary, the presence of such impurities will make it difficult to use the dye extracts directly in some dyeing machines because of possibility of the impurities causing blockage to certain machine parts which can lead to machine damage. Also as observed in this research the presence of such impurities makes it difficult to actually calculate the dye percent uptake.

The dye extracts appeared to be direct dyes having affinity for cotton fabric. But for effective dyeing with the *uri* dye, dyeing temperature has to be above room temperature and perhaps close to boiling depending on the depth of colour shade required. It has been reported in some literature that *Baphia nitida* plant dye contains flavones thus making it a mordant dye, but based on this research work *uhie* dye was found not to be mordant dye. Furthermore, the colour fastness tests

showed that the *uri* dye has a better rub fastness than the *uhie* dye. Both dyes do not have a very good wash fastness except when used on a pre-mordanted cotton fabric.

Finally, the extraction of dye from *uhie* (*Baphia nitida* plant) cakes and dry *uri* plant fruit is novel. *Uhie* cakes are used majorly for cosmetics, medicinal and magical purposes especially in Nigeria while dry *uri* plant fruit was not considered useful since only juice from the fresh fruit was used for body decoration and traditional medicine. Based on this research, both *uhie* and *uri* dyes can be used to dye cotton fibre with a good degree of wash and rub fastness.

5.2 Recommendations

Following the outcome of this research work it becomes pertinent to make some recommendations for future work.

- i. For the extraction of dye from dry *uri* fruit and *uhie*, 1% sodium hydroxide solution should be used. However, further research should be carried out using other alkali solutions to ascertain their effectiveness with these plant powders.
- ii. It is important to seek for ways to purify the dye extracts or ways of getting a pure dye extract powder so that they can be industrially applied using

sophisticated dyeing machines. The dye extracts should also be purified to enable correct calculation of percent dye uptake, the effect of dyeing time and other dyeing parameters without interference of impurities.

- iii. More tests should be carried out to ascertain the actual structures of *uri* and *uhie* dye extracts.
- iv. *Rothmannia whitfieldii* and *Baphia nitida* plant should be cultivated to save the plants from extinction in Nigeria in particular.
- v. Further research should be carried out in order to ascertain if *uhie* and *uri* dye extracts can be used to dye other natural and synthetic fibres.

5.3 Contribution to Knowledge

This research work has shown that:

- i. Natural dye can be extracted from mature dry *Rothmannia whitfieldii* fruit (*uri*) with 1% sodium hydroxide solution but not extractible with water, organic solvents such as iso-propanol and organic acids like citric acid. The dye appears not to be a vat or mordant dye but a direct dye having a hue with wavelength of maximum absorption of 670nm.

- ii. FTIR analysis of *uri* dye also revealed the possible presence of conjugated double bonds and phenol groups (tannins) in the molecular structure.
- iii. *Uri* dye can be used to dye cotton fibre at temperatures above room temperature ($27 \pm 2^{\circ}\text{C}$) with a reasonable degree of wash and rub fastness.
- iv. *Baphi nitida* locally prepared cakes (*uhie*) sold in Nigerian markets is a good source of dye. The dye can be extracted with 1% sodium hydroxide solution and organic solvents like iso-propanol but not with water or organic acids such as citric acid.
- v. *Uhie* dye hue has a wavelength of maximum absorption of 620nm and appears not to be a vat or mordant dye but rather a direct dye.
- vi. FTIR spectroscopy of *uhie* dye revealed the possible presence of conjugated double bonds in its molecular structure.

REFERENCES

- Acquaviva, S., D'Anna, E., De Giorgi, M L., Della Patria, A., & Baraldi, P. (2010). Physical and chemical investigations on natural dyes. *Applied Physics A*, 100 (3), 823 – 828.
- AsianSecrets, (2012) *Natural Dye - How is it extracted?* Retrieved from www.asiansecrets.hubpages.com 30th Dec. 2014
- Banerjee, A & Mukherjee, A.K. (1981). Chemical aspects of santalin as a histological stain. *Stain Technology*, 56 (2), 83-85.
- Bittar, K. (2015) Cellulose Retrieved from www.courses.sens.buffalo.edu 31st March, 2015
- Bowman, A. (1992). The Condition of the World's Tropical Forests, And Its Impact On Furniture Conservation. New York: *WAG Postprints*
- Burch, P.E. (2005). *Natural Dyes* Retrieved from www.pburch.net
- Cardon, D. & Jansen, P.C.M., (2005). *Baphia nitida* Lodd. in: Jansen, P.C.M. and Cardon, D. (ed.). *PROTA 3: Dyes and tannins/Colourants et tanins*. PROTA, Wageningen, Netherlands Retrieved from WWW.database.prota.org

Cardon, D., Borus, D & Lemmens, R. H. M. J. (2006). PROTA 3: Dyes and tannins. *INTERNATIONAL SYMPOSIUM / WORKSHOP ON NATURAL DYES* Hyderabad, India, november 2006 organised by UNESCO/Crafts Council of India. Retrieved from www.underutilized-species.org

Chanayath, N; Lhieochaiphant, S; & Phutrakul, S. (2002). Pigment Extraction Techniques from the Leaves of *Indigofera tinctoria* Linn. and *Baphicacanthus cusia* Brem. and Chemical Structure Analysis of Their Major Components. *CMU Journal*, 1(2), 149-160.

Christie R. M. (2001). *Colour Chemistry*. Royal Society of Chemistry, Cambridge.

Classification of Natural dyes and Synthetic dyes –By structure and by colour.

(n.d) Retrieved from www.nptel.ac.in 20th Nov. 2014

Coates, J. (2000). Interpretation of Infrared Spectra, A practical Approach” in R. A. Meyers, (ed.), *Encyclopedia of analytical Chemistry* (pp. 1-23), Chichester: John Wiley and Sons ltd.

Colour Bridge. (n.d). *Hessler Printing*. Retrieved from www.2.bp.blogspot.com
14th March, 2016

Colour fastness to rubbing. (2001). *ISO 105-X12:2001(E)*. Retrieved from www.textileinstruments.net

- Colour fastness to Washing with soap or soap and soda. (2006). *ISO 105-C10:2006(E)*. Retrieved from www.textileinstruments.net
- Crews, P. C. (1987). The Fading Rates of Some Natural Dyes. *Studies in Conservation*, 32 (2), 65-72.
- Divya, E., Madhumitha, T., Nandini, R., Pooja, R & Manickam, A. (2013) Extraction of Natural Dyes from Forest Trees and their Application in Textiles. *International Journal for Scientific Research and Development (IJSRD)*, 1, (3), 589-593.
- Drivas, I. (2008). Chemical modification of natural dyes and their application in textiles. *Ph. D. dissertation, ProQuest Dissertations & Theses Full Text*
- Ellis, C. (2013). The science of natural dyes. *Surface Design Journal*, 37 (3), 26 – 31.
- Encyclopedia Britannica (2011). Major Industrial Polymers. <http://www.britannica.com/EBchecked/topic/468678/industrial-polymers>.
- Fasan, F. A. (1972) Camwood (*Baphia nitida*) Extract as a Histological Stain for Interglobular Dentine, Striated Muscle, and Counterstaining. *Biotechnic & Histochemistry*, 47 (5), 223-227.

Ferreira, E. S. B., Hulme, A. N., McNab, H. & Quye, A. (2004). The natural constituents of historical textile dyes. *Chemical Society reviews*, 33(6), 329-336

General introduction to the chemistry of dyes. (n.d) *IARC MONOGRAPHS* 99, 55 – 67 Retrieved from www.monographs.iarc.fr 6th Nov. 2015

Gilles, K.N., Djakalia, Q., Léopold, A.A., Dédéou, S., Bamba, K., & Edouard, N.K. (2011). Anti-inflammatory and cicatrizing activity of *Baphia nitida* Lodd. Exudates. *International Journal of Biosciences (IJB)*,1(5), 45-50.

Grover, N. & Patni, V. (2011). Extraction and application of natural dye preparations from the floral parts of *Woodfordia fruticosa* (Linn.) Kurz. *Indian Journal of Natural Products and Resources*, 2(4), 403-408.

Haar, S., Schrader, E. & Gatewood, B. M. (2013). Comparison of Aluminium Mordants on the Colourfastness of Natural Dyes on Cotton. *Clothing and Textiles Research Journal*, 31 (2), 97-108.

Hansen, C. M. (2000). Solubility Parameters - An Introduction. in. *Hansen Solubility Parameters: a User's Handbook*. USA: CRC Press.

Hatch, K. L. (1993). *Textile Science*. New York: West Publishing Company.

Hedge, R. R., Dahiya, A. & Kamath, M.G. (2004). Nylon Fibres. Retrieved from [http://www.engr.utk.edu/msc/Textiles/Nylon fibres.htm](http://www.engr.utk.edu/msc/Textiles/Nylon%20fibres.htm)

Hemanthraj, K.P.M., Desai, S. M. & Bisht, S. S. (2014). Optimization of Extraction Parameters for Natural Dye from *Pterocarpus santalinus* by using Response Surface Methodology. *International Journal of Engineering research and Application*, 4(9), 100-108.

Hubbe, M.A., Beck, K. R., O' Neal, W.G., & Chsharma, Y. (2012). Dye biosorption: Review. *Bioresources*, 7(2), 2592 – 2687.

