

Investigations into Light Scattering by Human Hair

by

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To my parents and Andrew

Abstract

The main aim of this thesis is to increase the current level of understanding of the factors which affect the scattering of light by human hair. In particular, this work has been undertaken with a view to assessing the appearance of hair in an objective and quantitative manner — which is a commercially useful procedure.

The beginning of the thesis contains a brief outline of the biological and chemical nature of human hair, and a review of previous studies into the optical properties of hair. The investigations described in this thesis divide into three main sections.

First, optical experiments on individual hairs are detailed — these are conducted to analyse the components which contribute to the total light-scattering distribution produced by laser and white light illumination of hair. Two orientations of a single hair with respect to the planes of incidence and detection are considered and it is shown that the distribution of light is sensitively dependent on both the level of pigmentation and the surface condition of a hair.

Second, a series of methods of measuring the refractive index of hair and its constituents are described. The values obtained are used in an optical model of hair developed on a computer, using raytracing techniques. In this section, both the orientations of a hair investigated experimentally are simulated, together with the effects of variations in pigmentation level, cross-sectional shape, and scale angle.

Third, using planar arrays of parallel hairs, experiments are conducted to investigate any wavelength dependence in the light-scattering distribution, and to assess the effects of chemical treatments on the appearance of hair. Calculations of contrast gloss and kurtosis index are made to evaluate objectively any changes caused by the treatments. Also, for arrays of hair orientated vertically, intensity enhancement of the scattered light has been observed in the backscatter direction.

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Chapter 1

Introduction

1.1 General Introduction

The considerable social importance attached to the appearance of human hair invokes much attention by commercial interests. The cosmetics industry markets a vast range of products aimed at enhancing the appearance of hair, but most of them have been developed empirically, without an understanding of factors which affect the scattering of light by hair, and thus they achieve widely varying degrees of success. A more reasoned approach could be taken to the development of such products if the nature of light scattering by hair were better understood.

This broadly based introductory chapter contains information which is intended to provide a useful background to the work presented in the remainder of this thesis. Both the structure and the composition of an object affect the way it scatters light so, as the detailed structure and composition of hair may be unfamiliar to anyone other than a biologist, I have begun this chapter with a brief outline of the biological and chemical nature of human hair.

Previous studies into the optical properties of hair, including some which utilize techniques originally developed for the textile industry, are summarized in a short literature survey. A subsection on goniophotometry and gloss measurements contains a review of the terminology commonly used in this field, together with a summary of the development of meters for measuring different types of gloss.

The last section of chapter 1 is a synopsis of the main subject matter of this thesis.

1.2 Biological and Chemical Structure of Hair

1.2.1 Introduction

Hair is one of the characteristic features which distinguish mammals from other vertebrates. A typical human hair (shown in figure 1.1) consists of three distinct layers of keratin material: the medulla, cortex, and the cuticle (or scale layer); all the cells that compose these layers are dead. Keratins are defined by Lundgren and Ward

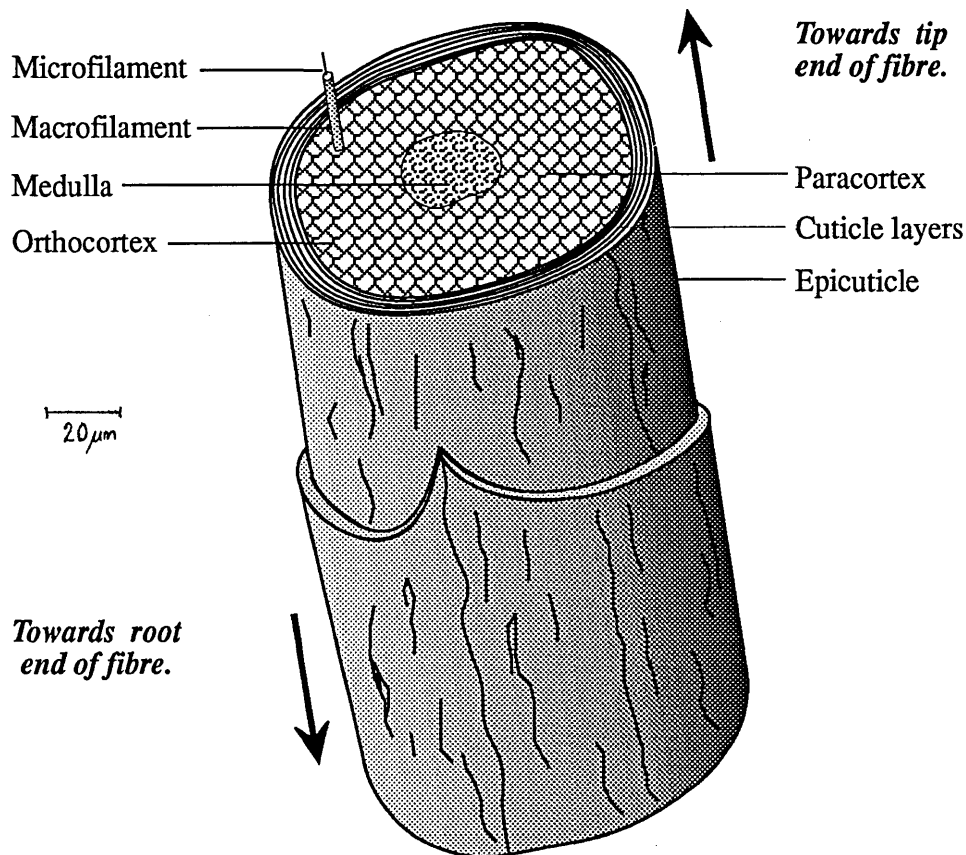


Figure 1.1: Cross-sectional structure of an individual hair fibre, illustrating its three distinct regions.

[1] as ‘natural, cellular systems of fibrous proteins cross-linked by cystine sulphur’ which are insoluble, forming a barrier against the environment. Two types of keratin exist: α keratins (coiled structures with many cystine* links) and β keratins (pleated sheet structures).

The constant addition of new cells at the base of the hair causes it to grow. Uncut hair may attain a length of 40 – 80 cm, with a growth rate of approximately

*Technical Note: cystine is a compound formed by the joining of two cysteine amino acids through a -Sulphur-Sulphur- linkage (a cystine link).

0.3 mm a day [2]. As a generalization, the curliness of a hair depends on the shape of its cross-section: circular is characteristic of straight hair, elliptical of wavy hair, and a flattened or kidney shape produces woolly hair [3].

1.2.2 Hair Follicle

The hair follicle, which is formed in the dermal layers of the skin, is a tubular epidermal structure, most often found surrounded by a well-developed capillary network, since a good blood supply is needed to provide the energy and chemicals required for growth and keratinization in the follicle. The process of keratinization (or cornification) involves the replacement of cell cytoplasm with keratin. As shown in figure 1.2, the follicle wall forms the inner and outer sheaths for the hair. The inner sheath, which grows up with the hair, consists of an outer Henlé layer and an inner Huxley layer [4, pages 10, 11]. Between the follicle wall and the hair, there is a thin layer of cells which act as a cuticle, interlocking with the scales of the hair.

1.2.3 Hair Formation in the Follicle

In the bulb of the follicle, each of the three distinct layers of hair and the two layers of sheath originates as a separate stream of cells; all cell division is confined to this germinative region of the follicle. Investigation has suggested that the size and shape of a papilla (see figure 1.2) are factors which influence the diameter of the hair the follicle produces [4, pages 10–12]. As the cortical cells proceed up the follicle they change shape; originally rounded, they become elongated as the pressure from cells below combined with the rigidity of the sheath wall squashes them.

During the stretching stage the cells are also becoming keratinized via the formation of cystine cross-links. In straight hairs the impregnation of keratin is fairly uniform around the circumference of the fibre; however, in crimped hairs asymmetries in this process have been observed [4, pages 12–14]. While the cortex is keratinizing, the medullary cells lose their nuclei and collapse, forming a soft keratin interspersed with a network of open spaces. Not all hairs possess medullas; they are most often formed during periods of vigorous growth when there exists a need to maintain hair diameter but minimize weight and conserve resources. The outermost cuticle cells are flat and overlap in a manner similar to the scales on a fish, for which reason they are often referred to as cuticle scales. In human hair the cuticle is several cell layers thick, with about one-sixth of the end of each cell exposed to the

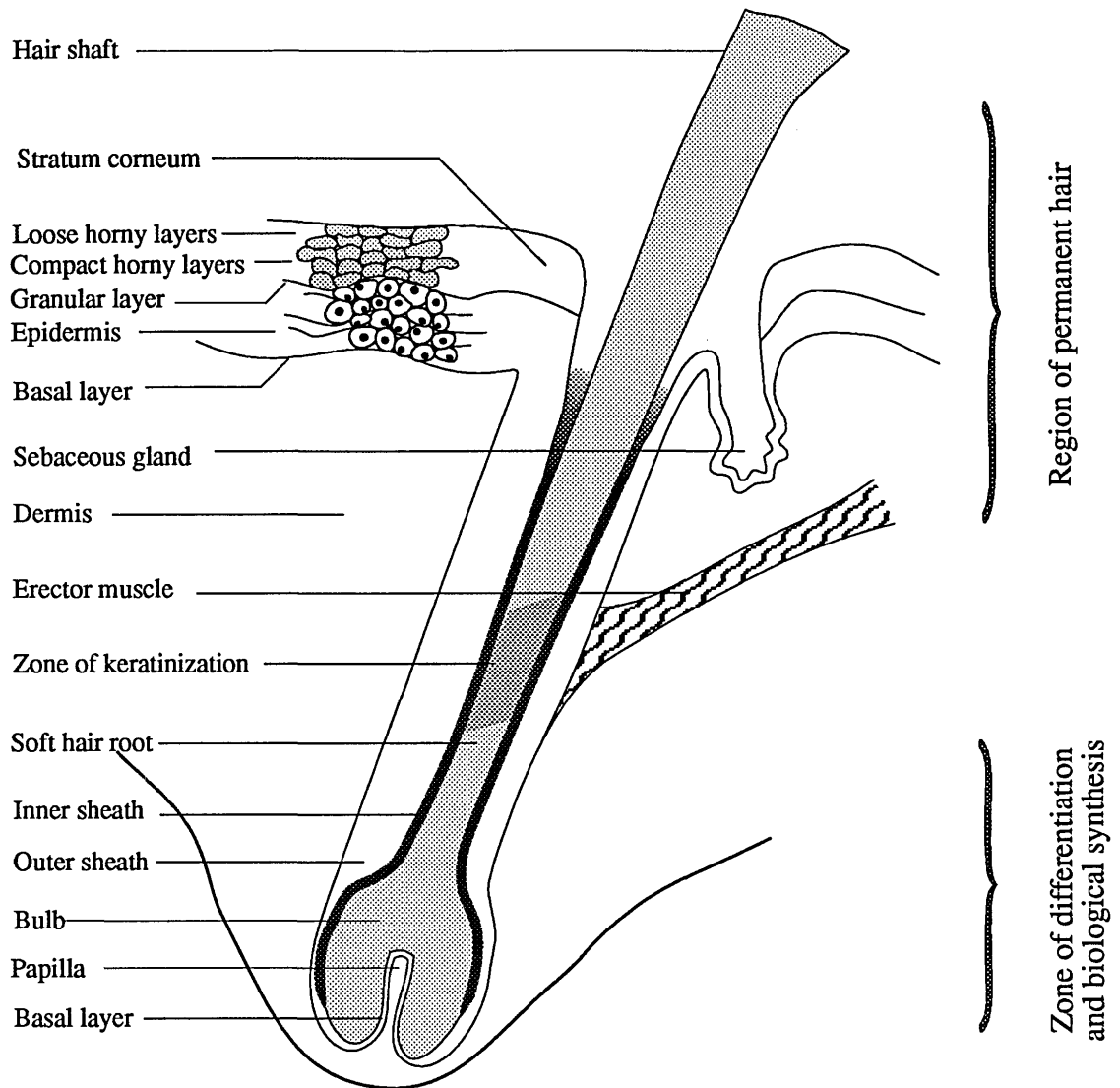


Figure 1.2: A vertical section through a hair follicle with hair fibre.

surface. Successive outer layers are forced over each other by upward movements in the inner sheath, therefore the overlapping edges of the cuticle always point towards the tip of the hair. The geometric arrangement of the scales is shown in figure 1.3. Before the hair emerges from the follicle it is coated with a secretion called sebum, produced by the sebaceous gland. Sebum acts as a greasing agent, endowing the hair with water-repelling properties. The multiplication of harmful bacteria and fungi is thought to be reduced by the fatty acids found in sebum [3, page 97].

1.2.4 The Gross Structure of Hair

Under an ordinary light microscope the gross structure of a single hair may be investigated. When a whole fibre is immersed in a suitable refractive-index-matching

medium, the microscope will reveal details of the outline of the hair and also provide some information on the interior. Surface casts of the hair made in thermoplastics allow the scale pattern along the fibre to be studied. Transverse and longitudinal sections of the hair reveal the internal structure.

1.2.5 The Detailed Structure of Hair

For a more detailed investigation of the three morphological regions of the fibre, techniques such as electron microscopy, X-ray diffraction, and chemical analysis need to be employed. Histologically, the cuticle cells comprise 10% of a fibre, the cortical cells about 88%, and the cell membrane complex the remaining 2% [5]. Each region of the hair is individually discussed below.

The Epicuticle

It was Allworden who first discovered that the epicuticle membrane, which is approximately $25\text{\AA}$ thick, covers the entire surface of the hair [6, pages 3–6]. While treating fibres with a solution of chlorine in water, he observed the formation of bubbles at the surface. These Allworden sacs, as they are now known, are formed as a result of the products of the chemical reaction between the protein membrane and the chlorine water being unable to diffuse back through the semi-permeable epicuticle membrane. Swelling occurs due to osmotic pressures producing the sacs, hence, revealing the presence of an outer membrane. Leeder and Bradbury have demonstrated that this membrane surrounds each individual cuticle cell. A relatively non-destructive technique of membrane extraction involves the use of hot ethanol. The presence of a lipid layer is as yet an unsubstantiated suggestion, although chemical analysis of epicuticle obtained by ethanol extraction indicates that the membrane contains both proteins and fatty acids (20–30%). After the extraction process the remainder of the hair fibre was found to be less resistant to chemical attack.

The Cuticle

This layer forms the outer cellular covering of the hair. It is a laminar structure (as shown in figure 1.3) generally composed of between 5–10 scales, which form a flexible radial mechanical constraint on the cortex [7].