Hunterlab (2008). Gray Change & Gray Stain Scales. *Applications Note*, 7(1), 1-3
Infrared Spectroscopy Absorption Table (n.d) Retrieved 10th March, 2016 from www.ochemonline.com

Infrared Spectroscopy. (n.d). Modern Chemical Techniques, Retrieved from [www.researchgate.net/MCT3 Infrared.pdf](http://www.researchgate.net/MCT3%20Infrared.pdf) (pp.62 - 91) 10th April, 2016.

Introduction to the Interpretation of Infrared Spectra. (n.d). Retrieved from www.chem.ucla.edu 14th March, 2016

Janani, L., Hillary, L. & Phillips, K. (2014). Mordanting Methods for Dyeing cotton fabrics with dye from *Albizia coriaria* plant species. *International Journal of Scientific and Research Publications*, 4(10), 1-6

- Jansen, P.C.M. (2005). *Rothmannia whitfieldii* (Lindl.) Dandy. in Jansen, P.C.M. & Cardon, D. (ed). PROTA (Plant Resources of Tropical Africa / Ressources végétales de l'Afrique tropicale), Wageningen, Netherlands. Retrieved from www.prota4u.org/search.asp
- Jansen, P.C.M., (2005). *Pterocarpus soyauxii* Taub. in Louppe, D., Oteng-Amoako, A.A. and Brink, M. (ed). PROTA (Plant Resources of Tropical Africa / Ressources végétales de l'Afrique tropicale), Wageningen, Netherlands. Retrieved from www.prota4u.org/search.asp.
- Kadolph, S. J. & Casselman, K. D. (2004). in the Bag: Contact Natural Dyes. *Clothing and Textiles Research Journal*, 22 (12), 15-21.
- Kasiri, M. B. & Safapour, S. (2014). Natural dyes and antimicrobials for green treatment of textiles. *Environmental Chemistry Letters*, 12(1), 1-13.
- Katz, D.A. (2011). Natural Plant Dyes. Retrieved from www.chymist.com
- Khatri, Z., Sheikh, G. Y., Brohi, K. M., & Uqaili, A.A. (2011). Effective Colour management for Textile Colouration – An instrumental way towards perfection. *Proceedings of the 2011 International Conference on Industrial Engineering and Operation Management Kuala Lumpur Malaysia Jan. 22 – 24, 2011* retrieved from www.iieom.org

Klemm, D., Schmauder, H., & Heinze, T. (n.d). *Cellulose* Retrieved from www.wiley-vch.de (pp. 275-287) 31st March, 2015.

Kouissa, B., Bouchouit, K., Abed, S., Essaidi, Z., Derkowska, B. & Sahraoui, B. (2013). Investigation study on the nonlinear optical properties of natural dyes: Chlorophyll a and b. *Optics Communications*, 293, 75

Kulkarni, S. S., Bodake U. M. & Pathade, G. R. (2011). Extraction of Natural Dye from Chili (*Capsicum Annum*) for Textile Colouration. *Universal Journal of Environmental Research and Technology*, 1, 58-63

Leube, H. (2003). Textile Dyeing. in K. Hunger (ed.), *Industrial Dyes: chemistry, properties, application* (pp.339-426). Weinheim Germani: WILEY-VCH Verlag GmbH & Co. KGaA.

Light Energy Output. (n.d) Retrieved 14th March, 2016 from www.lumigrow.com

Mahmudi, A., Mawardi, A.K., Putri, E.S., Alharis, R.U., Sari, R.P., Hidayati, N., Harismah, k., & Fuadi, A. *Extraction of Natural Dyes from Dadap Flower (Erythrina fusca L.) and Its Application in Dyeing of Cotton and Silk*. Retrieved from www.academia.edu 31st Dec.2014

Maiwa Handprints, (2015) *The Maiwa guide to Natural dyes: what they are and how to use them*. Retrieved from www.maiwa.com 1st Nov. 2015

- Manhita, A., Ferreira, T., Candeias, A. & Barrocas, D. C. (2011) Extracting natural dyes from wool—an evaluation of extraction methods. *Analytical and Bioanalytical Chemistry*, 400(5), 1501-1514
- McKahan, C. L. (2000). Goldenrod: A natural dye plant. *Countryside and Small Stock Journal*, 84(6), 80- 89
- Meena Devi. V. N., Ariharan V. N. & Nagendra P. P. (2013). Annatto: Eco-Friendly and Potential Source For Natural Dye. *International Research Journal of Pharmacy*, 4, 106-108
- Mennicke, W. (2003). Metal Complexes as Chromophores. In K. Hunger (ed), *Industrial Dyes: chemistry, properties, application*. Weinheim Germani: WILEY-VCH Verlag GmbH & Co. KGaA (pp.85-106)
- Mihalick, J. E. & Donnelly, K.M. (2006). Using Metals To Change the Colours of Natural Dyes. *Journal of Chemical Education*, 83(10), 1550-165
- Mirjalili, M., Nazarpour, K. & Karimi, L. (2011). Eco-friendly dyeing of wool using natural dye from weld as co-partner with synthetic dye. *Journal of Cleaner Production*, 19(9), 1045-1051.
- Mishra, S.P. (2014) *Dyeing with Natural Dyes*. Retrieved from www.scribd.com
31st Dec.

Morton, W.E. & Hearle, J.W.S (1975). *Physical properties of Textile Fibres*.

London: Heinemann and The Textile Institute

Nam, K. Y. & Lee, J. S. (2013). Dyeing Properties and Functionality of Methanol Extract from *Juniperus chinensis* Heartwood. *Textile Colouration and Finishing*, 25(3), 194-205.

Oda, H. (2012). Improving light fastness of natural dye: photostabilisation of gardenia blue. *Colouration Technology*, 128(1), 68-73.

Okoro, I.S. (2012). Antimicrobial Effect of Root Extracts of Cam Wood (*Baphia nitida*) on Some Human Pathogens. *Journal of Biological Science and Bioconservation*, 4, 93-100.

Orwa, C., Mutua, A., Kindt, R., Jamnadass, R. & Anthony, S. (2009) “Agroforestry Database: a tree reference and selection guide version 4.0” Retrieved from www.worldagroforestry.org/sites/treedbs/treedatabases.asp

Osabohien, E. (2009). Extraction and Utilization of Natural Dyestuffs from Dongoyaro Plant. *Advanced Natural and Applied Science Research*, 7, 187-190

Osemeobo, G. J. & Ujor, G. (1999). The Non-Wood Forest Products of Nigeria.

European Commission Directorate-General Viii Development: a report of the EC-FAO Partnership Programme (1998-2000)- ProjectGCP/INT/679/ECData Collection and Analysis for Sustainable Forest Management in ACP Countries - Linking National and International Efforts.

Park, S. & Jung, S. (2014). Technical approaches of a natural dye extracted from *Phytolacca americana* L.-berries with chemical mordants. *Technology and health care*, 22, (3), 339- 345

PERP Program (2011). *Nylon 6 and Nylon 6.6*. Retrieved from http://www.chemsystems.com/.../items/PERP070856_Nylon6.Cfm

Photometry_chpt1. (n.d). *Basic Techniques of Experimental Biochemistry*, pp. 15-24. Retrieved from www.chem.uky.edu 16th Dec. 2015

Practical Action, (n.d). *Natural dyeing of Textiles*, pp. 1- 11. Retrieved from www.practicalaction.org 3rd Nov. 2014

Pragati, J. S. (2013). Eco-friendly Antibacterial Printing of Wool Using Natural Dyes. *Journal of Textile Science & Engineering*, 4, (2), 112-117

Ramea Ova, A. A., Sokolova, R., Tarabek, J. & Degano, I. (2013). The oxidation of luteolin, the natural flavonoid dye. *Electrochimica Acta*, , 646-653.

- Ratnapandian, S., Fergusson, S. M. & Wang, L. (2012). Application of acacia natural dyes on cotton by pad dyeing. *Fibres and Polymers*, 13 (2), 206-211
- Rungruangkitkrai, N. & Mongkholrattanasit, R. (2012). Eco-Friendly of Textiles Dyeing and Printing with Natural Dyes. *RMUTP International Conference*. Bangkok Thailand: Textiles & Fashion July 3-4, 2012,
- Samanta, A. K. & Agarwal, P. (2009). Application of Natural Dyes on Textile. *Indian Journal of Fibre and Textile Research*, 34, 384-399
- Samanta, A.K. & Konar, A. (2011). *Dyeing of Textiles with Natural Dyes*
Retrieved from www.intechopen.com
- Satyanarayana, D.N.V. & Ramesh C, K. (2013). Dyeing Of Cotton Cloth with Natural Dye Extracted From Pomegranate Peel and its Fastness. *International Journal of Engineering Sciences & Research Technology*, 2, 2664-2669
- Saxena, S. & Raja, A. S. M. (2014). *Natural Dyes: Sources, Chemistry, Application and Sustainability Issues*. Retrieved from www.springer.com
14th Nov. 2014

- Schonberger, H. & Schafer, T. (2003). Best available Techniques in Textile Industry. *Federal Environment Agency*, (pp.50–51), Retrieved from www.umweltdaten.de
- Sequin-Frey, M. (1981). The chemistry of Plant and Animal Dyes. *Journal of Chemical Education*, 58 (4), 301-305.
- Shahid, M.; Shahid-Ul-Islam & Mohammad, F. (2013). Recent advancements in natural dye applications: a review. *Journal of Cleaner Production*, 53 310-331.
- Shahin, M.F. & Ahmed, R.M. (2014). Optimizing the Dyeing Process of Alkali-Treated Polyester Fabric with Dolu Natural Dye. *International Journal of Engineering Research and Applications*, 4, 35-40
- Shams-Nateri, A., Hajipour, A., Dehnavi, E. & Ekrami, E. (2014). Colourimetric Study on Polyamides Dyeing With Weld and Pomegranate Peel Natural Dyes. *Clothing and Textiles Research Journal*, 32 (2), 124-135.
- Singh, S. V. & Purohit, M.C. (2012). Applications of Eco-Friendly Natural Dye on Wool Fibres Using Combination of Natural and Chemical Mordants. *Universal Journal of Environmental Research and Technology*, 2 (2), 48-55.
- Solutions-Chapter 14* (n.d). Retrieved from www.chem.ccu.edu 24th Feb.2016

Spectroscopy Data Tables. (n.d). Retrieved from www.researchgate.net (pp.1-19)

10th April, 2016

Surowiec, I., Nowik, W. & Trojanowicz, M. (2004). Identification of "insoluble" red dyewoods by high performance liquid chromatography-photodiode array detection (HPLC-PDA) fingerprinting. *Journal of separation science*, 27 (3), 209-216.