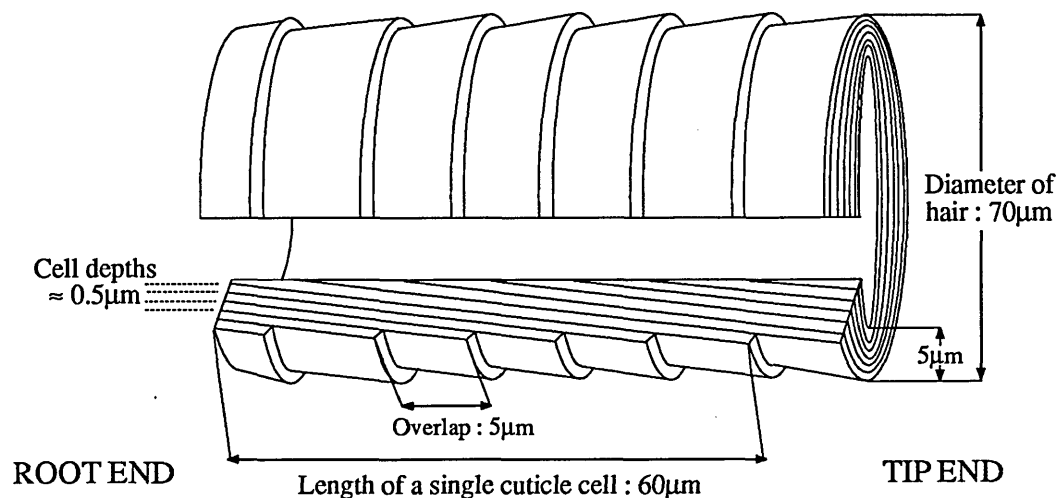


Figure 1.3: A schematic representation of the geometric arrangement of human hair cuticle.

Each cell (or scale) is quite flat, usually only 0.5 micron thick but up to 45 microns long. The gaps between scales contain natural sebum which maintains flexibility and adds a moisture-resistant oil film. The thin outer membrane of each cell varies in thickness from $50\text{\AA}$ to $250\text{\AA}$ and within this there seem to be three distinctive layers. The outer or 'A' layer has a high cystine content which makes it the most chemically resistant to attack (as demonstrated by Geiger [6, pages 1–3]), next comes the exocuticle and then, finally, the endocuticle. The overlap or scale margin in human hair is generally described as 'crenated', with the distance between scale margins depending on the rate of growth. Five distinctly different patterns have been observed [8], corresponding to a range of growth rates — these are shown in figure 1.4. For average growth rates of human hair the pattern usually seen is 'near', although both 'distant' and 'close' patterns are not uncommon. Studies of human hair has also revealed individual variations in scale pattern which seem to be inherited in a genetically simple Mendelian fashion. Thus, like fingerprints, hair may be used for identification.

The Intercellular Material

Alexander and Earland developed a method of isolating the intercellular complex by oxidizing the fibres with peracetic acid [6, pages 7, 8]. About 15% of the fibre mass is made up of this complex, which is called *b*-keratose and referred to as the *d*-band. It acts as the intercellular cement between cells, where it is approximately $50\text{\AA}$ thick, and is highly resistant to alkali and reducing agents but susceptible to

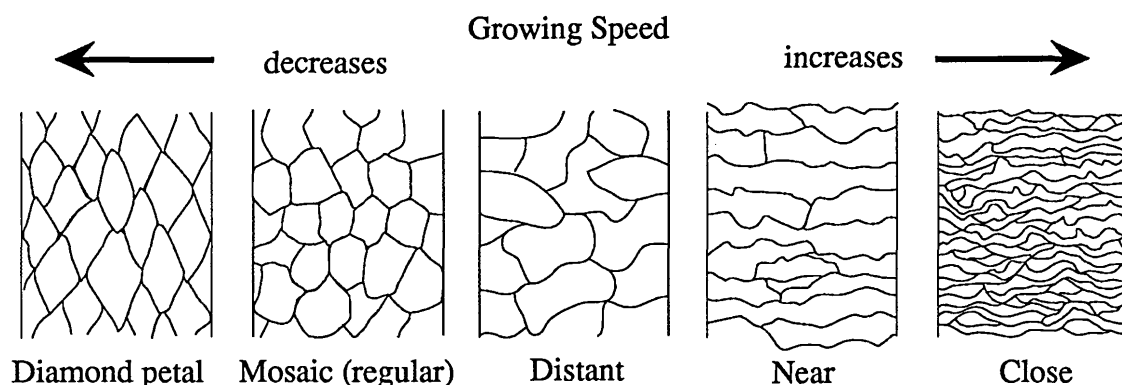


Figure 1.4: Morphological changes in cuticular cells with speed of growth.

attack by proteolytic enzymes. This is in direct contrast to the properties of the intracellular proteins (g-keratose) of the cortex. These proteins have a high proportion of sulphur in comparison with the intercellular material, which may partly explain the difference in chemical reactions.

The Cortex

The cortex is the major component in human hair, supplying strength and elasticity. Under a light microscope it *appears* to be a rigid, homogeneous, hyaline[†] mass, but, in fact, it actually consists of a central core of para-cortical cells which is surrounded by one or two layers of the more chemically reactive ortho-cortical cells. Negro hair tends to have a higher proportion of the ortho-type cells compared to Caucasian hair [5].

Individual cortical cells, polygonal in shape, may be isolated by shaking in formic acid or by enzymatic digestion using the enzyme trypsin. During keratinization the cells dehydrate and shrink, causing the sides of the cells to become serrated. This means that they can interlock with adjacent cells. All cortical cells are found to have spindle-shaped fibres, called macrofibrils, and nuclear remnants, whilst many also contain pigment granules. An idealized representation of a cortical cell is shown in figure 1.5. Macrofibrils run parallel to the hair axis. They vary in diameter between 0.1 and 0.4 microns. Under an electron microscope it is possible to investigate the sub-structure of the fibrils. It has been found that they are made up of smaller spiralling filaments, called microfibrils, about $60\text{\AA}$ in diameter, embedded in an amorphous matrix of randomly coiled polypeptide chains. The matrix

[†]Technical Note: hyaline (*adj.*) meaning glasslike, vitreous, transparent.

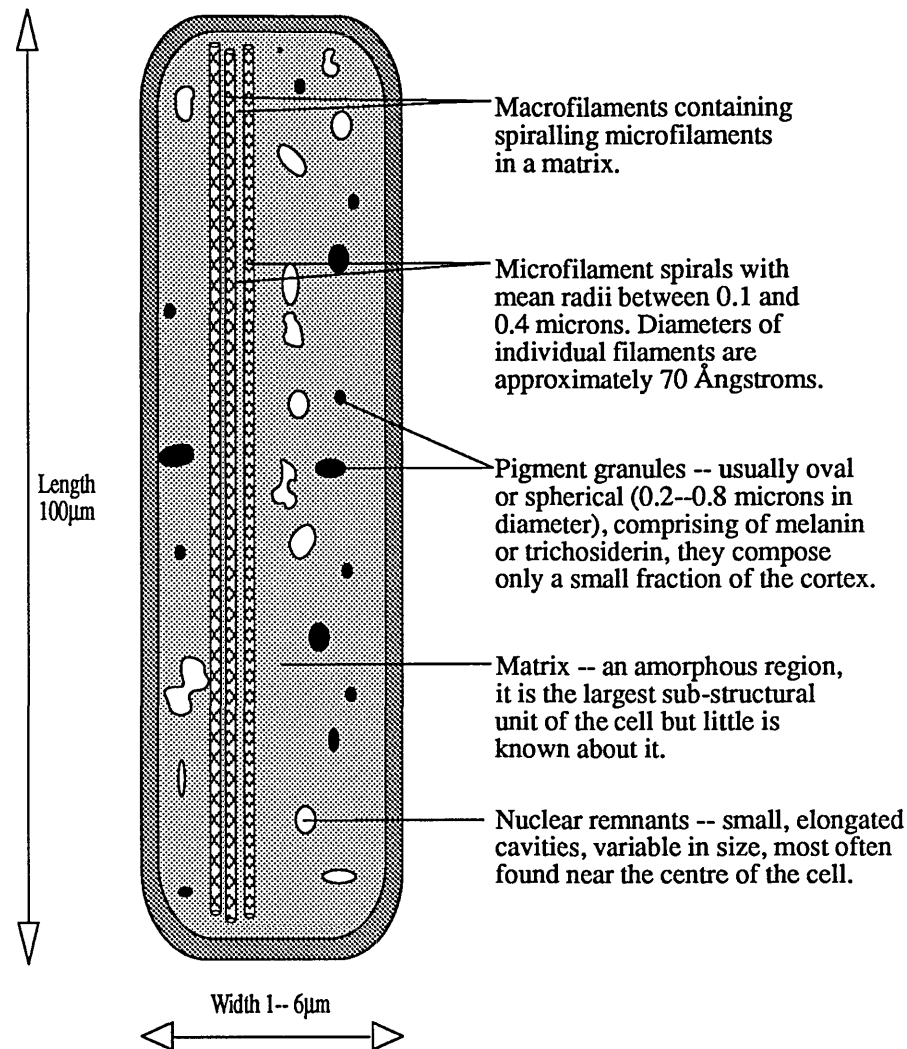


Figure 1.5: A longitudinal section through an idealized single cortical cell.

has higher cystine content than the microfilaments it surrounds. Further evidence suggests that the microfibrils are themselves subdivided into protofibrils (approximately $20\text{\AA}$ in diameter), although the exact arrangement of their structure is still under debate. Filshie and Rogers [6, page 9] proposed the standard '9+2' configuration, as observed in cilia and flagella. Since then, Fraser, MacRae and Rogers [6, page 9] have found that the microfilaments contain short sections of α -helical in a three-stranded, coiled formation. These, it is suggested, form a tubular ring with a central core. This structure is probably stabilized through a variety of intramolecular and intermolecular forces, including hydrogen bonds, van der Waals forces, dipolar interactions and hydrophobic bonds [9].

The Medulla

This central column region, not always present, is most often found in thick hair. The cells that form the medulla are often cuboidal in shape. In human hair, non-latticed medullas occur which are narrower and denser than the latticed variety more common in goats. A characteristic of non-latticed medulla is that it may be interrupted by the cortex, or become fragmented. In fibres with an intermittent medulla, cells emanating from the same point of origin may develop into either medullary cells or cortical cells, according to the degree of keratinization at their particular position in the hair. In a medulla cell the normal synthesis process which completely fills a cortical cell with keratin fails to occur. Thus, as the hair grows, instead of elongating under pressure, the medulla cells collapse; their contents condense around the nuclei and a region of 'soft' keratin interspersed with interconnecting air-filled cavities is formed [10].

1.2.6 Pigmentation of Hair

Hair colour is determined by melanin pigment granules found mainly in the cortex. Two kinds of melanin are known to be present in human hair: phæmelanin, which in appearance is yellow-red, and eumelanin, which is brown-black. The varying shades and colours observed in human hair are probably due to differences in distribution, size, and density of the pigment granules; for example, the pigment granules found in Negro hair are generally larger in size than those found in Caucasian and Oriental hair.

Melanocytes, which are the cells that form the granules, are mostly found in the basal layer of the epidermis and the outer sheath — they do not enter the fibre; instead, the cortical cells actively ingest the dendritic processes of the melanocytes, acquiring the granules before they die. This is referred to as phagocytosis [4, pages 17, 18]. The melanin pigment itself is produced by the oxidation of tyrosine (an amino acid), which is catalysed by the enzyme tyrosinase. In human hair the high density of pigment around the periphery of the fibres is often used as a means of identification, although both streaked and granular longitudinal distributions of pigment may occur.

Photons of light at visible wavelengths have energies between 1.6 eV and 3.2 eV, which are rather on the low side for ordinary electron excitation and on the high side for excitation via molecular vibration [11, pages 89–91]. Pigment molecules achieve

preferential absorption of visible wavelengths by forming conjugated systems of long-chain molecules which contain mobile pi electrons. These electrons are not bound to a specific site, but are able to range freely over the relatively large dimensions of the molecular chain. In quantum mechanical terms, the energy required to raise these pi electrons into higher excited states corresponds to that which may be provided by visible wavelength photons. The close proximity of other atoms in the molecule leads to a broadening of the discrete energy levels available for each atom, thus the spectrum range over which the pigment may absorb is wider than might first be anticipated.

1.2.7 Weathering of Hair

Weathering describes the cumulative effect of climate exposure on the physical and chemical structure of the hair shaft. In practice, it is difficult to differentiate between natural weathering and the changes resulting from the trauma inflicted for appearance's sake. Natural weathering processes include:-

- Photodegradation of keratin by exposure to sunlight (refer to [12]).
- Erosion of hair surface caused by friction between hairs (refer to [13]).
- Exposure to the atmosphere, e.g. wind, rain, dust and other air pollutants (refer to [14]).
- Repeated wetting of hair by seawater (particularly in conjunction with exposure to sunlight).

The following cosmetic processes and treatments cause damage:-

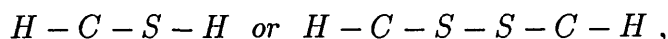
- Daily grooming, which embraces brushing, combing, and backcombing. This gradually chips away the scale edges. It has been reported [15] that combing reduces the scale margins of hair by $0.5\mu\text{m}$ per 2,000 comb strokes.
- Cleaning. Frequent washing with strong detergents will remove sebum, leaving hair dry and brittle. Normal shampoo abrades cuticle at the rate of $1\text{--}2.5\mu\text{m}$ per 50 treatments. Brushing wet hair may damage it 5–10 times faster than when it is dry [16]. The cuticle cortex boundary is the zone of weakness when the hair is wet.

- Mechanical rubbing action of towel-drying wet hair. This causes attrition of the scale edges (refer to section 1.2.8).
- Heat from the use of a hair-dryer or heated rollers.
- Chemical alteration of hair by bleaching, permanent waving (cold or hot waving), and dyeing (temporary and permanent). Chlorine (invariably added to water in swimming-pools) also has a deleterious effect on hair. In each treatment the pH of the solution will affect the degree to which hair suffers damage [17, 18].

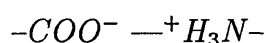
Unweathered hair has smooth scale edges. As weathering begins, the edges become jagged and partial scale erosion occurs. The pattern of weathering seems to depend on the cross-section of the hair; a hair with a circular cross-section will tend to wear evenly, but on a hair with a highly elliptical cross-section the pattern of wear is often sinusoidal (referred to as a chevron pattern). The amplitude of this sinusoidal variation in scale erosion increases with increasing distance from the root end of the hair, leading to the obvious conclusion that the prominent parts of the fibre are worn away at a faster rate than the rest. Eventually, complete scale erosion may lead to the fibre splitting into two roughly hemi-cylindrical parts. The unbound cortex then splits into fibrous elements (a 'split' end). Obviously the condition and structure of its cuticle affect the appearance of a hair, as it is with the hair's surface that the light first interacts. Therefore, many researchers [2, 15, 19, 16, 20, 21] have tried to quantify the effects of each kind of 'weathering' to determine which are the most significant. The effectiveness of compounds developed to minimize and/or repair such damage has also been investigated.