Texanlab (n.d). Colour fastness to washing. *Texanlab laboratories pvt. ltd.* (pp.1-9). Retrieved from <http://admin.umt.edu.pk/.../colour%20fastness.pdf> 27th Dec. 2015.

Texanlab (n.d). Colour fastness to Rubbing. *Texanlab laboratories pvt.ltd.* (pp.1-8). Retrieved from www.texanlab.com/.../4.pdf 27th Dec. 2015.

Textile Calculations and Equations. (2014). Prepared by Sheshir, M. H. Retrieved from www.slideshare.net/sheshir 8th Jan. 2015.

Thermo Nicolet, (2001). Introduction to Fourier Transform Infrared Spectrometry, *Thermo Nicolet Corporation*. Retrieved from www.thermonicolet.com

Visible Spectrum. (n.d) Retrieved from www.images.tutorcircle.com 14th March, 2016

- Wang, C., Xu, C., Tian, A., Fu, S & Wang, C. (2013). Extraction of natural dyes from *Alpinia blepharocalyx* K. Schum. for dyeing of silk fabric. *Colouration Technology*, 129, (1), 32-38.
- Wet processing calculations. (2001) *Complete Textile Glossary*. New York: Celanese Acetate.
- Whewell, C.S. (2011). Textile Dyeing Process. *Encyclopedia Britannica Online*: retrieved from [http://www. Encyclopedia Britannica.com/EBchecked /topic/589392/textile 15936/Dyeing Anchor](http://www.EncyclopediaBritannica.com/EBchecked/topic/589392/textile%2015936/DyeingAnchor).
- Wilson, H. W. (1999). Colours to dye for: preparation of natural dyes. *Journal of Chemical Education*, 76(12), 1688
- Wu, J.H. & Ke, J. (2011). Dyeability of PLA Fabric with Natural Dye Emodin. *Advanced Materials Research*, 183-185, 2000-2004
- Zheng, G. H., Fu, H. B. & Liu, G. P. (2011). Application of Rare Earth as Mordant For The Dyeing Of Ramie Fabrics With Natural Dyes. *Korean Journal of Chemical Engineering*, 28, (11), 2148-2155
- Zvezdina, S. V., Berezin, M. B. & Berezin, B. D. (2010). Natural dyes based on chlorophyll and protoporphyrin derivatives. *Russian Journal of Coordination Chemistry*, 36 (9), 711-714

APPENDIX A

ISO 105X12: COLOUR FASTNESS TO RUBBING TEST

INTERNATIONAL STANDARD

ISO 105-X12

Fifth edition
2001-05-01

Corrected version

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Textiles — Tests for colour fastness —

Part X12:

Colour fastness to rubbing

Textiles — Essais de solidité des teintures —

Partie X12: Solidité des teintures au frottement

Reference number
ISO 105-X12:2001(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 105 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 105-X12 was prepared by Technical Committee ISO/TC 38, *Textiles*, Subcommittee SC 1, *Tests for coloured textiles and colorants*.

This fifth edition cancels and replaces the fourth edition (ISO 105-X12:1993), which has been technically revised.

ISO 105 was previously published in thirteen "parts", each designated by a letter (e.g. "Part A"), with publication dates between 1978 and 1985. Each part contained a series of "sections", each designated by the respective part letter and by a two-digit serial number (e.g. "Section A01"). These sections are now being republished as separate documents, themselves designated "parts" but retaining their earlier alphanumeric designations. A complete list of these parts is given in ISO 105-A01.

This corrected and reprinted version of ISO 105-X12:2001 incorporates the following corrections in subclause 6.2 on page 3.

The sequence of the rubbing cycle has been clarified. The text now indicates that the total number of cycles is 20:10 to and 10 fro as opposed to 20 than 10 to and fro.

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ISO 105-X12:2001(E)

NOTE 1 Difficulty may be experienced in making assessments of the degree of staining on the rubbing cloth when pile fabrics are tested using the $(16 \pm 0,1)$ mm diameter rubbing finger due to heavier staining occurring on the circumference of the stained area, i.e., haloing. The rubbing finger described in 4.1.1 will eliminate the haloing with many types of pile fabrics.

Even with the use of the crock block, difficulty may be experienced in assessing staining when fabrics with high pile are tested.

NOTE 2 A suitable apparatus for pile fabrics is described in *Journal of the Society of Dyers and Colourists*, **87** 1971, 155; **88** 1972, 259.

4.1.2 For other textiles: rubbing finger comprised of a cylinder of $(16 \pm 0,1)$ mm diameter moving to and fro in a straight line along a (104 ± 3) mm track on the specimen and exerting a downward force of $(9 \pm 0,2)$ N.

NOTE A suitable apparatus is described in the *Technical Manual of the American Association of Textile Chemists and Colorists*, Test Method 8, for 4.1.2, and Test Method 165 for 4.1.1. Other devices can be used, provided that the same results are obtained as with the apparatus described in clause 4. There is no known correlation of results between the two methods described.

4.2 Cotton rubbing cloth, desized, bleached, without finish, cut into 50 mm squares (± 2) mm for the finger used in 4.1.2. For the finger described in 4.1.1, a 25 mm $\times$ 100 mm ± 2 mm cloth is used. See ISO 105-F09.

4.3 Soft-back waterproof abrasive paper, or grating of stainless steel wire 1 mm in diameter and mesh width about 20 mm.

NOTE Attention should be paid to the characteristics of the grating or abrasive paper used to hold the specimen as they may leave an imprint through the textile which would cause a false rating to be made. The use of the abrasive paper may be preferred for testing textile fabrics.

4.4 Grey scale, for assessing staining, in accordance with ISO 105-A03.

Verification on the operation of the test and the apparatus shall be made routinely and the results kept in a log. Use an in-house or established rubbing specimen and conduct three (3) dry tests.

5 Test specimens

5.1 If the textile to be tested is a fabric or textile floor covering, two pieces not less than 50 mm $\times$ 140 mm are required for dry rubbing and two for wet rubbing. Additional specimens may be used when higher precision is needed. One specimen of each pair shall have the long direction parallel to the warp yarns, (or in the direction of manufacture), the other parallel to the weft (or filling yarns or at right angles to the direction of manufacture). An alternate method of cutting specimens is to cut the long dimension diagonally to warp and weft. If the pile lay of a carpet specimen is distinguishable, cut the specimen with the pile lay pointing in the long direction.

5.2 If the textile to be tested is yarn or thread, knit it into fabric to provide specimens at least 50 mm $\times$ 140 mm or form a layer of parallel strands by wrapping it lengthways on a cardboard rectangle of suitable dimensions.

5.3 Before testing, condition the specimen and rubbing cloth for at least 4 h in an atmosphere of (20 ± 2) °C and (65 ± 2) % RH by laying each test specimen and each piece of rubbing cloth separately on a screen or perforated shelf. Some fabrics such as cotton or wool may require longer periods of conditioning.

5.4 For best results, testing should be conducted under standard atmosphere for testing textiles (see ISO 139).

6 Procedure

6.1 General

Fasten each test specimen by means of clamps to the baseboard of the testing device so that the long direction of the specimen follows the track of the device. Between the baseboard of the testing device and the specimen, place a piece of wire mesh or soft-back waterproof abrasive paper to help reduce movement of the specimen. Test the specimens prepared in clause 5 according to the procedures in 6.2 and 6.3.

When testing multi-coloured textiles, care should be taken to position the specimens in such a way that all colours of the design are rubbed in the test using the device described in 4.1.2. Alternatively, if the areas of colour are sufficiently large, more test specimens may be taken and the individual colours assessed separately. If the areas of colour are small and run together, a choice to test using a rotary device, as described in ISO 105-X10, is advised.

6.2 Dry rubbing

Place the conditioned rubbing cloth, (see 4.2 and 5.3), flat over the end of the finger with the weave parallel to the direction of rubbing finger. At a rate of one cycle per second, rub to and fro in a straight line 20 times, 10 times to and 10 times fro, along a track (104 ± 3) mm long on the dry specimen, with downward force of $(9 \pm 0,2)$ N (see 4.1.1 and 4.1.2). Remove test square and condition as in 5.3 above. Remove any extraneous fibrous material that might interfere with the rating.

6.3 Wet rubbing

Establish a technique for preparing rubbing cloth by weighing a conditioned piece of cloth, then thoroughly soak in distilled water and reweigh to ensure take-up of 95 % to 100 %. Follow the instructions for rubbing in 6.2.

NOTE As the level of soak of the rubbing cloth may dramatically affect ratings, other levels may be used. An example of a very commonly used level of soak is (65 ± 5) %.

6.4 Drying

Air dry the test cloth.

7 Evaluation

7.1 Back each tested rubbing cloth with three layers of white rubbing cloth while evaluating.

7.2 Assess the staining of the cotton rubbing cloths with the grey scale for staining (4.4) under suitable illumination (see clause 13 of ISO 105-A01:1994).

8 Test Report

The test report shall contain the following information:

- reference to this part of ISO 105; i.e., ISO 105-X12;
- which finger and force were used in the test;
- whether dry or wet rubbing was performed along with the percentage of soak;
- the time of conditioning of the specimens and rubbing cloth as well as the atmospheric conditions during testing;
- identification of the long direction of the specimen mounting, i.e., warp, weft or oblique;
- the numerical rating for staining for each test specimen.

APPENDIX B

ISO 105C10: COLOUR FASTNESS TO WASHING WITH SOAP TEST

INTERNATIONAL STANDARD

**ISO
105-C10**

First edition
2006-06-15

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Textiles — Tests for colour fastness — Part C10: Colour fastness to washing with soap or soap and soda

Textiles — Essais de solidité des teintures —

Partie C10: Solidité des teintures au lavage au savon ou au savon et à la soude



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 105-C10 was prepared by Technical Committee ISO/TC 38, *Textiles*, Subcommittee SC 1, *Tests for coloured textiles and colorants*.

ISO 105 was previously published in thirteen "parts", each designated by a letter (e.g. "Part A"), with publication dates between 1975 and 1985. Each part contained a series of "sections", each designated by the respective part letter and by a two-digit serial number (e.g. "Section A02"). These sections are now being republished as separate documents, themselves designated "parts", but retaining their earlier alphanumeric designations. A complete list of these parts is given in ISO 105-A01.

This first edition of ISO 105-C10 cancels and replaces ISO 105-C01:1989, ISO 105-C02:1989, ISO 105-C03:1989, ISO 105-C04:1989 and ISO 105-C05:1989, which have been technically revised.

Textiles — Tests for colour fastness —

Part C10:

Colour fastness to washing with soap or soap and soda

1 Scope

This part of ISO 105 specifies five methods intended for determining the resistance of the colour of textiles of all kinds and in all forms to washing procedures, from mild to severe, used for normal household articles.

This part of ISO 105 is designed to determine the effect of washing only on the colour fastness of the textile. It is not intended to reflect the result of the comprehensive laundering procedure.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 105-A01, *Textiles — Tests for colour fastness — Part A01: General principles of testing*

ISO 105-A02, *Textiles — Tests for colour fastness — Part A02: Grey scale for assessing change in colour*

ISO 105-A03, *Textiles — Tests for colour fastness — Part A03: Grey scale for assessing staining*

ISO 105-A04, *Textiles — Tests for colour fastness — Part A04: Method for the instrumental assessment of the degree of staining of adjacent fabrics*

ISO 105-A05, *Textiles — Tests for colour fastness — Part A05: Instrumental assessment of change in colour for determination of grey scale rating*

ISO 105-F, *Textiles — Tests for colour fastness — Part F: Standard adjacent fabrics*

ISO 105-F01, *Textiles — Tests for colour fastness — Part F01: Specification for wool adjacent fabric*

ISO 105-F02, *Textiles — Tests for colour fastness — Part F02: Specification for cotton and viscose adjacent fabrics*

ISO 105-F03, *Textiles — Tests for colour fastness — Part F03: Specification for polyamide adjacent fabric*

ISO 105-F04, *Textiles — Tests for colour fastness — Part F04: Specification for polyester adjacent fabric*

ISO 105-F05, *Textiles — Tests for colour fastness — Part F05: Specification for acrylic adjacent fabric*

ISO 105-F06, *Textiles — Tests for colour fastness — Part F06: Specification for silk adjacent fabric*

ISO 105-F07, *Textiles — Tests for colour fastness — Part F07: Specification for secondary acetate adjacent fabric*

ISO 105-F10, *Textiles — Tests for colour fastness — Part F10: Specification for adjacent fabric: Multifibre*

ISO 105-J01, *Textiles — Tests for colour fastness — Part J01: General principles for measurement of surface colour*

ISO 105-J03, *Textiles — Tests for colour fastness — Part J03: Calculation of colour differences*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Principle

A specimen of the textile in contact with one or two specified adjacent fabrics is mechanically agitated under specified conditions of time and temperature in a soap, or soap and soda solution, then rinsed and dried. The change in colour of the specimen and the staining of the adjacent fabric, or fabrics, are assessed with reference to the original fabric, either with the grey scales or instrumentally.

4 Apparatus

4.1 Suitable mechanical laundering device, consisting of water bath containing a rotatable shaft which supports, radially, stainless steel containers [(75 mm ± 5 mm diameter) × (125 mm ± 10 mm high)] of capacity (550 ± 50) ml, the bottom of the containers being (45 ± 10) mm from the centre of the shaft.

The shaft/container assembly is rotated at a frequency of (40 ± 2) r/min. The temperature of the water bath is thermostatically controlled to maintain the test solution at the prescribed temperature ± 2 °C.

Other mechanically devices may be used for this test, provided that the results are identical with those obtained by the apparatus described in 4.1. Be aware of possible contamination (see the note in 7.2).

4.2 Balance, accurate to ± 0,01 g (see ISO 105-A01).

4.3 Mechanical stirrer, minimum 16,667 s⁻¹ (1 000 r/min) to ensure thorough dispersion and prevent settling.

4.4 Non-corrodible (stainless) steel balls, approximately 6 mm in diameter.

4.5 Means of heating the soap solution, such as a hot plate.

5 Reagents and materials

5.1 Soap, containing not more than 5 % moisture and complying with the following requirements based upon dry mass:

- free alkali, calculated as Na₂CO₃: 0,3 % maximum;
- free alkali, calculated as NaOH: 0,1 % maximum;
- total fatty matter: 650 g/kg minimum;
- titre of mixed fatty acids, prepared from soap: 30 °C maximum;
- iodine value: 50 maximum.

The soap shall be free from fluorescent brightening agents.

5.2 Sodium carbonate, anhydrous (Na_2CO_3).

5.3 Soap solution, containing 5 g of soap (5.1) per litre of water (5.4) for test conditions A and B and 5 g of soap (5.1) and 2 g of sodium carbonate (5.2) per litre of water (5.4), for test conditions C, D and E.

It is recommended to vigorously disperse the soap using a mixer (4.3) in grade 3 water at $(25 \pm 5) ^\circ\text{C}$ and stir for (10 ± 1) min.

5.4 Grade 3 water, complying with ISO 3696.

5.5 Adjacent fabrics (see ISO 105-A01), either 5.5.1 or 5.5.2

5.5.1 Multifibre adjacent fabric, complying with ISO 105-F10, according to the temperature used:

- Type DW multifibre adjacent fabric containing wool and acetate (for tests at $40 ^\circ\text{C}$ and $50 ^\circ\text{C}$ and, in certain cases, to be indicated in the test report, at $60 ^\circ\text{C}$);
- Type TV multifibre adjacent fabric not containing wool and acetate (in certain tests at $60 ^\circ\text{C}$ and in all tests at $95 ^\circ\text{C}$).

5.5.2 Two single-fibre adjacent fabrics, complying with the relevant clauses of ISO 105-F01 to ISO 105-F07.

One of the adjacent fabrics shall be made of the same kind of the fibre as that of the textile to be tested or that predominating in the case of blends. The second piece shall be made of the fibre as indicated in Table 1 or, in the case of blends, of the kind of fibre second in order of predominance or as otherwise specified.

Table 1 — Pairs of adjacent fabrics

If first piece is	Second piece	
	For test at $40 ^\circ\text{C}$ and $50 ^\circ\text{C}$	For test at $60 ^\circ\text{C}$ and $95 ^\circ\text{C}$
Cotton	Wool	Viscose
Wool	Cotton	—
Silk	Cotton	—
Viscose	Wool	Cotton
Acetate	Viscose	Viscose
Polyamide	Wool or cotton	Cotton
Polyester	Wool or cotton	Cotton
Acrylic	Wool or cotton	Cotton

5.6 Non-dyeable fabric, if required (e.g. polypropylene).

5.7 Grey scales, for assessing change in colour and staining (ISO 105-A02; ISO 105-A03), or a spectrophotometer for assessing change in colour and staining complying with ISO 105-J01, ISO 105-A04 and ISO 105-A05.

6 Test specimen

6.1 If the textile to be tested is fabric, either

- attach a specimen 100 mm × 40 mm to a piece of the multifibre adjacent fabric (5.5.1), also 100 mm × 40 mm, by sewing along one of the shorter edges, with the multifibre adjacent fabric next to the face side of the specimen, or
- attach a specimen 100 mm × 40 mm between the two single-fibre adjacent fabric (5.5.2), also 100 mm × 40 mm by sewing along one of the shorter edges.