1.2.8 Chemical Composition of Hair

Human hair contains several different chemical species. Depending on the moisture content (which may vary up to 32%), it consists of protein (65–95%), lipids, pigment, and trace elements in compound form. At least 21 different amino acids have been found to be present in hair. X-ray diffraction has revealed that these amino acids are arranged in long helical chains of protein molecules [4, pages 23–25]. Many of the side groups on these amino acids (particularly cystine) contain sulphur in the form of:–



where $H \equiv$ hydrogen atom, $C \equiv$ carbon atom, and $S \equiv$ sulphur atom. Disulphide crosslinks and hydrogen bonds hold the protein molecules together, giving the hair its shape and strength. When hair is wet the hydrogen bonds are reversibly broken, reforming when the hair dries [22]. Thus, wet hair is less structurally robust and more vulnerable to mechanical damage. Additional linkages are sometimes found via the ionization of a carboxyl ($COOH$) group and an amino (NH_2) group to form 'salt' links:-



The natural weathering processes, such as sunlight and atmospheric exposure, seem to have an oxidizing effect on hair, and it has been observed that the cystinyl groups become oxidized to higher states along the length of the hair [23]. In the distal section of the fibre there exists a much higher proportion of cysteic acid than in the root. A poor protein diet will reduce the amount of cystine in the hair initially, whilst brushing, combing, and cosmetic chemical treatments such as bleaching and permanent waving, tend to erode cuticle and also reduce the cystine content in the fibres, at the same time increasing the cysteic acid content. This provides evidence supporting Zahn's theory [6, pages 18–39] that the reaction of the chemical agents with human hair proteins is primarily at the disulphide bond.

1.2.9 Function of Hair

Hair, being an epidermal structure, functions mainly as a mechanical protection. In the areas of the body where hairs grow, the epidermis is thinner. Eyelashes protect the eyes, and hair in the nostrils and external ear protects against the entry of foreign bodies. Associated with the hair follicle is the involuntary erector muscle, a dermal structure whose contraction causes the hair to stand on end. This action increases the amount of air trapped as an insulating layer around the skin, and is thus a mechanism of homeostasis.

1.2.10 Hair Growth Cycles

It is almost certain that no single hair fibre grows continuously — sooner or later individual follicles enter a resting stage. There appear to be three stages in the

cycle of hair growth: the first, anagen, includes follicle regeneration and active hair growth; the second, catagen, is the retrogressive stage; and then finally there is telogen, the inactive or resting period. During catagen the hair narrows and there is often a loss of pigmentation [4, pages 42, 43].

1.2.11 Hair Replacement Patterns

There are three main types of hair growth cycle: seasonal, wave, and mosaic. In man, hairs are replaced irregularly with each follicle having its own cycle, apparently independent of the rest of its neighbours. This replacement pattern enables a constant length of hair to be maintained and is called ‘mosaic’. The cycle for human hair is probably between 18 months and 7 years [2], with nearly 90% of the scalp follicles being active at any given time. Therefore the period of growth must be long compared to the period of rest [4, pages 45, 46].

1.2.12 Differentiation Between Root and Tip

A hair fibre grows with a pointed tip — a shape it will retain for its lifetime, provided there is no excessive wear. As a consequence of the way the hair grows out of the scalp, the scale edges always point towards the tip. This means that if the hair is pulled between the fingers from root to tip it will feel smooth, in the opposite direction the scales will provide resistance and so the hair will feel ‘rubbery’ [4, pages 19, 20]. A growing hair has a soft, tapering root — easily visible under a light microscope — which takes up dyes readily.

1.3 Literature Survey (Previous Optical Studies of Hair, Including Equipment and Techniques Used)

The optical properties of human hair include its colour (brightness, purity, and dominant wavelength), refractive index, birefringence, and lustre. Each of these properties, together with the hair’s anatomy, influences the way in which it scatters light. This literature survey reviews the techniques which have been used to investigate the optical and structural properties of human hair with regard to its appearance. In particular, colorimetry, light microscopy (polarized and unpolarized), electron microscopy, and goniophotometry have been examined.

1.3.1 Colorimetry

One of the factors which dominate the appearance of hair is its colour. As a consequence of this, efforts have been made for many years to classify the natural colours of human hair. In 1934, Gardner and MacAdams [24, 25], using the recording spectrophotometer developed by A. C. Hardy, studied a large number of hair samples for the purpose of classifying naturally occurring hair colours. The curves obtained showed that all the hairs produced a simple reflectance/wavelength relationship across the visible region of the spectrum. For black and blond hairs the curves were found to be almost straight lines, but the curves produced by red hairs showed an upward curvature at the green end. It was also evident from their results that the differences in hair colour are due to reflectance at the red rather than the violet end of the spectrum. However, subtle variations in colour within the red and brown hairs were found to occur due to changes in reflectance in the blue/green range. A complete colorimetric specification of 20 hairs was also made following the standard objective method suggested by Judd [24]. The three criteria considered were:—

- The lightness (further discussed in section 1.3.5) or luminosity of a sample. It is defined as the fraction of incident light the surface of the object reflects back in the direction of observation. It is measured by comparing the brightness of a sample relative to that of a Lambertian diffuser. Sometimes referred to as the luminance factor, it is a measure of relative luminosity.
- The dominant wavelength. This may be visualized as the one most closely resembling the sample colour; it is directly related to the hue of the sample.
- The purity of the sample — this is a measure of the degree of similarity between its colour and the colour of monochromatic light at the dominant wavelength of the sample; the greater the similarity, the higher the purity. A term often used instead of purity is ‘saturation’, which signifies the dilution of the colour with white light, i.e. the degree to which the dominant wavelength is pre-eminent.

Gardner and MacAdams found that, in general, the relative brightness of the samples with respect to a magnesium oxide reflector (taken to behave as a Lambertian diffuser) was in the range of 2% to 20%; with purities of less than 60% in all cases. The dominant wavelength was found for all samples to lie between $580\mu\text{m}$ and $595\mu\text{m}$.

Bleaching with peroxide was found to increase the purity and brightness but did not alter the dominant wavelength.

Although hair classification based on reflection spectra is possible, it is an expensive (cost of spectrophotometer) and protracted method of assessment. It also does not take into account the change in hair colour with angle of incidence, reflection, and viewing. Den Beste and Moyer [26] built and used a specially designed scanning gonireflectometer to characterize natural hair colours, using the C.I.E.[†] tristimulus system of notation.

Briefly, this is a scheme by which colours are described in terms of the amount of red, green, and blue light they reflect. Thus each sample undergoes three measurements (one at each wavelength), and the data are used to calculate the tristimulus chromaticity co-ordinates, which provide a mathematical representation of colour. Purity and dominant wavelength may also be deduced from the data.

Again the dominant wavelength of each tested sample lay between $586\mu\text{m}$ and $589\mu\text{m}$, the purity between 10% and 60% and the luminosity between 2% and 90%. As a generalization, they found that hair colours with low purity were ash or drab, while those of high purity were red or warm; also, that the measured luminosity had some correlation with the subjective assessment of dark or light hair — hair of low luminosity appeared dark, and hair of high luminosity appeared light or blond.

Their luminosity results were, however, in comparison with those produced by other workers, consistently high, but, in view of the results presented in chapter 3, this may have been because the method they adopted for separating the component of light containing the colour information from the total light scattered was not quite correct. Further discussions about this proposal are given in chapters 3 and 5.

A recent paper by Gerrard [27] which presented measurements of hair colour, using a Minolta Chromameter, was based on a study of 65 hair samples still attached to the heads of volunteers. The results were analysed following the C.I.E. 1976 (L^* a^* b^*) uniform colour space and colour-difference formula (for more information refer to [28]). The author found that on the lightness scale L^* all the hairs produced values which varied between 17 and 67 (note: $L=0$ is black and $L=100$ is white) and that all the subjects had hair in which yellow and red hues dominated. (Only one commercially supplied tress of grey hair — of dubious past history — exhibited a result indicating a green hue, which was then confirmed subjectively. It was thought

[†]C.I.E. $\equiv$ Commission Internationale de l'Eclairage.

that this hair may have been subjected to chemical treatment.) The main advantage of this method of determining hair colour was felt to be the rapid and reproducible results it provided.

1.3.2 Light Microscopy

Hair is difficult to study in detail under an ordinary light microscope, because it is, in effect, a cylinder which is vastly longer than it is wide. Being also very thin (typically 80 microns in diameter), high magnifications are required to resolve detail on the hair, and at these magnifications the depth of focus is less than the diameter of the hair. Since the small field of view limits the length of the fibre portion that may be studied without moving the sample stage, searching for congenital abnormalities or the effects of a treatment or test along the length of the fibre is time consuming and difficult. Sectioning of hair in some circumstances can be helpful but may involve a loss of information.

However, as hair, like many other natural fibres, is birefringent, a technique involving polarized light microscopy has been used by several medical and anthropological researchers [29, 30] for quickly assessing the condition of a hair shaft. This is useful for the early identification of a number of diseases. In the main, three kinds of abnormality are appropriate for study using this technique:—

- changes in thickness of hair shaft, e.g. nodules, constrictions and twists;
- structural abnormalities;
- orientation of fibrils inside the hair — in healthy, normal hair they are usually aligned to within $\pm 2^\circ$ parallel to the fibre axis.

The optical anisotropy (birefringence) of hair arises primarily from its inner structural arrangement (flattened keratinized cells all lie parallel to the fibre axis) but the ordinary arrangement of the α -keratin crystals also contributes. The optic axis is collinear with the fibre axis of the hair shaft, with each region of the hair displaying a slightly different birefringence, depending on its degree of keratinization. Fraser [31] reported an average birefringence value for hair of 0.007. (Note: numerical birefringence equals phase retardation divided by sample thickness,

$$\frac{2\pi}{\lambda}(n_2 - n_1) = \frac{\Delta}{d} , \quad (1.1)$$

where n_2 and n_1 are the refractive indices in orthogonal directions, λ is the wavelength of light, Δ is the amount of retardation in the phase of one wave with respect to the other, and d is the thickness of the sample.) By monitoring the birefringence value, studies have been made on the elasticity and condition of hair [31, 32].

In particular, the relative humidity (R.H.) was found to affect the birefringence of hair: at 0% R.H. the numerical birefringence was measured as 0.01, whilst at 100% R.H. it was found to be 0.006 [32]. Hairs absorb moisture according to the ambient relative humidity; the swelling of the hair has been reported to be as much as 16% radially but only 1.2% longitudinally.

1.3.3 Electron Microscopy

Two types of electron microscope are available for use in examining hair. The transmission electron microscope (T.E.M.) is capable of achieving very high magnifications (200,000X) and allows the study of fine details. However, it requires extremely thin, specially prepared samples which are time consuming to produce and then only small sections of a hair may be studied. It is useful for monitoring the ultrastructure of the hair through its cross-section and assessing any changes as a result of cosmetic treatments [33]. For surface examination a replica of the sample is generated [34] by spraying the hair's surface with a layer of plastic and carbon.

The scanning electron microscope is better suited for studying hair as, compared to a light microscope, it has a great depth of focus and high magnification but does not require the extensive sample preparation necessary when using a T.E.M. However, it cannot in general reach such high magnifications (limited to around 10,000X) as the latter. It has been used extensively for evaluating the surface condition of hair and changes due to treatments (pharmaceutical and cosmetic) as well as for studying hair breakage and damage [2, 16, 35, 36, 37]. In the work of Gerdes and Brown [38], it was noted that strict standardization in sample collection, treatment, and preparation, as well as pictorial representation (photographs), is required to avoid confusion and misleading results. For instance, the tilt angle of the hair at the time of recording data can greatly influence the apparent separation of the scale margins along its length.

When hair is examined under an S.E.M it is normally necessary to vacuum coat it with a thin layer of metal to prevent charging occurring — hair is naturally a non-conducting, dielectric material. When 'before and after' data are required in

order to quantify the subtler effects of grooming and weathering, the hairs must be examined without coating, and therefore low electron-accelerating potentials (2kV instead of the usual 10 or 20kV) have been employed [15, 35]. In one case [35] the hairs were actually left attached to the volunteer's head during the entire procedure.

Several researchers [19, 21] have used both types of electron microscope to produce an extensive study into the effects of grooming on the ultrastructure of hair. Using an S.E.M., an attempt has been made to classify the morphological alteration of hair shafts according to the extent and type of damage sustained [39].

1.3.4 Light Diffraction Experiments on Hair

The optical diffraction patterns produced by hair have been used to measure their diameters and investigate their structural properties. In 1954, Raman and Bhatt [40] used a pencil of sunlight to observe the pattern produced by a selection of natural and synthetic fibres. Polarized light was used to try to determine from birefringence effects the molecular structure of the fibres, and the authors observed that a wide variety of noticeably different patterns were displayed, even from the same fibre.

In the textile and toiletry industries, the diameter of a fibre is considered an important quantity. Several techniques have been used to determine this quantity, such as the use of vibrascopes, micrometer calipers, and projection microscopes, but all have tended to be of limited use as they are either time consuming or open to inaccuracies. This has led to the development of a light-diffraction technique to determine fibre diameter. In general, the method used has been based on the Fraunhofer calculations of the far-field diffraction pattern formed by light scattering from a single slit.

When a plane, monochromatic wave is incident on a single slit (aperture width typically of the order of a few hundred wavelengths, and length of several centimetres), the majority of the light is diffracted perpendicular to the orientation of the slit edges. In the far-field (Fraunhofer) region a diffraction pattern may be observed. The intensity distribution of the diffraction pattern is represented mathematically by:-

$$I(\theta) = I(0) \left(\frac{\sin \beta}{\beta} \right)^2, \quad (1.2)$$

where θ is the scattering angle, $I(0)$ is the intensity when $\theta = 0$, i.e. at the centre

of the diffraction pattern, and

$$\beta = \frac{\pi d \sin \theta}{\lambda}, \quad (1.3)$$

where d = diameter of the slit, and λ = wavelength of the incident radiation. By invoking Babinet's theorem (similar diffraction patterns are produced by two complementary screens, the opaque portions of one corresponding to the transparent portions of the other), the diffraction patterns produced by a slit and an opaque, conducting cylinder may be considered to be equivalent. Lundberg [41] demonstrated this idea in his paper 'Light scattering from large fibres at normal incidence'. Good agreement was found to exist for diameters of gold wire calculated using the Fraunhofer diffraction theory and then measured via electron microscopy. However, this was not found to be true for transparent, dielectric fibres. For these fibres there is an addition to the diffracted light as it is possible for light to be transmitted through the fibre via refraction. Thus, the optical diffraction pattern observed for such fibres cannot simply be described in terms of its geometrical profile but must also include terms relating to its refractive index. Any measurements of dielectric fibre diameter calculated from the diffraction pattern using the equations derived for a single slit will be in error, the amount depending on the refractive index of the fibre. An alternative model for dielectric fibres uses Rayleigh's equations, which give an exact solution for a uniform dielectric cylinder of constant refractive index. In practice, when Lundberg applied this model to the light-scattering patterns produced by nylon fibres he achieved good agreement over only small ranges of scattering angles.