6.2 Yarn may be knitted into fabric and tested in this form. Where yarns or loose fibres are to be tested, take a mass of the yarn or loose fibres approximately equal to one-half of the combined mass of the adjacent fabrics and either

- place it between a 100 mm × 40 mm piece of the multifibre fabric (5.5.1) and a piece of the non-dyeable fabric (5.6) and sew them along all four sides (see ISO 105-A01), or
- place it between a 100 mm × 40 mm pieces of the two specified single-fibre fabrics (5.5.2) and sew them along all four sides.

6.3 Determine the mass, in grams, of the composite specimen using the balance (4.2) to aid accurate liquor ratio volumes.

7 Test procedures

7.1 Prepare the soap solution (5.3) according to the test used.

7.2 Place the composite specimen in the container together with the specified number of steel balls (Table 2). Add the necessary amount of soap solution (5.3) preheated to the test temperature ± 2 °C, according to Table 2, to give a liquor ratio of 50:1 ml/g. Close the container and operate the machine at the temperature and for the time specified in Table 2. Begin timing as soon as the container is closed.

Table 2 — Test conditions

Test number	Temperature °C	Time	Number of steel balls	Sodium carbonate
A (1)	40	30 min	0	—
B (2)	50	45 min	0	—
C (2)	60	30 min	0	+
D (4)	95	30 min	10	+
E (5)	95	4 h	10	+

Care should be taken to differentiate clearly between containers used for testing with and without fluorescent brighteners.

NOTE Containers (see 4.1) could be contaminated by the fluorescent brightening agents present in other test detergents and in commercial detergents. This could affect the colour fastness ratings of test specimens if such contaminated containers were subsequently used for tests using a detergent without fluorescent brighteners.

7.3 For all tests, remove the composite specimen at the end of the wash and place it in a 4 l beaker half filled with grade 3 water (5.4) at ambient temperature. Gently agitate, rinse for 1 min and then place the beaker under a cold running tap for 1 min.

7.4 For all methods, extract the excess water from the composite specimen by squeezing the test specimen by hand.

Open out the composite specimen by cutting the stitching except on one of the shorter sides if necessary.

7.5 Dry the specimen by pressing it flat between new filter papers to remove excess water. Then dry by hanging it in air at a temperature not exceeding 60 °C, with the parts in contact only at the line of stitching.

7.6 Assess the change in colour of the specimen and the staining of the adjacent fabric with reference to the original specimen using either the grey scales or instrumentally. See ISO 105-A02; ISO 105-A03; ISO 105-A04; ISO 105-A05; ISO 105-J03.

8 Test report

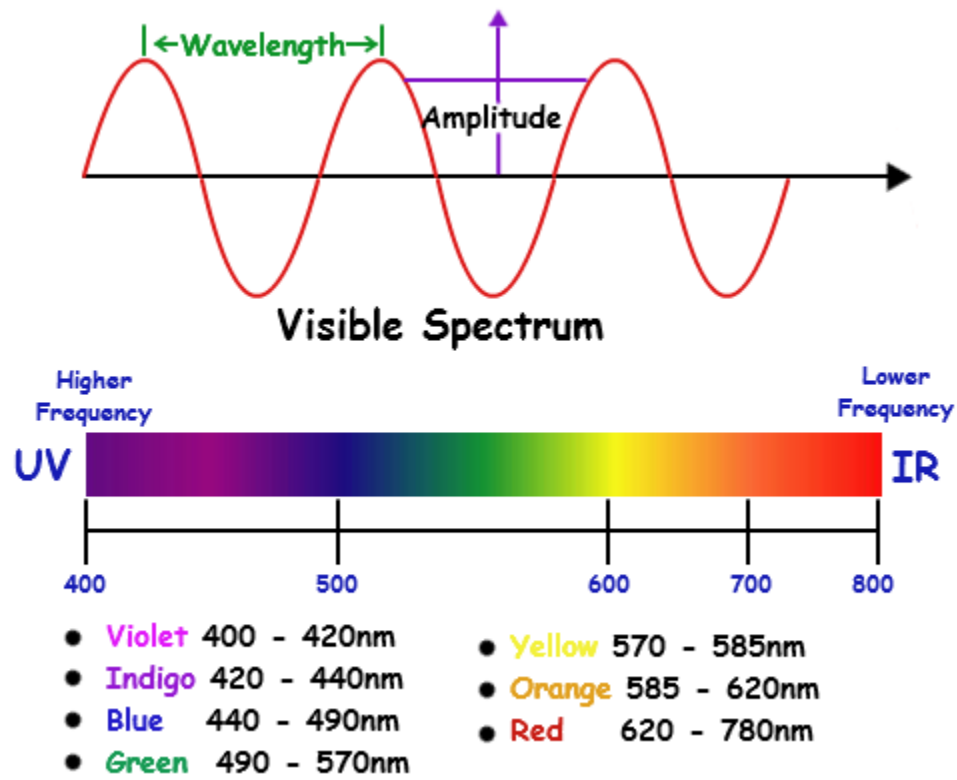
The test report shall include the following information:

- a) a reference to this part of ISO 105 (ISO 105-C10:2006);
- b) all details necessary for complete identification of the sample tested;
- c) the test conditions/test number used from Table 2;
- d) the numerical grey scale rating and/or instrumental assessment for the change in colour of the specimen;
- e) if single-fibre adjacent fabrics were used, the numerical rating for staining of each kind of adjacent fabric used;
- f) if a multifibre adjacent fabric was used, the staining of each type of fibre in the multifibre adjacent fabric, and the type of multifibre adjacent fabric used;
- g) any deviation, by agreement or otherwise, from the procedure specified.

APPENDIX C

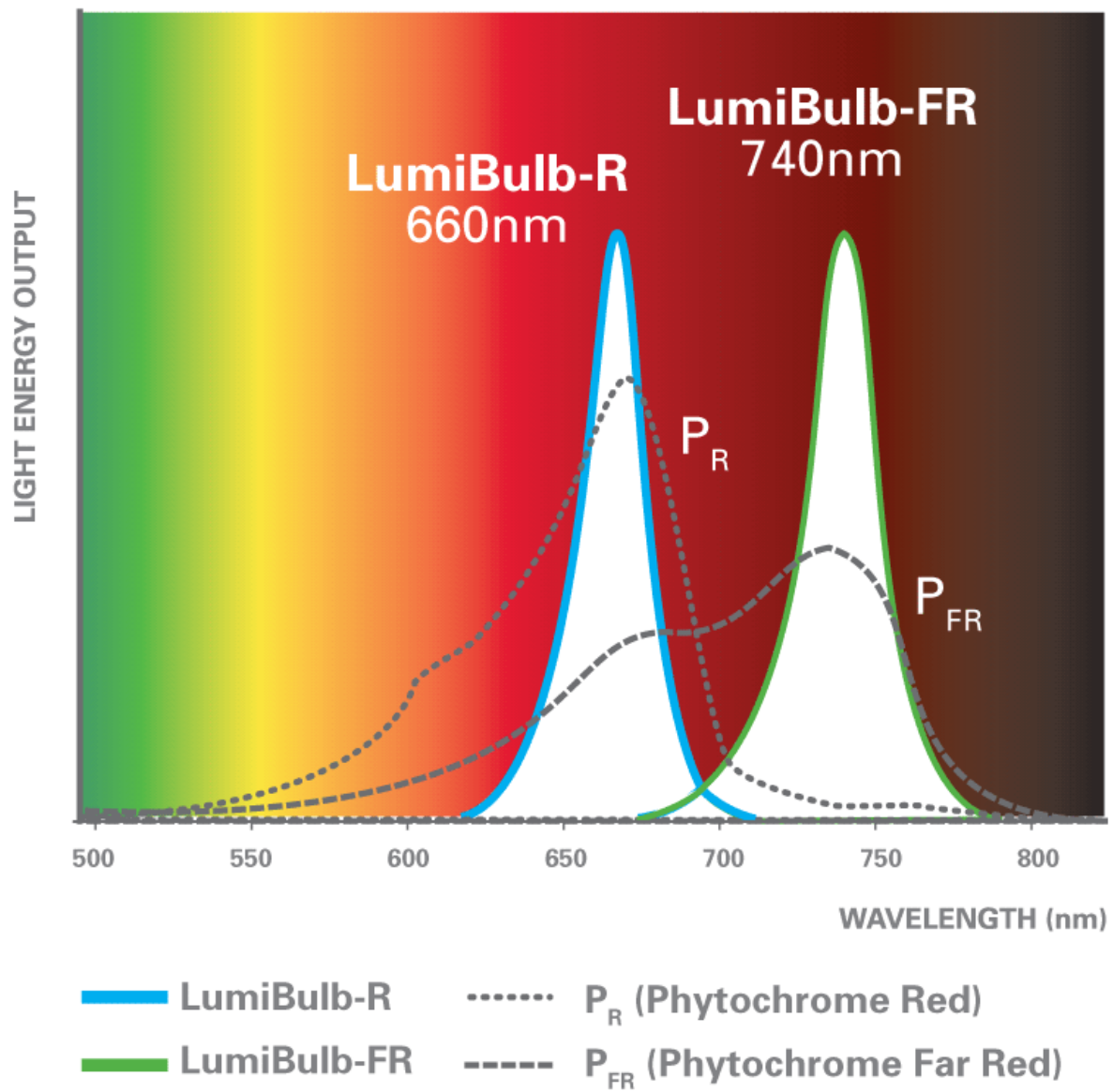
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A



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For the purpose of this study, the authors used the following definitions of the variables:

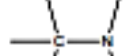
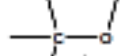
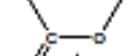
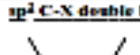
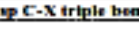
APPENDIX D

TABLE OF CHARACTERISTIC INFRA-RED ABSORPTIONS

Infrared Tables (short summary of common absorption frequencies)

The values given in the tables that follow are typical values. Specific bands may fall over a range of wavenumbers, cm^{-1} . Specific substituents may cause variations in absorption frequencies. Absorption intensities may be stronger or weaker than expected, often depending on dipole moments. Additional bands may confuse the interpretation. In very symmetrical compounds there may be fewer than the expected number of absorption bands (it is even possible that all bands of a functional group may disappear, i.e. a symmetrically substituted alkyne!). Infrared spectra are generally informative about what functional groups are present, but not always. The ^1H and ^{13}C NMR's are often just as informative about functional groups, and sometimes even more so in this regard. Information obtained from one spectroscopic technique should be verified or expanded by consulting the other spectroscopic techniques.

IR Summary - All numerical values in the tables below are given in wavenumbers, cm^{-1} **Bonds to Carbon (stretching wave numbers)**

<u>sp^3 C-X single bonds</u>			<u>sp^2 C-X single bonds</u>		
					
not used	1000-1350 not very useful	1050-1150 alkoxy C-O	not very useful	1250	1100-1350 acyl and phenyl C-O
<u>sp^2 C-X double bonds</u>			<u>sp C-X triple bonds</u>		
					
1600-1680	1640-1690	1640-1810 expanded table on next page	2100-2250	2240-2260	

Stronger dipoles produce more intense IR bands and weaker dipoles produce less intense IR bands (sometimes none).

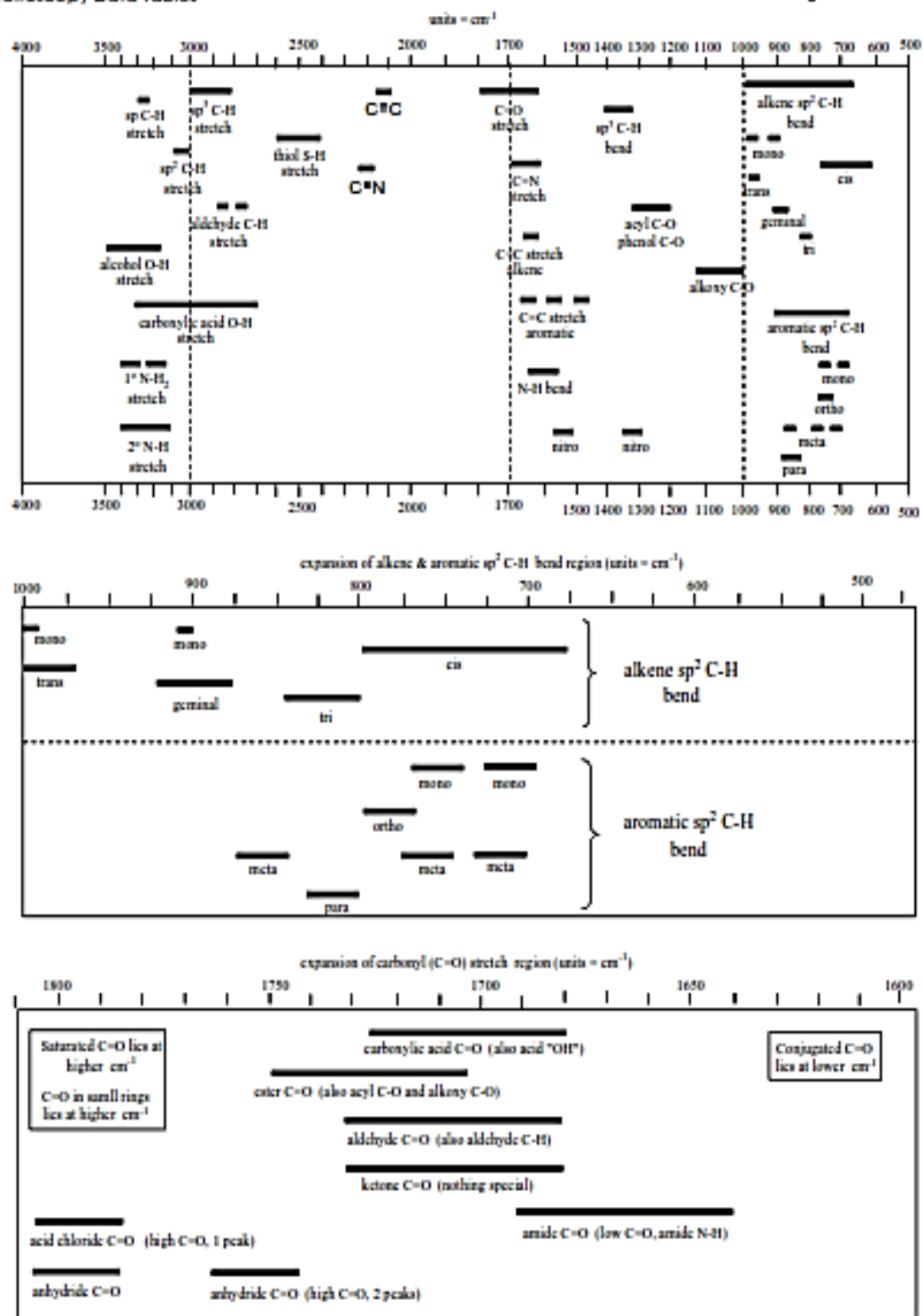
Bonds to Hydrogen (stretching wave numbers)

2850-3000 sp^3 C-H	3000-3100 sp^2 C-H (see sp^2 C-H bend patterns below)	3300 sp C-H	2700-2760 2800-2860 aldehyde C-H (two bands)
3100-3500 primary NH_2 (two bands)	3100-3500 secondary N-H (one band)	3200-3400 alcohol O-H	2500-3400 acid O-H
amides = strong, amines = weak			2550-2620 (very weak) thiol S-H

Carbonyl Highlights (stretching wave numbers)

Aldehydes	Ketones	Esters	Acids
saturated = 1725 conjugated = 1690 aromatic = 1700	saturated = 1715 conjugated = 1680 aromatic = 1690 6 atom ring = 1715 5 atom ring = 1745 4 atom ring = 1780 3 atom ring = 1850	saturated = 1735 conjugated = 1720 aromatic = 1720 6 atom ring = 1735 5 atom ring = 1775 4 atom ring = 1840	saturated = 1715 conjugated = 1690 aromatic = 1690
Amides	Anhydrides	Acid Chlorides	Nitro
saturated = 1650 conjugated = 1660 aromatic = 1660 6 atom ring = 1670 5 atom ring = 1700 4 atom ring = 1745 3 atom ring = 1850	saturated = 1760, 1820 conjugated = 1725, 1785 aromatic = 1725, 1785 6 atom ring = 1750, 1800 5 atom ring = 1785, 1865	saturated = 1800 conjugated = 1770 aromatic = 1770	asymmetric = 1500-1600 symmetric = 1300-1390
Very often there is a very weak C=O overtone at approximately $2 \times \nu$ ($\approx 3400 \text{ cm}^{-1}$). Sometimes this is mistaken for an OH or NH peak.			

sp^2 C-H bend patterns for alkenes			sp^2 C-H bend patterns for aromatics		
alkene substitution pattern	descriptive alkene term	absorption frequencies (cm^{-1}) due to sp^2 CH bend	aromatic substitution pattern	descriptive aromatic term	absorption frequencies (cm^{-1}) due to sp^2 CH bend
	monosubstituted alkene	985-1000 900-920		monosubstituted aromatic	690-710 730-770
	cis disubstituted alkene	675-730 (broad)		ortho disubstituted aromatic	735-770
	trans disubstituted alkene	960-990		meta disubstituted aromatic	680-725 750-810 880-900 (sometimes)
	geminal disubstituted alkene	880-900		para disubstituted aromatic	790-840
	trisubstituted alkene	790-840	Aromatic compounds have characteristic weak overtone bands that show up between 1650-2000 cm^{-1} . Some books provide pictures for comparison (not here). A strong C=O peak will cover up most of this region.		
	tetrasubstituted alkene	none			



IR Flowchart to determine functional groups in a compound (all values in cm^{-1}).