The diffraction technique has been extended to measuring roughly the average diameter of a group of fibres — again, each individual fibre was considered equivalent to a slit. Edmonds [42] studied the diffraction patterns produced by a randomly orientated group of fibres whilst Onions and Ellingham [43] considered a group of parallel-orientated fibres, sufficiently separated so that they were not touching. In each case, the mean diameter and corresponding standard deviation of the group of fibres was determined. Typical diameter sizes that have been investigated using this method range between 10 and 80 times the wavelength.

Lynch and Thomas [44] investigated the optical diffraction profiles of individual fibres, including hair, using a helium-neon laser. In this experiment the fibre could be rotated about its axis and traversed horizontally through the narrow beam. By mounting a photographic film on a rotating drum, which had its axis of rotation orthogonal to the axis of the hair, a record of the diffraction profile from each point

along the length of hair was made; gold-coating the hair was reported to improve the clarity and resolution of these profiles. Lynch [45, 46] later published tables of values of fibre diameters calculated from their diffraction patterns. He used the Fraunhofer relationship derived for a single slit relating the angular position of the first minimum (θ_1) to the diameter (d):–

$$d = \frac{\lambda}{\sin(\theta_1)} , \quad (1.4)$$

where λ is the illuminating wavelength. However, depending on the refractive index of the material, he replaced λ with an effective wavelength λ' , which he calculated by measuring the diameter at one position using an independent method.

If absolute measurements of fibre diameter are not required (for instance, if it is the changes in diameter which are of interest) then the diffraction method may be particularly useful. Brancik et al. [47] calculated the swelling effects of solvents, and Buras et al. [48] the effects of humidity, on the diameter of human scalp hair. Buras et al. found that pristine hair exhibited an 8% increase in diameter over the full range of relative humidity (0 to 100%), the curve being sigmoid[†] in shape. Descaled hair followed a similar trend, except at very high relative humidities where the expansion was less; this may be accounted for by the missing cuticle scales, which usually tend to spread out as they absorb water. Bleached hair also followed the same trend except that the curve was a different shape (no point of inflection); the chemical changes in bleached hair (more cysteic acid) were thought to explain this difference.

1.3.5 Goniophotometry and Gloss Measurements

The appearance of a head of hair is often described in terms of its gloss, lustre and shine. However, these terms are usually applied subjectively. Even when a new hair product is being tested in a salon its effect on the shininess of hair is made subjectively by a panel during a ‘half-head test’. A half-head test involves the application of the product under evaluation to one half of a subject’s hair whilst a mild detergent shampoo is applied to the other. A subjective judgement on the relative appearance of the two halves is then made by the panel.

In everyday life most materials we encounter have a characteristic gloss but normally it is not consciously noticed; subconsciously, people do react to the appearance

[†]Technical Note: Sigmoid (*adj.*) meaning curved like the letter *S* in shape.

of objects and form opinions about what they see. The quantity called gloss is an important factor in the appearance of an object and so over the years much effort has been made to measure it. The motivation behind developing methods of defining and quantifying gloss, thus enabling articles to be classed according to their glossiness, is often commercial.

Review of Terms and Definitions

In this field there reigns some confusion over the terms gloss, glossiness, sheen, and lustre, as well as over the types of gloss that exist. For the purpose of my research I shall adopt the following:—

1. **Specular Reflection.** At an ideal mirror surface, the angle of reflection of light striking it is equal and opposite to the angle of incidence — the normal to the surface and the angles of incidence and reflection all lying in a plane; that is, all the light incident in the same given direction to the surface is returned at a single angle of reflection. Light reflected from the surface satisfying this condition is referred to as *specularly reflected*, and this type of reflection occurs with mirror surfaces. In terms of its visual appearance, a plane specular surface would be observed to be mainly dark, exhibiting highlights only at particular angles, i.e. possessing high angular contrast.
2. **Diffuse Reflection.** Many surfaces exist that do not behave as mirrors. Instead, under a single angle of illumination, light is returned over a wide range of angles. In most cases this light is the result of a combination of reflection, refraction, and scattering taking place on the surface and within the medium of the object. On the surface, irregular discontinuities (roughness) act as random scatters, whilst inside a medium, small particles of differing refractive indices act as centres of scattering. A diffuse surface might appear to an observer to be composed of graduated regions of lightness and darkness, i.e. possessing low angular contrast. A special type of diffuse surface is Lambertian Diffuser which scatters light equally in all directions irrespective of the angles of illumination or viewing, i.e. it will appear equally bright when viewed from all directions.
3. **Gloss.** This is an inherent property of the surface which defines its ability to reflect light specularly, i.e. it is a measure of how close its behaviour approxi-

mates that of an ideal mirror surface. In practice, it is usually difficult (except in special cases) to separate specular reflectance from the diffuse component of scattered light. Thus, to measure gloss unambiguously, under experimental conditions, the parameters of the adopted method must be described in detail. According to Hunter [49], the three most important parameters are:—

- ‘direction and aperture* of both incidence and view’
- ‘spectral composition of the light’
- ‘polarization of the light’

* The aperture of incidence in this context may reasonably be interpreted as the angular spread of illumination of the beam at the sample, whilst the aperture of view almost undoubtably pertains to the solid angle of detection.

4. **Glossiness.** This is the appearance of a surface resulting from its inherent gloss; the apparent glossiness, which is a transient property of a surface, will depend on the conditions of illumination and viewing and therefore can change as they vary.
5. **Lightness.** A specimen is described as having regions of lightness if some areas reflect back a larger fraction of the incident light than others. For instance, an ideal white object reflects back all the light incident on it and an ideal black object reflects back none. The lightness index is one of the three attributes (the other two being hue and saturation) which completely describe a colour [28].

Gloss itself seems to have been further classified into six types [49]. This classification has arisen from the various attempts to categorize materials in terms of their gloss and hence describe their different visual aspects. It has been found that for two materials of the same general appearance it is meaningful to determine their relative glosses, but for materials of widely differing appearance it is not, and so they cannot be graded. Indeed, as will be mentioned later, fibres and yarns which vary in colour (or, more precisely, lightness) often produce confusing relative gloss measurements. Several of the definitions of gloss types are based on measurements of the specularly and diffusely scattered light. While, for practical purposes, the term specularly reflected light has a definite meaning, it is less certain what is meant by diffusely scattered light. Therefore, as stated by Hunter, it is difficult to separate

the specular from the diffuse reflectance, and it is important to state the solid angle of detection over which these quantities are measured. Bearing this in mind, the following is a review of six gloss types mentioned in the literature:-

1. **Specular Gloss** is seen as a brightness of specularly reflected light – highlights. It is more often used to describe medium-gloss surfaces such as paints and dark, chromatic objects.

Quantitatively, its reflectance function is defined as:-

$$G_s = \frac{S}{I}, \quad (1.5)$$

where S is the specular reflection and I is the incident light.

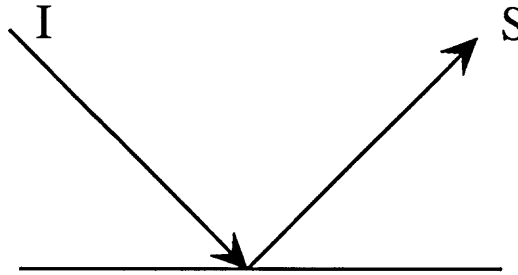


Figure 1.6: Specular gloss

2. **Sheen** manifests itself as shininess at grazing angles (high angles of incidence with respect to the surface normal) on otherwise mat surfaces. This effect occurs commonly for low-gloss surfaces such as papers and paints. Sheen has a reflectance function defined similarly to that of specular gloss:-

$$G_{sh} = \frac{Sh}{I}, \quad (1.6)$$

where Sh is the reflection at grazing angles and I is the incident light, and may be thought of as a special case of specular gloss.



Figure 1.7: Sheen

3. **Contrast Gloss** may be evaluated by making a contrast between the areas which are specularly reflecting and those which are not; textiles and mat and light-coloured surfaces are all examples of low-gloss surfaces best described using this definition. Its reflectance function was originally defined as:-

$$G_c = \frac{S}{D}, \quad (1.7)$$

where S is the specular reflection and D is the diffuse reflection. D is usually measured by convention at the normal to the surface as indicated in figure 1.8. This definition of G_c would mean that G_c tends to infinity as D tends to zero,

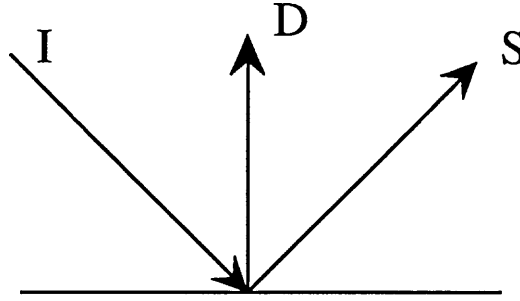


Figure 1.8: Contrast gloss

therefore Nickerson [50] suggested that an alternative form should be used for contrast gloss measurements:-

$$G_c = \frac{(S - D)}{S} \quad (1.8)$$

or

$$G_c = 1 - \frac{D}{S}, \quad (1.9)$$

where D and S have the same definitions as before. Thus when $D = 0$, $G_c = 1$ and when $D = S$, $G_c = 0$. For the types of surfaces that this gloss measurement is suitable for (surfaces that produce a specular reflection) the case of $D > S$ is not considered likely to occur in practical terms.

4. **Absence-of-bloom Gloss** is a 'milky' appearance surrounding reflected highlights and images. It is also sometimes called an absence of haze or excess of semi-specular reflection. It applies to surfaces with high- or semi-gloss in which highlights may be viewed. Its reflectance function is defined as:-

$$G_h = \frac{(B - D)}{I}, \quad (1.10)$$

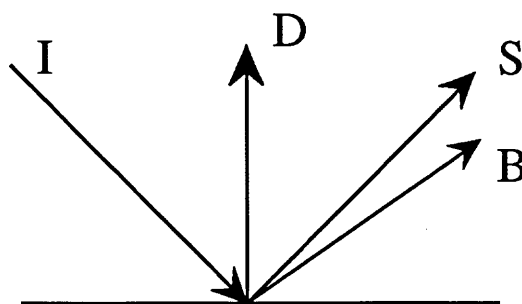


Figure 1.9: Absence-of-bloom gloss

where I is the incident light, D is the diffuse reflection, and B is the semi-specular reflection adjacent to specular light.

5. **Distinctness-of-image Gloss** occurs in high-gloss, smooth, mirror-like surfaces such as enamels and lacquers. It is an indication of the sharpness of mirror images in a surface. A statistical analysis, applicable to reflection from these types of surfaces, has been developed and used by Nimeroff [51] and is discussed in greater detail in chapter five, section 5.3.1.
6. **Surface Uniformity Gloss** appears in surfaces which exhibit an evenness or a lack of texture. Usually arises in medium- to high-gloss surfaces of many varieties and is independent of the reflectance.

In the literature surveyed, this type of gloss does not seem to have been as thoroughly studied as the first five. Of course, there are still other surfaces whose classification is not covered in the aforementioned categories and so this is by no means a definitive list of gloss types.

The definition of lustre has been given by many researchers. R. S. Hunter [49], regarded as somewhat of an historical expert on gloss, considered the terms gloss, lustre and shininess to be synonymous. Indeed, D. Nickerson states in her paper [50], on measuring the lustre of textile yarns, that lustre is merely the textile trade's name for gloss. In a paper by J. S. Christie [52], there is an appendix summarizing accepted definitions of terms related to the geometric attributes of reflectance. Here he distinguishes between specular gloss (shininess) and lustre, defining lustre as 'the appearance characteristic of a specimen associated with a change in intensity of reflected light when the viewing angle is changed'. On consideration of this information it appears that lustre is equivalent to the type of gloss usually referred to as 'contrast gloss'.

As hairs are similar to textile fibres, contrast gloss measurements have been applied to them. However, hair fibres tend to produce a much more restricted range of contrast gloss values than textile yarns. This is because the diffuse measurement is very small, or below the range of response of the equipment.

It was also noticed by D. Nickerson [50], whilst making goniophotometric measurements on yarns of differing colours, that the colours of the yarns alter the apparent gloss. A dark-coloured, low-grade (low reflectance) sample was computed to have a higher gloss than a light-coloured, high-grade (high reflectance) sample. She concluded that the level of reflectance of a sample is associated with its colour and that this must be considered when comparing relative lustres.

History and Development of Glossmeters

Although, as already mentioned, it would require a perfect mirror surface for specular reflection only to occur, and for all other surfaces the specular and diffuse components of reflection are virtually inseparable, it is often still useful to obtain a measure of the light reflected within a certain solid angle which includes the direction of direct specular reflection [53]. A glossmeter is an instrument designed to measure the scattered light detected over a certain specified solid angle at one or two fixed angular positions. As long as the same instrument is used, although the values obtained are arbitrary they are comparable with one another. A goniophotometer is an apparatus capable of illuminating a surface over a range of angles and collecting scattered light over a range of angles. Thus, a goniophotometer can provide more information about the light-scattering properties of the surface than a glossmeter. Despite this, most instruments used to determine the gloss of a range of specimens have often been designed empirically, because the experimenter has not been able to study goniophotometric data pertinent to the materials. Hunter recommended that the best approach for determining the gloss of a new range of samples was to build a goniophotometer and characterize the range of responses that the objects produced. From such data the most appropriate type of gloss measurement could be chosen and hence the most effective glossmeter could be built.

In 1945, Harrison [54] published a book entitled 'Definition and Measurement of Gloss' in which he reviewed the field up to that time; he then went on to carry out further extensive work himself on the measurement of gloss. This resulted in the development of the Harrison method of gloss assessment by means of the calcu-

lation of a gloss number G . He used a goniophotometer to take three photometric measurements per sample — one at the angle of specular reflection, one 5° nearer the normal, and one at the normal to the surface — and these were combined to produce the gloss number. His results yielded good agreement with visual assessments of grades of glossy paper, but did not work for all viewing conditions and all observers [55].

Many types of glossmeter have been developed to measure the different types of gloss; a short list of examples follows:—

1. Polarization Glossmeters. Their principle of operation relies on the fact that specularly reflected light from a flat dielectric sample is partly polarized. At one angle of incidence (the Brewster angle) almost all the light that is scattered into the plane of incidence is polarized, but the light diffusely scattered out of this plane is unpolarized. Since unpolarized light reflected from metal surfaces is not usually polarized, these glossmeters are mainly used for classifying paper and ceramics. Examples of polarization glossmeters are:—
 - Ingersoll Glarimeter. Surface is viewed along the direction of incidence.
 - Jones Glossmeter. Same principle of operation as the Ingersoll Glarimeter except that the surface is viewed normally instead of along the direction of incidence.
2. Contrast Glossmeters. The sample is illuminated at a fixed angle to the normal, and light intensity is measured in the specular direction and in the direction of the normal to the surface (diffuse component). A comparison is made to determine the gloss. Examples of these types of meter are:—
 - Ostwald Klughart Meter. Fixed angle chosen was 45° to the normal.
 - Trotter Gloss Tester. The direction chosen for measuring the diffuse component was not always normal to the surface.
 - Cotton Lustermeter. Specially designed by Hunterlabs and used by Nickerson [50] to measure low values of contrast gloss of textile fibres and yarns.
3. Objective Glossmeters. These compare specularly reflected light from a test sample with that from a standard surface usually made of highly polished,

plane, black glass. Often used to measure gloss of paints and enamels. Examples of these types of meter are:-

- Pfund Glossimeter. An early, adjustable, visual, specular glossmeter, also capable of measuring sheen.
 - Schreckengust and Gowing direct-reading glossmeter. Built to satisfy the American Society for Testing and Materials standard D523-62T.
4. Distinctness-of-Image Glossmeter. This type of glossmeter can be used to evaluate the appearance of metallic surfaces.
- Hunter gloss comparator. Early meter which compared the distinctness of the image formed by a standard reflector with that produced by a sample surface.
 - Hunterlab D47 Dori-Gon Glossmeter (developed by Christie). This later model was made with high precision to measure the effective gloss of extremely shiny surfaces. It was reported that it gave excellent agreement with visual assessments [56].

Of course, there is little practical point in measuring changes in gloss which are undetectable to the human eye. Estimates of visual sensitivity to changes in gloss also vary slightly from one researcher's paper to that of another, but the general consensus of opinion seems to be that a trained eye can detect changes of as little as 2% of the full scale range (for specular, sheen, contrast, and absence-of-bloom glosses the physically sensible range of values is from zero to one).

Goniophotometric Measurements on Hair

In 1968, during an investigation into the classification of natural hair colour [26], it was noticed that the light scattered from a parallel array of fibres into the region surrounding the specular direction was formed into two peaks, neither of which occurred at the 'ideal' or 'mirror' angle of reflection. In 1976, researchers at Clairol [57] continued the work using arrays of hairs and a white light source. They proposed that the larger, sharper peak was due to the light specularly reflected at the near side air/cuticle interface (front-face), and the second, more-diffuse peak was attributed to internal reflection at the cuticle/air interface at the far side of the fibre (rear-face). As confirmation of this interpretation of the results, a black hair (highly pigmented

and thus heavily absorbing of light) was examined; it was found that for such a dark hair the diffuse peak was not present. They also suggested that the displacement of the front-face peak was due to the angle of inclination of the cuticle cells to the cortex of the hair (scattering measurements on hairs have predicted an average angle of inclination of approximately 3°). When the detector was replaced by the human eye it was found that the front-face peak appeared to consist of 'white light' and the rear-face peak appeared to be the colour of the hair itself.

Some workers claim that in their experiments they have found the presence of an 'equal-angle peak' at the 'ideal' or 'mirror' angle of reflection (measured with respect to the fibre axis); this peak, only detectable at high angles of incidence (50° or greater) or with crossed polarizers, was thought to have been previously masked by the other, stronger peaks. They also made several attempts, with varying success, to encapsulate the hairs in a resin to negate the effects of the scales (cuticle cells).

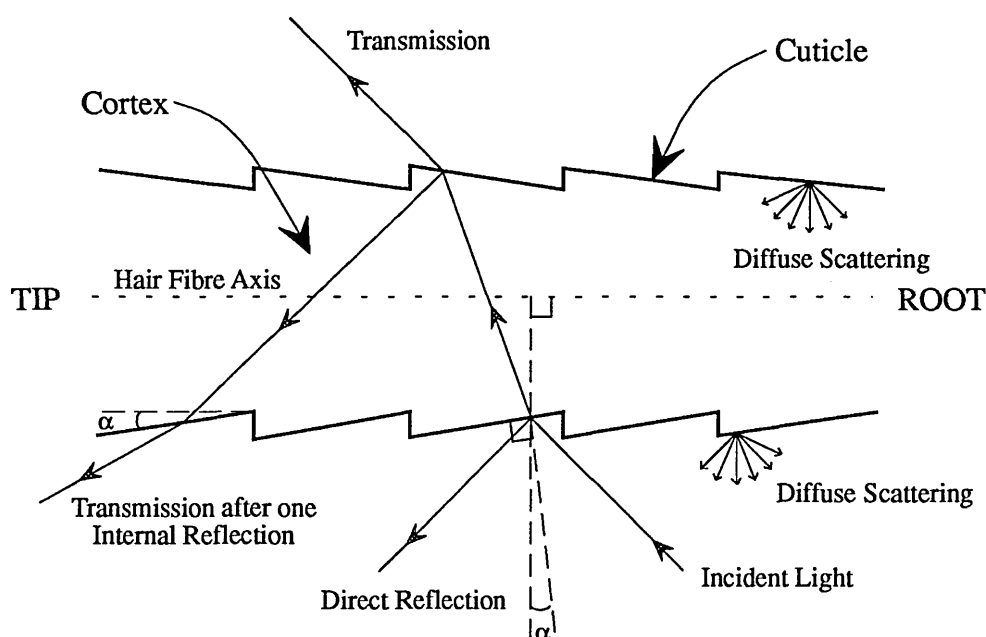


Figure 1.10: Simple optical model of a hair, light incident from the right with the fibre orientated with its root end to the right.

On the theoretical side, two optical models of hair were postulated to try to explain the angular position of the peaks observed experimentally; this required a knowledge of the refractive index of the hair. By employing the Becke line method (see chapter four, section 4.2.1) it was determined that the refractive index of a whole hair fibre was $1.548 (\pm 0.001)$ at a wavelength of 589.3nm . The first optical model consisted of a plane section through a solid fibre of one refractive index, as

shown in figure 1.10. By applying Snell's law the path of a single ray incident at angle θ (chosen to equal the angle of incidence of the beam during experimentation) was traced through this planar section of a hair. This model was found to predict two peaks, not three. The angular position of the front-face peak was in agreement with experimental results, but a similar comparison for the angular position of the diffuse peak revealed that it was in error by 15%. The second model introduced a thin wedge of air or low-refractive-index material between the cuticle and cortex in model 1. Tracing a ray through this model produced the 'equal-angle peak' but still did not correctly predict the angular position of the rear-face peak. Neither model was able to account for the broad widths of the peaks or the relative heights of the front and rear peaks.

A second paper by the same authors [58] attempted to evaluate the lustre (contrast gloss) of human hair fibres. After a short review of the types and definitions of gloss, they adopted Nickerson's contrast gloss (or lustre) measurement as a method of assessing the gloss of hair. Spot values of the contrast gloss were calculated as follows:-

$$g_c = \frac{(s - d)}{s}, \quad (1.11)$$

where lower-case s and d were used to represent spot-value measurements of the specular and diffuse scattering. Note: it was stated that the detector was usually operated with a 1° slit in front of its aperture, and the angular resolution was reported as being 'adequate'. Integrated contrast gloss values were calculated similarly:-

$$G_c = \frac{(S - D)}{S}, \quad (1.12)$$

where upper-case S and D were reserved for representing the integrated values of specular and diffuse scattering. In this case, they took $S + D$ to be the total area under the goniophotometric curve, and found D by 'drawing' an imaginary line between the ordinate values at 0° and 75° and then calculating the area beneath this line. Hence, S and $S - D$ were calculated by subtraction. The contrast gloss values g_c determined from spot measurements were found to have high precision but a low sensitivity to changes. In comparison the integrated contrast gloss values G_c , which used all data points, exhibited a wide range of values with a precision that was high enough for the method to be valuable in making assessments of contrast gloss of hair by an objective instrumental method. The objective gloss results on hair samples were compared with subjective judgments made under carefully controlled conditions

by a random selection of untrained people. It was found in their experience that an untrained human eye could easily detect changes of 0.2 in value of contrast gloss of hair (full possible range extends from zero to unity) but had difficulty with changes in contrast gloss values of 0.05 or less.

In conclusion, Stamm et al. stated that the factors that influence the contrast gloss of hair are, in order of decreasing importance, high specular reflectivity, straightness, low diffuse scattering, alignment, and colour.

The most recent paper produced on this subject was published in 1987. Again the method of investigation took the form of goniophotometric experiments [59] on arrays of parallel hair fibres enclosed in a chamber where the climatic conditions (temperature, relative humidity, etc.) were controlled. Optical fibres were used to connect two telescopes to the illuminating and detecting systems. In this paper Guiolet et al. adopted the first optical model of a hair proposed by Stamm et al. [57]. Each set of experimental goniophotometric curves was then decomposed into 3 components: specular reflection (s), internal reflection (ir), and diffusion (d). A new optical parameter in relation to the hair was defined as the transparency of a hair:-

$$T = 10 \times \frac{ir}{s}, \quad (1.13)$$

i.e. the ratio between the maximum intensity of the internal reflection peak (ir) and the maximum intensity of the specular reflection (s), all multiplied by a factor of 10 to prevent excessively low values in dark hair. The gloss values of the hair samples were calculated using Hunter's unmodified version of the reflectance function for contrast gloss:-

$$G = \frac{s}{d}. \quad (1.14)$$

The average cuticle scale angle was determined from the graphical data and was used, together with the gloss measurements, to monitor the effects of bleaching, dyeing, and stretching on the hair fibres. The authors reported that both gloss and scale angle decreased with increasing strain, and bleaching was found to flatten the scales against the cortex; this was suggested to be due to the extraction of intercellular cement from the cuticle. The average scale angle was not affected by dyeing treatments. It was concluded that, although measuring these parameters was useful for monitoring the condition of hair, goniophotometry alone could not be used to assess the lustre value of a head of hair as it cannot take into account 'the

collective dimension of the hair style’.

1.4 Thesis Synopsis

The following chapters contain the experimental and theoretical investigations which have been undertaken to increase the current level of understanding of the optical properties of human hair.

Chapter two is devoted to a description of the experimental equipment built for examining the intensity distribution of light scattered by human hair, and it also includes details of sample preparation and mounting, and a consideration of the radiometry of the goniophotometer. Established in the chapter are definitions and terms of reference with regard to polarization notation and orientation of an individual hair with respect to the planes of incidence and detection.

Chapter three contains a summary of the optical experiments on individual hairs and is subdivided according to the illuminating source and the orientation of the hair fibre. The results are analysed with a view to explaining the major features in terms of the biological structure of hair. This chapter also deals with any variations in diameter along extended lengths of single hairs, measured via the formation of far-field diffraction patterns.

The theoretical aspects of the investigation are dealt with in chapter four. In the first section, several methods of measuring the refractive index of hair (whole and part) are described, together with a consideration of the absorbing effects of melanin pigment granules included in the hair’s keratin matrix. The results of this first section are then used in the following two sections, where raytracing techniques are applied to develop an optical model of human hair. The two orientations of hair considered experimentally in chapter three are modelled: for hairs orientated vertically, a range of incident angles and variations in hair cross-section (circular and elliptical) are investigated; and for hairs orientated horizontally, the effects of absorption and the possibility of a range of scale angles present along the hair are included. In both cases comparisons are drawn with experimental results.

Chapter five contains the second set of experimental results, which summarizes the goniophotometric results from arrays of hairs strung parallel. It includes investigations into the effects on the light-scattering distribution produced by hair of varying the incident wavelength of the illumination source (laser) and a calculation, from goniophotometric data, of the tri-stimulus chromaticity co-ordinates of four

hair samples via two different analytical methods. As with chapter three, the results are subdivided according to orientation of the hairs and type of illumination. Single- and double-layer arrays of hair orientated vertically were found to exhibit enhancement of intensity in the direction of backscatter. Simple explanations are proposed to indicate the mechanism which may account for the presence of this enhancement in some cases and for its absence in others. Also in this chapter, the various methods of objectively evaluating the appearance of hair are assessed and applied to sets of data collected from hair arrays orientated horizontally to the plane of incidence and illuminated with a quartz halogen lamp. Assessments are made on samples of virgin hair as well as those exposed to ultraviolet irradiation and a selection of chemical (cosmetic) treatments.

The last chapter closes the thesis with a review and summary of the main results and conclusions derived from this body of work. In particular, it highlights the precautions that need to be taken when experimenting with human hair, and stresses the essential requirement of repetition for gaining meaningful results.

Chapter 2

The Goniophotometer

2.1 General Introduction

Before an investigation into the scattering of light by human hair could be undertaken it was necessary to assemble a suitable scattering-rig. This chapter contains a description of the design, construction, and testing of an automated goniophotometer dedicated to this purpose. The permanent set-up consisted of a sample stage, detection system, and control equipment; interchangeable light sources, illumination optics, and sample mounts were substituted as required. To a certain extent a restricted budget and the availability of hardware already present in the laboratory influenced the final construction of the rig. A schematic overhead view of the goniophotometer is presented in figure 2.1; in this diagram the scattering-rig is set up with a quartz halogen lamp. The goniophotometer was situated on a holography table, and this, in terms of vibrational isolation, was more than adequate.

In an investigation into the scattering of light by human hairs, many possibilities exist for the orientation of the hairs with respect to the incident beam. Two orthogonal orientations were chosen and they are illustrated in figure 2.2 for an individual hair fibre but also apply to an array of parallel hairs. To accommodate mounting the hairs in such orientations three different sample-holders were designed.

Also described in this chapter are the nomenclature and conventions adopted for various light-scattering quantities. The response of the goniophotometer has been characterized using a white reflectance standard whose light-scattering properties closely approximate a Lambertian diffuser.