IR Spectrum	
has C=O band (1650-1800 cm^{-1}) very strong	does not have C=O band
aldehydes  1725-1740 (saturated) 1660-1700 (unsaturated) aldehyde C-H 2860-2900 2760-2700 (both weak) sometimes lost in sp^3 C-H peaks	alkynes  ~ 2250 sharp, stronger than alkynes, a little lower when conjugated
ketones  1710-1720 (saturated) 1680-1700 (unsaturated) 1715-1810 (rings: higher in small rings)	nitriles  ~ 2250 sharp, stronger than alkynes, a little lower when conjugated
esters - rule of 2  1735-1750 (saturated) 1715-1740 (unsaturated) 1735-1820 (higher in small rings) acyl C-O 1150-1350 (acyl, strong) alkoxy C-O (1000-1150, alkoxy, medium)	alkenes  2150 (variable intensity) not present or weak when symmetrically substituted, a little lower when conjugated sp^2 C-H stretch 3300 sharp, strong sp^2 C-H bend 620
acids  1700-1730 (saturated) 1715-1740 (unsaturated) 1680-1700 (higher in small rings) acyl C-O 1210-1320 (acyl, strong) acid O-H 2400-3400, very broad (overlaps C-H stretch)	All IR values are approximate and have a range of possibilities depending on the molecular environment in which the functional group resides. Resonance often modifies a peak's position because of electron delocalization (C=O lower, acyl C-O higher, etc.). IR peaks are not 100% reliable. Peaks tend to be stronger (more intense) when there is a large dipole associated with a vibration in the functional group and weaker in less polar bonds (to the point of disappearing in some completely symmetrical bonds).
amides  1650-1680 (saturated) 1745 (in 4 atom ring) 3350 & 3180, two bands for 1° amides, one band for 2° amides, stronger than in amines, extra overtone sometimes at 3100 N-H 1550-1640, stronger in amides than amines	alkene sp^2 C-H bending patterns monosubstituted alkene (985-1000, 900-920) geminal disubstituted (960-990) cis disubstituted (675-750) trans disubstituted (880-900) trisubstituted (790-840) tetrasubstituted (none, no sp^2 C-H)
acid chlorides  1800 (saturated) 1770 (unsaturated) Inductive pull of Cl increases the electron density between C and O.	Aromatic sp^2 C-H bending patterns monosubstituted (750-770, 690-710) ortho disubstituted (735-770) meta disubstituted (880-900, sometimes, 750-810, 690-725) para disubstituted (790-840)
anhydrides  1760 & 1820 (saturated) 1725-1785 (unsaturated) two strong bands acyl C-O 1150-1350 (acyl, strong)	There are also weak overtone bands between 1660 and 2000, but are not shown here. You can consult pictures of typical patterns in other reference books. If there is a strong C=O band, they may be partially covered up.
	alkanes sp^3 C-H stretch 2850-3000 sp^3 C-H bend 1460 & 1380 C-C not useful
	alkenes sp^2 C-H stretch 3000-3100 sp^2 C-H bend 650-1000 (see table for spectral patterns) C=C 1600-1660 weak or not present
	aromatics sp^2 C-H stretch 3050-3150 sp^2 C-H bend 690-900 (see table), overtone patterns between 1600-2000 C=C 1600 & 1480 can be weak
	alcohols alcohol O-H 2600-3500 alkoxy C-O 1000-1260 ($3^\circ > 2^\circ > 1^\circ$)
	thiols thiol S-H ~ 2550 (weak) (easy to overlook)
	amines  3300 - 3500, two bands for 1° amines, one band for 2° amines, weaker than in amides, N-H bend, 1550-1640, stronger in amides than amines N-C 1000-1350 (uncertain)
	ethers alkoxy C-O 1120 (aliphatic) 1040 & 1250 (aromatic)
	nitro compounds  1500-1600, asymmetric (strong) 1300-1390, symmetric (medium)
	carbon-halogen bonds  usually not very useful X = F, Cl, Br, I

Table of Characteristic IR Absorptions

wavenumber, cm⁻¹	Bond	functional group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	primary, secondary amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C(triple bond)C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	Aromatics
3100–3000 (m)	=C–H stretch	Alkenes
3000–2850 (m)	C–H stretch	Alkanes
2830–2695 (m)	H–C=O: C–H stretch	Aldehydes
2260–2210 (v)	C(triple bond)N stretch	Nitriles
2260–2100 (w)	–C(triple bond)C– stretch	Alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	alpha,beta-unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	alpha,beta-unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	Alkenes
1650–1580 (m)	N–H bend	primary amines
1600–1585 (m)	C–C stretch (in-ring)	Aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	Aromatics
1470–1450 (m)	C–H bend	Alkanes
1370–1350 (m)	C–H rock	Alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds

1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag ($-\text{CH}_2\text{X}$)	alkyl halides
1300–1150 (m)	C–H wag ($-\text{CH}_2\text{X}$)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	$=\text{C}-\text{H}$ bend	Alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	primary, secondary amines
900–675 (s)	C–H "oop"	Aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	Alkanes
700–610 (b, s)	$-\text{C}(\text{triple bond})\text{C}-\text{H}$: C–H bend	Alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Infrared spectroscopy absorption Table

From OChemOnline

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The following Table lists **infrared spectroscopy absorptions** by frequency regions.

4000-3000 cm ⁻¹						
3700-3584	medium sharp	O-H	stretching	alcohol		free
3550-3200	strong broad	O-H	stretching	alcohol		intermolecular bonded
3500-3400	medium	N-H	stretching	primary amine		
3400-3300	medium	N-H	stretching	aliphatic primary amine		
3330-3250						
3350-3310	medium	N-H	stretching	secondary amine		
3300-2500	strong broad	O-H	stretching	carboxylic acid	usually centered on 3000 cm ⁻¹	
3200-2700	weak broad	O-H	stretching	alcohol		intramolecular bonded
3000-2800	strong broad	N-H	stretching	amine salt		
3000-2500 cm ⁻¹						
3333-3267	strong sharp	C-H	stretching	alkyne		
3100-3000	medium	C-H	stretching	alkene		
3000-2840	medium	C-H	stretching	alkane		
2830-2695	medium	C-H	stretching	aldehyde		doublet
2600-2550	weak	S-H	stretching	thiol		
2400-2000 cm ⁻¹						
2349	strong	O=C=O	stretching	carbon dioxide		
2275-2250	strong broad	N=C=O	stretching	isocyanate		

2260-2222	weak	C≡N	stretching	nitrile	
2260-2190	weak	C≡C	stretching	alkyne	Disubstituted
2175-2140	strong	S-C≡N	stretching	thiocyanate	
2160-2120	strong	N=N=N	stretching	azide	
2150		C=C=O	stretching	ketene	
2145-2120	strong	N=C=N	stretching	carbodiimide	
2140-2100	weak	C≡C	stretching	alkyne	Monosubstituted
2140-1990	strong	N=C=S	stretching	isothiocyanate	
2000-1900	medium	C=C=C	stretching	allene	
2000		C=C=N	stretching	ketenimine	
2000-1650 cm⁻¹					
2000-1650	weak	C-H	bending	aromatic compound	overtone
1870-1540 cm⁻¹					
1818-1750	Strong	C=O	stretching	anhydride	
1815-1785	Strong	C=O	stretching	acid halide	
1800-1770	Strong	C=O	stretching	conjugated acid halide	
1775-1720	Strong	C=O	stretching	conjugated anhydride	
1770-1780	Strong	C=O	stretching	vinyl / phenyl ester	
1760	Strong	C=O	stretching	carboxylic acid	monomer
1750-1735	Strong	C=O	stretching	esters	6-membered lactone
1750-1735	Strong	C=O	stretching	δ-lactone	γ: 1770
1745	Strong	C=O	stretching	cyclopentanone	
1740-1720	Strong	C=O	stretching	aldehyde	
1730-	Strong	C=O	stretching	α,β-unsaturated ester	or formates

1715					
1725-1705	Strong	C=O	stretching	aliphatic ketone	or cyclohexanone or cyclopentenone
1720-1706	Strong	C=O	stretching	carboxylic acid	dimer
1710-1680	Strong	C=O	stretching	conjugated acid	dimer
1710-1685	Strong	C=O	stretching	conjugated aldehyde	
1690	Strong	C=O	stretching	primary amide	free (associated: 1650)
1690-1640	medium	C=N	stretching	imine / oxime	
1685-1666	Strong	C=O	stretching	conjugated ketone	
1680	Strong	C=O	stretching	secondary amide	free (associated: 1640)
1680	Strong	C=O	stretching	tertiary amide	free (associated: 1630)
1650	Strong	C=O	stretching	δ -lactam	γ : 1750-1700 β : 1760-1730

1670-1600 cm⁻¹

1678-1668	Weak	C=C	stretching	alkene	disubstituted (trans)
1675-1665	Weak	C=C	stretching	alkene	Trisubstituted
1675-1665	Weak	C=C	stretching	alkene	Tetrasubstituted
1662-1626	medium	C=C	stretching	alkene	disubstituted (cis)
1658-1648	medium	C=C	stretching	alkene	Vinylidene
1650-1600	medium	C=C	stretching	conjugated alkene	
1650-1580	medium	N-H	bending	amine	
1650-1566	medium	C=C	stretching	cyclic alkene	
1648-1638	Strong	C=C	stretching	alkene	Monosubstituted
1620-1610	Strong	C=C	stretching	α,β -unsaturated ketone	

1600-1300 cm⁻¹

1550-1500	Strong	N-O	stretching	nitro compound	
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1372-1290					
1465	medium	C-H	bending	alkane	methylene group
1450-1375	medium	C-H	bending	alkane	methyl group
1390-1380	medium	C-H	bending	aldehyde	
1385-1380-1370-1365	medium	C-H	bending	alkane	gem dimethyl