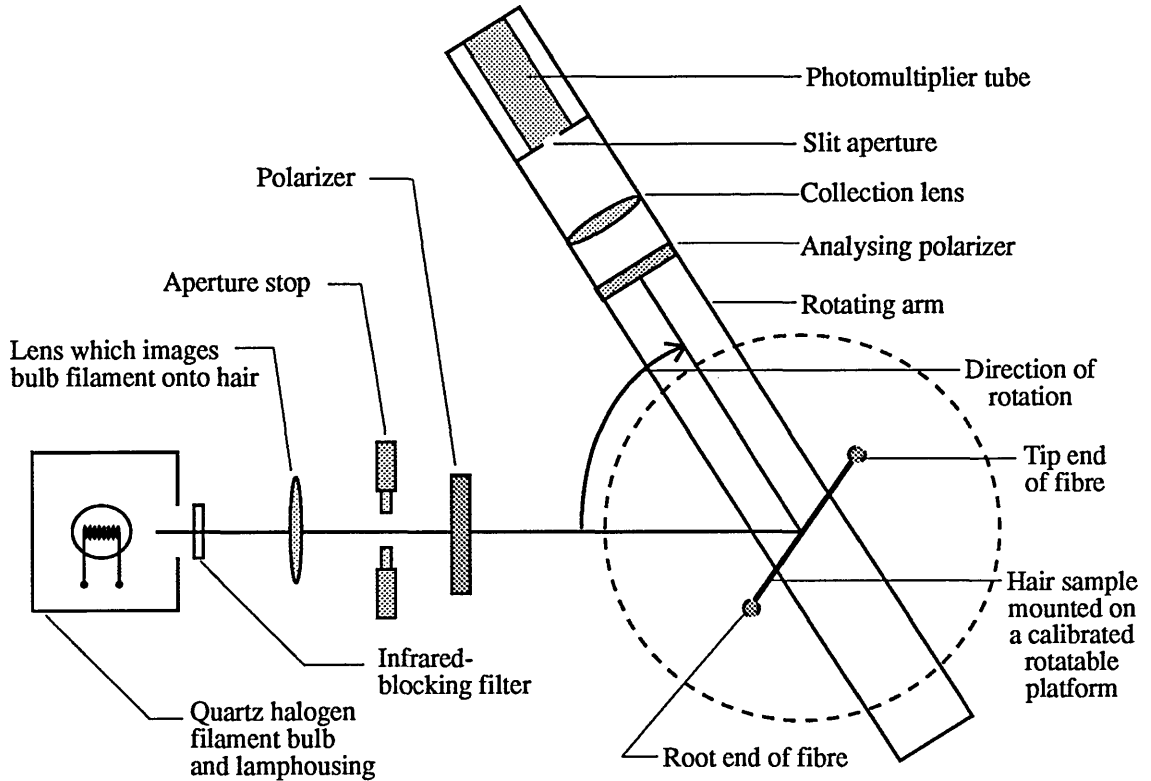


Figure 2.1: Experimental arrangement of goniophotometer shown in two dimensions.

2.2 Illumination Optics

2.2.1 Introduction

Three light sources were available to this project: a helium-neon laser (10mW), an argon-ion laser (4W), and a quartz halogen filament lamp (6V, 18W). As this work was motivated by the desire to gain a better understanding of the *appearance* of hair, the investigation was restricted to the visible region of the electromagnetic spectrum.

2.2.2 Laser Illumination

Three wavelengths were chosen in the visible spectrum for experimentation: two from an argon-ion laser at 457.9nm and 514.5nm, and one from a helium-neon laser at 632.8nm. The intensity of light was controlled using fixed-value neutral density filters. Both of the lasers are C.W. (continuous working) and produce linearly polarized radiation. For the argon-ion laser, the plane of polarization was set at 45° using a periscope mirror and then a dichroic sheet polarizer was rotated to select the

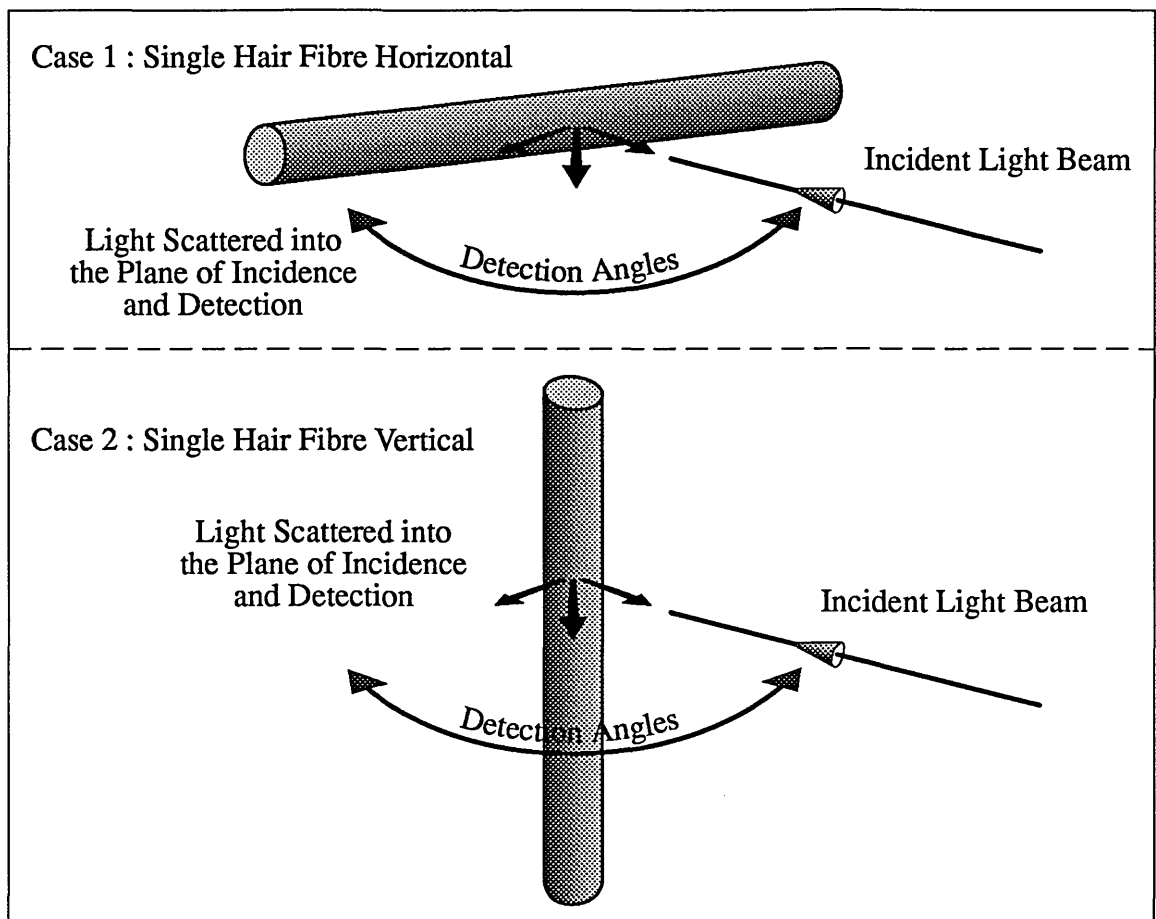


Figure 2.2: Orthogonal arrangements of a hair fibre: Case 1. Hair orientated horizontally to lie in the plane of incidence and detection. Case 2. Hair orientated vertically perpendicular to the plane of incidence and detection. [Note: this plane is defined uniquely in section 2.7]

required polarization; the smaller, cylindrical helium-neon laser was itself rotated to align the polarization state of the light.

Before continuing further with a discussion on the illumination arrangements, it may be useful to consider the consequences of using laser illumination to investigate the light-scattering properties of hair. A laser is an almost ideal source of coherent monochromatic radiation, and a hair has an outer laminar structure of irregularly shaped cells (as mentioned in section 1.2.5) which may be considered at visible wavelengths to constitute a 'rough' surface.

When coherent monochromatic radiation impinges on a rough surface it is scattered, and as a result the surrounding region is filled with a stationary interference pattern, called a speckle pattern. If this speckle pattern is observed on a screen, it appears to consist of randomly arranged small regions of high intensity set against a dark background; the speckle pattern overlies the average intensity distribution of

the scattered light. The ‘size’ (statistical average of the distance between adjacent regions of maximum and minimum brightness) of the individual speckles will depend on the area of the object illuminated, the illuminating wavelength (λ), and the distance from the object to the plane of detection (d). Assuming that the incident beam has a Gaussian profile, then the correlation length (s) of a speckle (which can be used as a measure of its size) may be calculated as:-

$$s = \frac{\lambda d}{r\pi\sqrt{2}} \quad (2.1)$$

where r is the $1/e$ radius of the intensity profile of the beam at the sample [60]. If the size of the speckles formed in the detection plane is large compared to the aperture of the detector, then, at each position during a scan, the detector will average over only a few speckles and the resulting signal will appear spiky and be difficult to interpret. From equation 2.1 it can be deduced that, at a fixed wavelength, to reduce the speckle size and thus increase the number of speckles that the detector averages over, either the distance from the detector to the sample must be decreased (d) or the size of the illumination area (r) increased.

When a laser beam is shone on an individual hair, the area of illumination in one dimension is generally determined by the diameter of the hair rather than the beam size (as the diameter of a hair is usually less than that of the incident beam); therefore, the speckle pattern formed consists of speckles elongated in a direction perpendicular to the orientation of the length of hair. In general, the speckle pattern has been observed to be confined to a broad band surrounding the diffraction pattern of the hair.

Increasing the diameter of the incident beam was considered as one means of reducing the speckle problem, but this is accompanied by a corresponding reduction in radiant intensity. For experiments on individual hairs, where only a small proportion of the illuminating beam impinges on the hair, any significant reduction in signal level would involve the use of a high-gain amplifier. Very high-gain amplifiers are often unstable (d.c. drift problems) and subject to electronic noise (low signal-to-noise ratios). A solution to this problem was found by arranging for the distance (d) from the hair to the detector to be short (0.08m). Normally, this would also reduce the angular resolution of the detector, but this was avoided by placing a simple optical system in front of the detector: details are given in section 2.3.2. In the experiments using lasers, the light was first spatially filtered and collimated, then expanded using a diverging lens and recollimated with a converging lens, as

shown in figure 2.3. For planar arrays of hairs, where low signals were not a problem as a greater percentage of the incident beam actually impinged on hairs, a beam size of 1cm diameter was used.

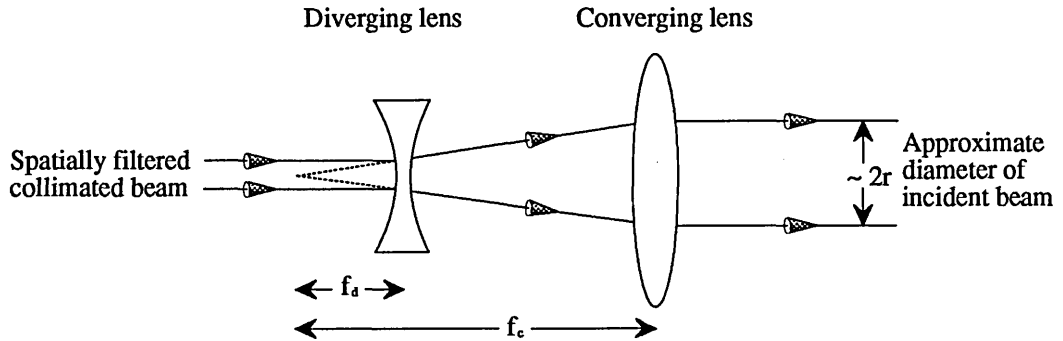


Figure 2.3: Optical arrangement used for illuminating single hair fibres with a laser source. For the illumination of single hairs $f_c = 0.25\text{m}$, $f_d = -0.083\text{m}$ and $r \approx 0.0025\text{m}$

Another scattering-rig [61, 62] was used for some of the measurements on hairs arranged vertically, particularly where the light scattered back in the direction of the incident beam was of interest. Normally, the detector itself would block the incident beam as it scanned through the backward scatter direction, but this ‘scatterometer’ was built to investigate the phenomena of enhanced backscatter and as such was specifically designed to collect data very close to the backscatter direction. In this rig the light was directed towards the sample via a periscope arrangement of mirrors. During a scan the detector would pass behind the last mirror, which was sliver-shaped, forming a narrow point in the detector plane to minimize its obstruction of the detector. This arrangement minimized the loss of data in the backscatter direction to approximately 1.5° degrees compared to 18° degrees on the goniophotometer (partially a consequence of a short detector-sample distance (d)). The scatterometer was also designed to have a large distance between the sample and the detector — approximately 0.65m — again minimizing angular obstruction of the detector at the backward scatter direction; however, to compensate for this in terms of speckle noise a large illuminating spot size of between $10 - 15\text{mm}$ was used. The typical number of speckles averaged over was 10^5 . Problems of low signal levels were avoided by chopping the laser beam at a reference frequency of 83Hz (and for very weak signals at 830Hz), the signal being retrieved using a phase-lock-in amplifier. The hairs were illuminated using a helium-neon laser at wavelength 633nm with a slightly diverging beam geometry ($\approx 1^\circ$ divergence at the sample), and the

angular resolution of detection was 0.5° ; therefore typical data collection intervals were 0.5° and, for courser scans, 1° . Further details of this equipment may be found in papers by O'Donnell et al. and Kim et al. [61, 62].

One modification essential when working with objects smaller than the cross-sectional area of an incident beam is the use of a 'beam dump' to avoid the detector seeing the undeviated beam reflecting off a surface further downstream. The beam dump used consisted of a high-value (4.0) neutral density filter placed at a 45° angle so that any light reflected from its surface fell onto a black card and could not be seen by the detector. This was checked by performing a detection scan without the hair sample in place.

2.2.3 Quartz Halogen Lamp Illumination

To approximate a 'white' light source, a quartz halogen filament bulb was mounted in a lamphousing with an infrared-blocking filter to prevent overheating of the sample. A stable level of light flux was maintained during measurements by using a d.c. regulated power supply (Oriel model 68735). This extended thermal source can be considered to consist of many non-monochromatic point sources. Each of these point sources will produce a different speckle pattern at each wavelength it contains; superposition of this large number of patterns smears out the speckle effect. Thus for this source there was no speckle problem.

For single-fibre illumination the lamp filament was imaged onto the hair fibre with an angular spread of illumination of approximately $\pm 0.3^\circ$, using a spherical lens and aperture stop as shown in figure 2.4. This arrangement was modified for a planar array of hairs by the introduction of a cylindrical lens to produce a 3mm wide strip of light across all the hairs. As in both cases this source produced unpolarized light, for polarization measurements a dichroic sheet linear polarizer was included in the set-up, positioned after the final lens.

2.3 Detection System

2.3.1 Introduction

The detection system consisted of a lens, analyser, slit, and photomultiplier tube. All the elements were suspended rigidly beneath a lightweight arm which was sup-

detector arm as it is ideally suited to applications that involve short, rapid moves in point-to-point positioning applications. In terms of cost it was also very economic, as no additional feedback components were required. After each step the stepper motor was designed to have a holding torque even when the permanent magnet rotors were not energized, thus this residual torque gave positional integrity. An R.S. stepper motor size 1 (RS332-947) was selected as having sufficient torque to move the arm and rotate it with a non-cumulative tolerance of 5 – 10% of the step, regardless of the number of steps advanced in the same direction. Unfortunately, the angular step size of the motor was 7.5° , which was too large an interval between data acquisitions, so, to achieve a smaller angular step size, a synchronous gearbox (RS336-416) was attached to the spindle of the stepper motor. A gear ratio of 250 : 1 reduced the angular size of step to 0.03° and the addition of a gearbox also had the effect of increasing torque and reducing the speed of movement but introduced the further problem of slack in the mesh of the gears. This resulted in a certain amount of play in the detector arm. To maintain positional integrity and reduce the amount of overshoot at each step, a weak coiled spring was used as a friction damping device, bringing the arm to rest in a shorter settling time. The spring was wound clockwise about the gearbox spindle and attached to the support arm. Data were then collected during clockwise scans so that the spring always opposed the forward motion and held the arm at one end of its free play.

2.3.2 Detection Optics

Originally a silicon photodiode was chosen as the detector, but problems involving low signal levels, with consequent high unstable amplification factors, prompted the change to a Hamamatsu photomultiplier tube (R647-01). A miniature photomultiplier tube was chosen as it is lighter and more compact for mounting below the arm. This particular photomultiplier tube has a significant signal response over the wavelength range 300nm to 650nm peaking at 420nm, and adequately covers the visible spectrum.

If the photomultiplier tube alone was mounted on the arm then the angular resolution of detection would be approximately equal to the size of the active area of the detector (a) divided by the distance from the sample to the detector (d). To produce a reasonable angular resolution it would require a large value for d or a small value for a , but, as mentioned in section 2.2.2, increasing d also increases the

speckle noise; decreasing the active area (a) of the detector would correspondingly reduce the signal level. To overcome this problem a collection lens was positioned at its focal length ($f = 22\text{mm}$) in front of the detector window to which a $150\mu\text{m}$ vertical slit had been fixed. This arrangement allowed only collimated light to be focused on the detector window, giving the system an angular resolution of 0.4° in the horizontal plane independent of d . By focusing all the collimated light incident on the lens aperture through the slit, an adequate signal level was detected. The arrangement of the collection optics is shown schematically in figure 2.6. It was possible to use a vertical slit rather than a pinhole as this would only have changed the resolution in the plane perpendicular to that occupied by the detector as it scans. A $150\mu\text{m}$ pinhole was tested in place of a vertical slit but the resulting trace differed only in the total amount of light detected. A narrower slit would have increased the angular resolution of the equipment but it would have been at the expense of signal level, which for some experiments may have caused problems. Although other slit widths were tested, a width of $150\mu\text{m}$ was found to be the best compromise; it is also equivalent to the angular resolution of the human eye one metre from an object, given a pupil diameter of 7mm (i.e. 0.4°), which might be considered to be a typical viewing distance from a head of hair during subjective salon evaluations of the appearance of hair.

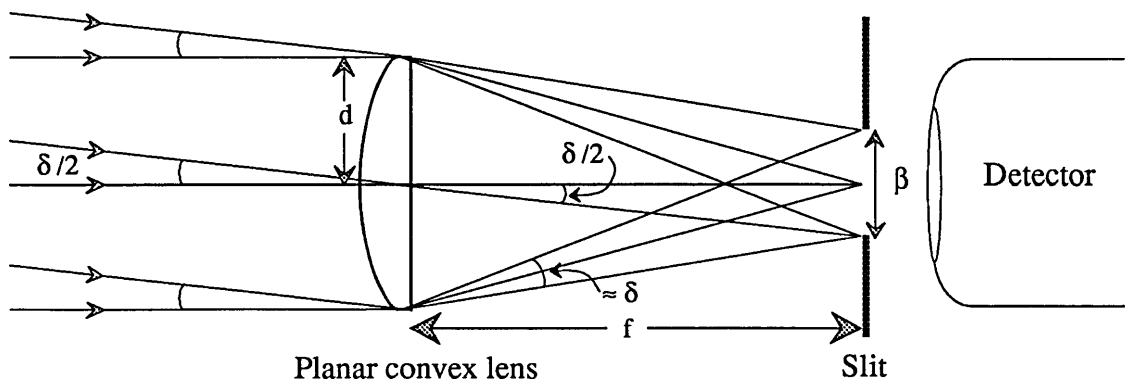


Figure 2.6: This arrangement of lens and slit, as viewed looking onto the plane of detection, produced an angular resolution of the detection system δ equal to the slit width β divided by the focal length f of the lens. $\delta = \beta/f \approx 0.4^\circ$

2.3.3 Data Acquisition

Once the illumination optics were set up, the detector was aligned with respect to the undeviated beam. Fixed neutral density filters were used to attenuate the beam

intensity sufficiently for the photomultiplier tube to scan the beam profile without overloading. The centre of the symmetrical beam profile was determined and its angular position in turn was used to ascertain the angular position of the detector arm. By entering this position into the software program, the computer was able to track the detector for the duration of the subsequent experiments. When the alignment procedure was periodically repeated to check that steps had not been lost, it was confirmed that the stepper motor was very reliable, any positional errors that occurred during data acquisition being below the resolution of the step size.

At each sampling position the detector was brought to rest and 500 readings were taken by the computer. The average of these readings was then calculated so as to produce one reading for that angular position. Although the smallest step size available to the experiment was 0.03° , this was much smaller than the angular resolution of the detection system, and it would therefore have been pointless to collect data at such small intervals; instead, typical data acquisition intervals were 0.45° and, for coarser scans, 0.9° .

As already mentioned, the positional integrity of the detector was very reliable, and the light sources, too, were quite stable after they had warmed up (for instance, the lamp power supply was regulated to within typically 0.2% over 8 hours, after a 30-minute warm-up period); it was not surprising then that, if a data set was remeasured without moving the sample between scans, the two sets of results when plotted on a screen or on paper would overlay one another, being virtually identical. Thus, no error bars are shown on the graphs of scattering data; instead, where possible, the plot symbol has been chosen such that it is always larger than the error associated with the point. Sources of random error which could affect the results may originate from the amplification and conversion stages of the signal processing between the photomultiplier tube and the computer. Errors were typically found to be less than 1% of the measured value for goniophotometric data.

2.4 Sample Preparation

Sample preparation was dependent on the source of the hairs. Ideally, the full history of the hair sample would be known, and this was possible in cases where a small number of hairs were required; for example, the single-fibre and the *untreated* fibre-array experiments. Each of these samples was cut, near the scalp, from the head of a volunteer (whose hair had not been treated, except for normal shampooing

and grooming), shampooed, dried, and stored in a sealed environment to minimize dust contamination. By wearing disposable plastic gloves contact with fingers was avoided, as this was found to affect the measurements [58].

For comparison tests into the effects of cosmetic treatments, several tresses of the same hair sample were required — these were supplied by SmithKline Beecham, who regularly bought tresses from a hair supplier (Banbury Postiche Ltd.). In their experience the hair description (virgin black, etc.) was reliable except for some of the lighter-coloured tresses which showed signs of bleaching [27]. Light-scattering experiments comparing hair samples before and after shampooing [59] have recorded increases in intensity of scattered light of up to 40% in the direction of specular reflection after cleaning. The hair samples were therefore divided into 1 gramme tresses (typically containing several hundred hairs) and washed using a mild herbal shampoo (Silvikrin Aloe Vera) in preparation for our investigations.

It was found that, in order to examine the extreme ends of single fibres, particularly at the root end where all hairs are least damaged, an extension to the fibre was required. A method of glueing nylon or cotton thread with a fast-drying contact adhesive to the ends of each hair fibre was developed. Small weights (brass nuts, each with a mass of 2.6 g) were then tied to the threads to allow the hair to be placed under a reproducible tension during measurements.

A technique of producing planar arrays of hairs was developed so that a 'surface' could be strung quickly, with the fibres at regular intervals (1mm apart) and held taut. A plastic photographic slide mount was employed as a frame, with the ends of the hairs embedded in two strips of double-sided adhesive tape and then sealed in place by a layer of single-sided tape. Ruled markings at 1mm intervals ensured the hairs were strung parallel and regularly. Double or 'thick' surfaces were also strung; they consisted of two layers of fibres arranged so that the second layer filled in the gaps created by the first.

Investigations into the tensile properties of hair have shown that dry hair may be subjected to strains of the order of 10% before their optical properties are significantly affected [63, 64, 59]. Indeed at 60% relative humidity, hair has been measured [6] to have an elastic modulus of $3.89 \times 10^5 \text{ Nm}^{-2}$ which corresponds to tensioning a $70\mu\text{m}$ diameter hair with a 75 gramme weight to achieve a strain of 5%. Thus hair must be placed under the stress of several Nm^{-2} to produce a level of strain that would influence the goniophotometric experiments. In view of these results no

attempt was made to precisely tension each hair as a surface of hairs was strung although each was secured tautly across the frame.

2.5 Sample Stage

To form an integral unit the supporting post for the detector arm and sample stage were bolted to an aluminium baseplate which was then fixed in position on the optical table by using magnetic mounts. The samples were positioned using a jack, rotation stage, translation stage, and kinematic-style mounting system, as shown in figure 2.7. This arrangement permitted each sample to be levelled, translated, and rotated, as required. The rotation stage was used to set the angle of incidence of the beam at the sample. Bolted to the translation stage was a smaller aluminium plate which formed the lower half of the kinematic-style set of interchangeable hair-holders. Each of these holders was sprayed matt black to minimize the effects of random reflections that might otherwise be detected during the experiments. Three holders were constructed: one to hold a single fibre horizontal (see figure 2.7), one to hold a single fibre vertical, and one to hold a planar array of hairs (see figures 2.8(a) and (b) respectively). Each holder was designed to comply as closely as possible with the following criteria:-

- Hair fibres should have minimum contact with the holder so that their surfaces do not become damaged or altered.
- Hair fibres must be kept under the same constant tension.
- Any section of the hair fibre may be examined, particularly the root region (at this end the effects of grooming and previous treatments on the fibre surface will be least). Hairs away from this region, even from the same head, may have developed very different surface conditions.
- Holders should be easily interchangeable with minimum realignment procedures between changes.

An inverted modified drawing compass was used as a basis for the design of the hair mount holding a single hair horizontally. The modifications included grooves for the fibre to sit in when it was strung across the holder, and a rotatable base for aligning it with respect to the incident beam. A simpler design of mount proved suitable

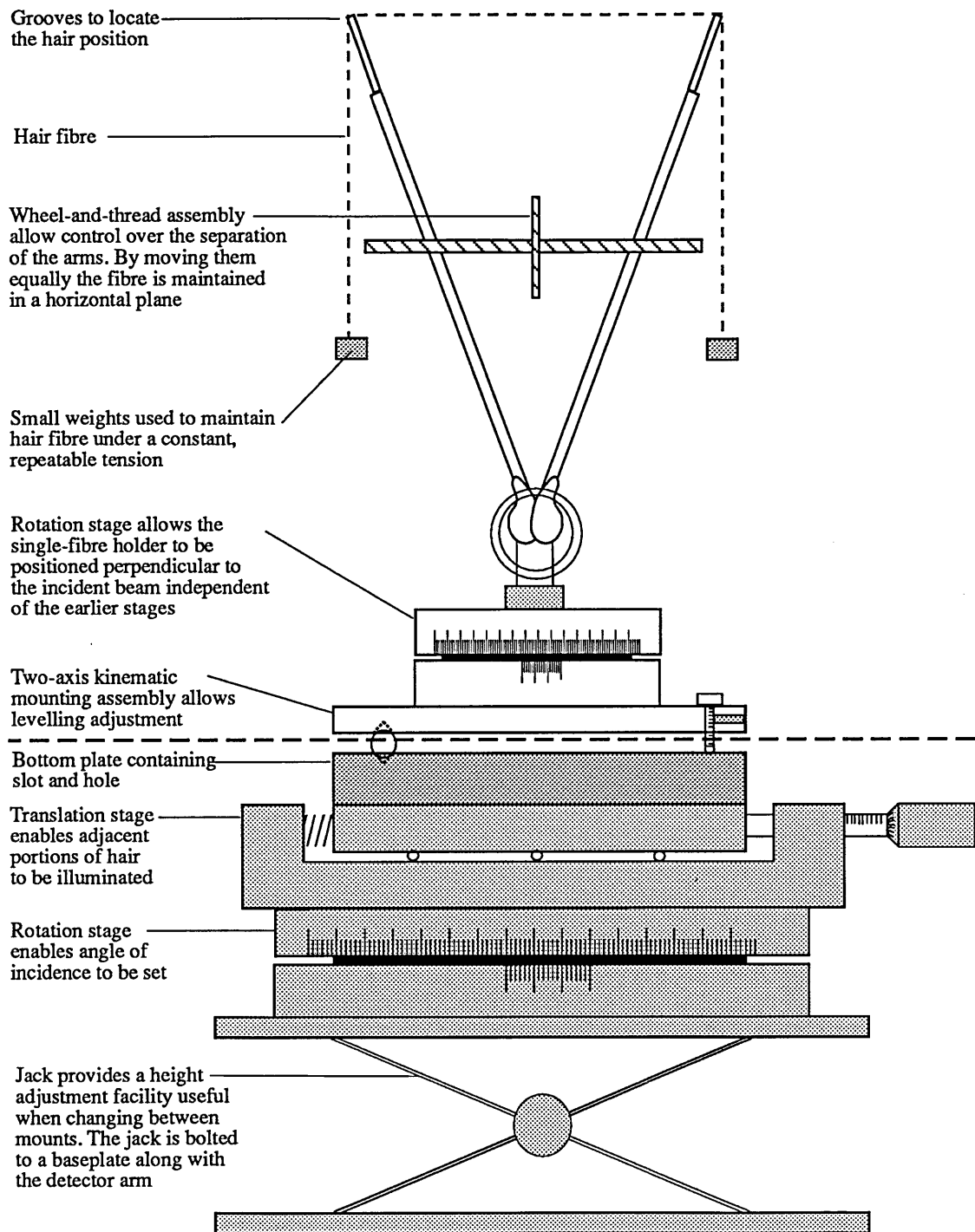


Figure 2.7: Sample stage and hair-fibre holder designed for experiments on individual hairs mounted horizontally with respect to the planes of incidence and detection. All the equipment above the dashed line is interchangeable with the other hair mounts which are shown separately in figures 2.8.