1400-1000 cm⁻¹

1440-1395	medium	O-H	bending	carboxylic acid	
1420-1330	medium	O-H	bending	alcohol	
1415-1380-1200-1185	Strong	S=O	stretching	sulfate	
1410-1380-1204-1177	Strong	S=O	stretching	sulfonyl chloride	
1400-1000	Strong	C-F	stretching	fluoro compound	
1390-1310	medium	O-H	bending	phenol	
1372-1335-1195-1168	Strong	S=O	stretching	sulfonate	
1370-1335-1170-1155	Strong	S=O	stretching	sulfonamide	
1350-1342-1165-1150	Strong	S=O	stretching	sulfonic acid	anhydrous hydrate: 1230-1120
1350-1300-1160	Strong	S=O	stretching	sulfone	

1120					
1342-1266	Strong	C-N	stretching	aromatic amine	
1310-1250	Strong	C-O	stretching	aromatic ester	
1275-1200	Strong	C-O	stretching	alkyl aryl ether	
1075-1020					
1250-1020	medium	C-N	stretching	amine	
1225-1200	Strong	C-O	stretching	vinyl ether	
1075-1020					
1210-1163	Strong	C-O	stretching	ester	
1205-1124	Strong	C-O	stretching	tertiary alcohol	
1150-1085	Strong	C-O	stretching	aliphatic ether	
1124-1087	Strong	C-O	stretching	secondary alcohol	
1085-1050	Strong	C-O	stretching	primary alcohol	
1070-1030	Strong	S=O	stretching	sulfoxide	
1050-1040	Strong broad	CO-O-CO	stretching	anhydride	
1000-650 cm⁻¹					
995-985	Strong	C=C	bending	alkene	Monosubstituted
915-905					
980-960	Strong	C=C	bending	alkene	disubstituted (trans)
895-885	Strong	C=C	bending	alkene	Vinylidene
850-550	Strong	C-Cl	stretching	halo compound	
840-790	medium	C=C	bending	alkene	Trisubstituted
730-665	Strong	C=C	bending	alkene	disubstituted (cis)
690-515	Strong	C-Br	stretching	halo compound	
600-500	Strong	C-I	stretching	halo compound	
900-700 cm⁻¹					
880 ± 20	Strong	C-H	bending	1,2,4-trisubstituted	

810 ± 20				
880 ± 20				
780 ± 20 (700 ± 20)	Strong	C-H	bending	1,3-disubstituted
810 ± 20	Strong	C-H	bending	1,4-disubstituted or 1,2,3,4- tetrasubstituted
780 ± 20 (700 ± 20)	Strong	C-H	bending	1,2,3-trisubstituted
755 ± 20	Strong	C-H	bending	1,2-disubstituted
750 ± 20	Strong	C-H	bending	monosubstituted
700 ± 20				benzene derivative

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Introduction to Interpretation of Infrared Spectra

IR Spectroscopy is an extremely effective method for determining the presence or absence of a wide variety of functional groups in a molecule. ([For a detailed listing, see the Table showing important IR absorptions of various functional groups.](#)) One way to begin analyzing an IR spectrum is to start at the high wavenumber end of the spectrum (typically 4000 cm^{-1}) and look for the presence and absence of characteristic absorptions as you move toward lower wavenumbers. Some of the most common, and distinctive, absorptions are organized into several regions below. This is the type of analysis that you should be able to do without consulting notes. If necessary, a more detailed analysis could then be attempted by consulting a text on IR interpretation.

Important Regions of the IR Spectrum

$3600\text{-}2700\text{ cm}^{-1}$

X-H stretch region

$3600\text{-}3300\text{ cm}^{-1}$	Alcohol O-H Amine or Amide N-H Alkyne C-H	The alcohol OH stretch is usually a broad and strong absorption near 3400 . The NH stretch is typically not as broad or strong as the OH, and in the case of an NH_2 it may appear as two peaks. The terminal alkyne C-H may be confirmed by a weak CC triple bond stretch near 2150 cm^{-1}
$3300\text{-}2500\text{ cm}^{-1}$	Acid O-H	This is normally a very broad signal centered near 3000 cm^{-1} .
$3200\text{-}3000\text{ cm}^{-1}$	Aromatic (sp^2) =C-H Alkene (sp^2) =C-H	The aromatic CH's usually appear as a number of weak absorptions, while the alkene C-H is one or a couple stronger absorptions.
$3000\text{-}2800\text{ cm}^{-1}$	Alkyl (sp^3) C-H	Almost all organic compounds have alkyl CH's so this is not usually too informative. However, the intensity of these peaks relative to other peaks gives a hint as to the size of the alkyl group.
$2850\text{ and }2750\text{ cm}^{-1}$	Aldehyde C-H	Two medium intensity peaks on the right hand shoulder of the alkyl C-H's. Look for confirming carbonyl C=O peak.

$2300\text{-}2100\text{ cm}^{-1}$

$\text{C}\equiv\text{X}$ stretch region

2260-2210 cm⁻¹	Nitrile C≡N	A sharp, medium intensity peak. Carbon Dioxide in the atmosphere may also result in an absorption in this area if not subtracted out.
2260-2100 cm⁻¹	Alkyne C≡C	This peak's intensity varies from medium to nothing. Since the intensity is related to the change in dipole moment, symmetrical alkynes will show little or no absorption here!

1850-1500 cm⁻¹

C=X stretch region

1850-1750 cm⁻¹	Anhydride C=O 3- 4 membered ring C=O	Anhydrides have two absorptions, one near 1830-1800 and one near 1775-1740. The absorption frequency increases as the ring size decreases. For example: cyclohexanone=1715, cyclopentanone=1745, cyclobutanone=1780, cyclopropanone=1850.
1750-1700 cm⁻¹	Aldehyde C=O Ketone C=O Ester C=O Acid C=O	This is usually the most intense absorption in the spectrum.
1700-1640 cm⁻¹	Amide C=O Conjugated C=O	Because of the weakening of the C=O due to resonance, amides and conjugated carbonyl's come slightly lower than "normal" C=O. In general, conjugation lowers the absorption by 20-50 cm ⁻¹ .
1680-1620 cm⁻¹	Alkene C=C	This absorption is not as intense as that seen for C=O. It is variable and may be fairly small in symmetrical, or nearly symmetrical cases. Look for confirming alkene C-H peaks above 3000.
1600-1400 cm⁻¹	Aromatic C=C	Multiple sharp, medium peaks. The pattern of peaks varies depending upon the substitution pattern. Usually there is one peak around 1600 and several others at lower wavenumbers. Look for confirming aromatic C-H peaks slightly above 3000.

1500-400 cm⁻¹

Fingerprint Region

1300-1000 cm⁻¹	C-O	A strong absorption.
1500-400 cm⁻¹	Various	Interpretation of peaks in the fingerprint region is complicated by the large number of different vibrations that occur here. These include single bond stretches and a wide variety of bending vibrations. This region gets its name since nearly all molecules (even very similar ones) have a unique pattern of absorptions in this region.

Other Helpful Characteristics to Keep in Mind When Interpreting IR Spectra

Wavenumber of Absorption

The absorption wavenumber for a stretching vibration is related to both the force constant between the two atoms (k) and the mass of the two atoms (m_1 and m_2) by the Hooke's Law equation:

From this relationship, two important trends in the wavenumber for stretching vibrations can be deduced.

1. As the bond strength increases, the wavenumber increases. For example:

Bond stretch	C—C	C=C	C≡C	C—H	=C—H	≡C—H
Wavenumber of Absorption (cm ⁻¹)	1200	1650	2150	2900	3100	3300
	CC stretch			CH stretch		

2. As the mass of one of the two atoms in the bond increases, the wavenumber decreases. (Assuming the change in bond strength is relatively small.) For example:

Bond stretch	C—H	C—D	C—C	C—O	C—Cl	C—Br	C—I
Wavenumber of Absorption (cm ⁻¹)	3000	2100	1200	1100	800	550	500

Intensity of Absorption

The intensity of an absorption in the IR spectrum is related to the change in dipole that occurs *during* the vibration. Consequently, vibrations that produce a large change in dipole (e.g. C=O stretch) result in a more intense absorption than those that result in a relatively modest change in dipole (e.g. C=C). Vibrations that do not result in a change in dipole moment (e.g., a symmetrical alkyne C triple bond C stretch) will show little or no absorption for this vibration.

Table of IR Absorptions

<i>Functional Group</i>	<i>Characteristic Absorption(s) (cm⁻¹)</i>	<i>Notes</i>
Alkyl C-H Stretch	2950 - 2850 (m or s)	Alkane C-H bonds are fairly ubiquitous and therefore usually less useful in determining structure.
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)	Absorption peaks above 3000 cm ⁻¹ are frequently diagnostic of unsaturation
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)	
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)	
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)	See "Free vs. Hyrdogen-Bonded Hydroxyl Groups" in the Introduction to IR Spectra for more information
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)	
Amine N-H Stretch	3500 - 3300 (m)	Primary amines produce two N-H stretch absorptions, secondary amides only one, and tetriary none.
Nitrile C≡N Stretch	2260 - 2220 (m)	
Aldehyde C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s)	The carbonyl stretching absorption is one of the strongest IR absorptions, and is

Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)	very useful in structure determination as one can determine both the number of carbonyl groups (assuming peaks do not overlap) but also an estimation of which types.
Amide N-H Stretch	3700 - 3500 (m)	As with amines, an amide produces zero to two N-H absorptions depending on its type.

All figures are for the typical case only -- signal positions and intensities may vary depending on the particular bond environment.

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