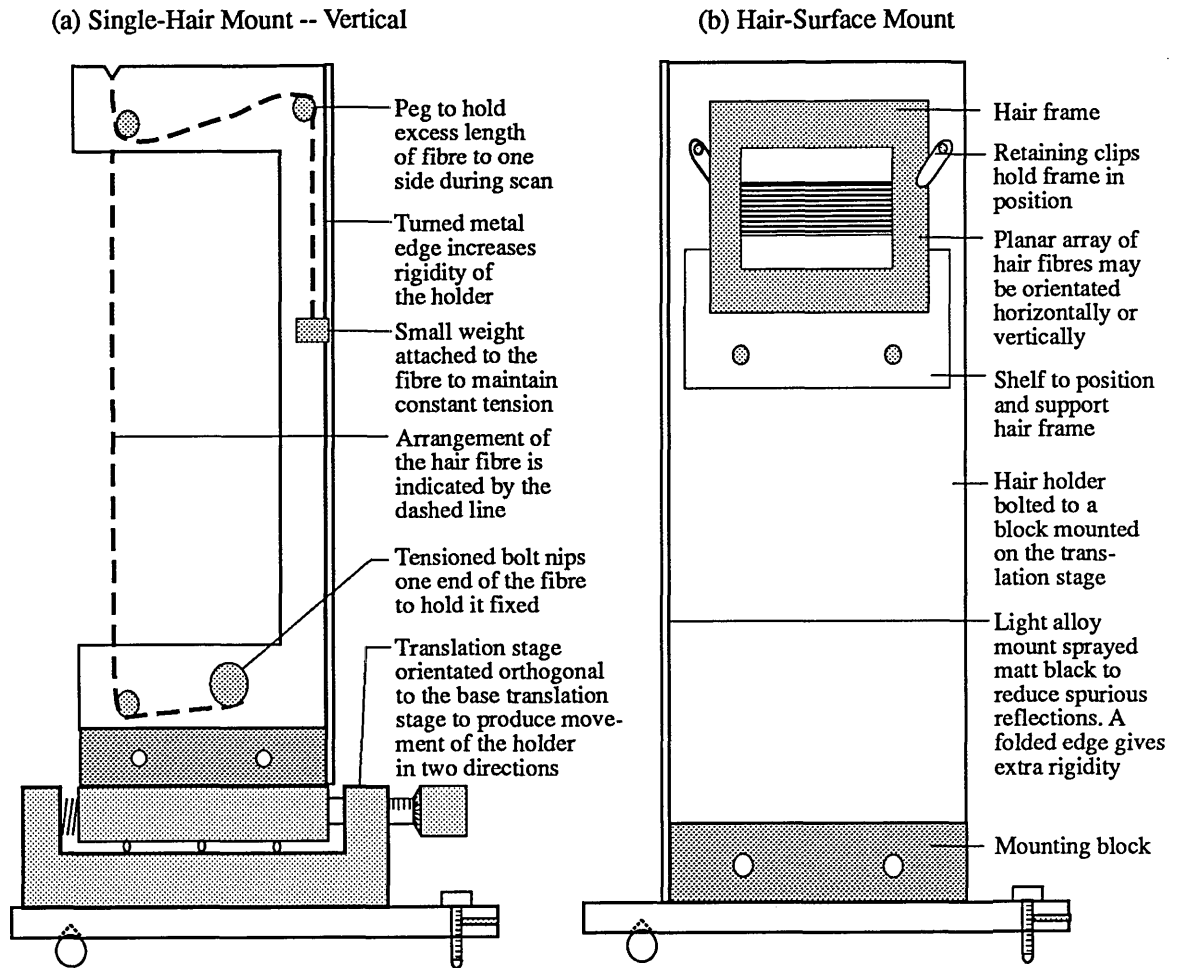


Figure 2.8: (a) Hair-fibre holder designed for experiments on individual hairs mounted vertically with respect to the plane of incidence and detection. (b) Hair-fibre holder designed for experiments on planar arrays of hair mounted either horizontally or vertically with respect to the plane of incidence and detection.

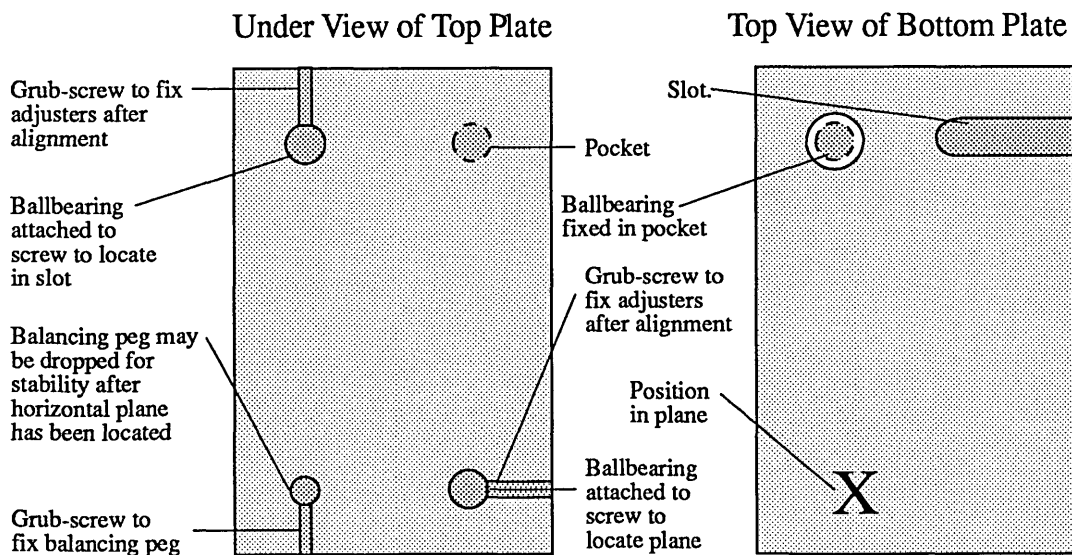


Figure 2.9: A plan view of the plates that form the kinematic mounting system.

for investigating hairs held vertically to the plane of incidence and detection: it consisted of a rigid aluminium plate with a series of clips and grooves to position the hair.

Plastic slide mounts were used as frames to hold planar arrays of hairs forming an open ‘surface’; these could then be mounted in a customized holder with the hairs aligned horizontally or vertically to the plane of incidence. The kinematic mounting assembly consisted of an interchangeable top plate and a lower plate into which a slot and hole had been machined, with a ballbearing glued into the hole. A plan view of the bottom plate and one of the top plates is shown in figure 2.9. Each hair mount was bolted to its own top plate, and the top plate had two Allen screws passing through it and, on its underside, a hole to locate the fixed ballbearing. The Allen screws had small ballbearings in their ends which located in the slot and on the plane of the bottom plate. The ballbearing-and-hole arrangement fixed the two translational degrees of freedom in the horizontal plane. By adjusting the height of the Allen screws, the mounts could be levelled to lie parallel with the plane of incidence; small grub screws enabled the Allen screws to be locked in position. Thus each top plate in turn could be fitted onto the bottom plate, levelled and locked. This guaranteed repositioning accuracy and fast changeover between sample-holders.

2.6 Radiometry

Having described the construction of the goniophotometer it is also appropriate to consider in formal terms the quantities that are measured when a detector observes the light scattered by an object. To do this it is necessary to introduce some concepts and terminology that exist in radiometry. This section is based for the most part on two papers by Nicodemus [65, 66] that provide an extensive framework of information about radiometric quantities and their definitions; the symbol used to represent a quantity will generally be the one recommended in the revised paper by Nicodemus [66]. I will begin in the same way as Nicodemus by introducing a basic quantity called *radiance*, conventionally represented by the symbol L , which is defined as ‘the radiant flux or power (P) per unit solid-angle- (Ω) -in-the-direction-of-a-ray per unit projected-area- $(A \cos \theta)$ -perpendicular-to-the-ray’,

$$L(\theta, \phi) = \frac{\partial^2 P}{\partial A \cos \theta \partial \Omega} \quad [W m^{-2} sr^{-1}]. \quad (2.2)$$

In an isotropic, lossless medium the radiance is a conserved quantity; that is, it

has the same value at all points along the ray. As the radiance, L , is a function of angular position it may be used to describe the *directional* variation in the scattering of light by a surface. In spherical co-ordinates the solid angle $d\Omega = \sin \theta d\theta d\phi$ where ϕ is the azimuth angle in the plane of dA and θ is the angle measured to the normal of the surface dA .

If one now considers what happens when light is incident on a surface, depending on the properties of the surface (e.g. its refractive index, particle size, etc.) and the illumination geometry (e.g. angle of incidence, collimation of beam), it is found that a certain proportion of the light will be scattered into the hemisphere above the surface. At this point it is noted that analogous results may be drawn for transmitted light, although this work will be confined to the reflected case only. It is possible to describe the power incident on and scattered by a surface in terms of this basic quantity, radiance. The radiant incident power, δP_{inc} , on a surface element of area δA through an incident beam which is collimated to within a solid angle $\delta\Omega_{inc}$, is then

$$\delta P_{inc} = L_{inc}(\theta_{inc}, \phi_{inc}) \delta A \cos \theta_{inc} \delta\Omega_{inc} \quad [W]. \quad (2.3)$$

Of this incident radiant power the amount scattered into an elementary solid angle $\delta\Omega_{scat}$ is

$$\delta P_{scat} = L_{scat}(\theta_{scat}, \phi_{scat}) \delta A \cos \theta_{scat} \delta\Omega_{scat} \quad [W]. \quad (2.4)$$

The reflecting properties of the elemental surface δA may be described geometrically by the bidirectional reflectance-distribution function f_r which is defined by Nicodemus as

$$f_r(\theta_{inc}, \phi_{inc}; \theta_{scat}, \phi_{scat}) \equiv \frac{L_{scat}}{\cos \theta_{inc} \delta\Omega_{inc} L_{inc}} \quad [sr^{-1}]. \quad (2.5)$$

Substituting into equation 2.5, using rearranged forms of equations 2.3 and 2.4 for the incident and scattered powers, this function may re-expressed in the following terms:-

$$f_r(\theta_{inc}, \phi_{inc}; \theta_{scat}, \phi_{scat}) = \frac{\delta P_{scat}}{\delta\Omega_{scat} \cos \theta_{scat} \delta P_{inc}} \quad [sr^{-1}]. \quad (2.6)$$

If these equations are now applied to the practical situation of a goniophotometer where near-collimated light (all surface elements of area δA are illuminated at the same angle) of power P_{inc} is incident on a surface of area A , then the physical

response of its detector subtending a solid angle $\Delta\Omega_{det}$ at the surface, working within the limits of linear response, may be written in radiometric terms as

$$R_{det} = \mathcal{C} \int_{\Delta\Omega_{det}} f'_r P_{inc} \cos \theta_{scat} \mathcal{W}(\theta_{scat}, \phi_{scat}) d\Omega_{scat} , \quad (2.7)$$

where $\mathcal{W}$ is a weight function which takes into account the vignetting of $\Delta\Omega_{det}$, for instance, $\mathcal{C}$ is a constant of proportionality which includes among other factors the conversion of the power impinging on the detector from watts into signal (measured in amps for a photomultiplier tube), and f'_r is the effective bidirectional reflectance-distribution function for the total surface area A illuminated as described above. It is given by:

$$f'_r = \frac{\delta P_{scat}}{\delta\Omega_{scat} \cos \theta_{scat} P_{inc}} \quad [sr^{-1}].$$

At this point I will introduce another useful quantity — the radiant intensity, I , which is defined as

$$I = \frac{dP}{d\Omega} \quad [Wsr^{-1}]. \quad (2.8)$$

It is now possible to re-express the detector response in terms of the radiometric intensity as

$$R_{det} = \mathcal{C} \int_{\Delta\Omega_{det}} I(\Omega_{scat}) \mathcal{W}(\Omega_{scat}) d\Omega_{scat} . \quad (2.9)$$

At this point the equation may be simplified if it is assumed that the integral of radiant intensity over the detector solid angle may be replaced by an average radiant intensity $\langle I_{scat} \rangle$ multiplied by an effective solid angle $\Delta\Omega'_{det}$, then

$$R_{det} = \mathcal{C} \langle I_{scat} \rangle \Delta\Omega'_{det} . \quad (2.10)$$

However, as the weighting function has been included in this effective solid angle it may vary with scattering angle θ_{scat} , depending on the geometry of the scattering equipment. Thus the detected signal is directly proportional to the mean radiant scattered intensity $\langle I(\Omega_{scat}) \rangle$ and so it is in terms of this quantity that the scattering of light by samples, as measured by the goniophotometer, will be described.

If the surface under investigation is a perfect conductor then the total light scattered over a hemisphere (*hemi*) above the surface could be normalized such that

$$\mathcal{C} \int_{hemi} \langle I_n \rangle d\Omega_{scat} = 1$$

where the normalized radiometric intensity

$$\langle I_n \rangle = \frac{\langle I_{scat} \rangle}{P_{inc}} \quad (2.11)$$

and

$$\int_{hemi} d\Omega_{scat} = \int_0^\pi d\phi_{scat} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin \theta_{scat} d\theta_{scat} .$$

However, problems of normalization arise for real conductors and dielectrics where the total amount of power scattered (in both reflection and transmission) does not equal the total power incident on the surface. Normalizing data from such samples requires a knowledge of the power incident on the surface. For human hair experiments the incident beam is many times greater in power than the light scattered by the samples, thus to measure it using the same detector without overloading it requires attenuation using fixed neutral density filters. The compound use of several neutral density filters often leads to errors in measurement and therefore in calculating P_{inc} , which makes any normalization procedures stemming from such a measurement unreliable. To complicate the problem further is the unavoidable fact that individual hairs are smaller in one dimension than the area of the illuminating beam. Thus, even if the power in the incident beam was measured accurately, it would not correspond to the incident power P_{inc} impinging on the hair. This would depend on the diameter of the hair, which, as shown in section 3.2.3, varies not only between hairs but also along the length of a hair, so it is only possible to determine an average diameter for the actual length of hair illuminated. However, by maintaining a fixed power in the incident beam during a set of measurements, the unnormalized light-scattering envelopes produced by each hair may be compared.

2.7 Polarization Notation

In this section I will introduce the polarization notation that will be used in the experiments detailed later. As already mentioned in section 2.2.2, it was arranged for the incident light to be linearly polarized with its electric vector either:-

- parallel to the plane of incidence, which is denoted as p-polarized (equivalent alternative notations would be T.M. (transverse magnetic), S-polarized or V-polarized),

or

- perpendicular to the plane of incidence, which is denoted as s-polarized (equivalent alternative notations would be T.E. (transverse electric), P-polarized or H-polarized).

The plane of incidence is defined as the plane which contains the incident beam and the outward normal to the surface. However, for single hair fibres which have rough, curved surfaces the definition of a unique outward normal is difficult, so, for the purpose of defining a plane of incidence the outward normal chosen is perpendicular to the fibre axis and lies in the horizontal plane containing the incident beam and the detector. This arrangement is shown in figure 2.10. After scattering, light which is detected with the same polarization state as the incident light will be referred to as the co-polarized return (*ss* or *pp*); and the light detected with the orthogonal polarization to the incident light will be referred to as the cross-polarized return (*sp* or *ps*).

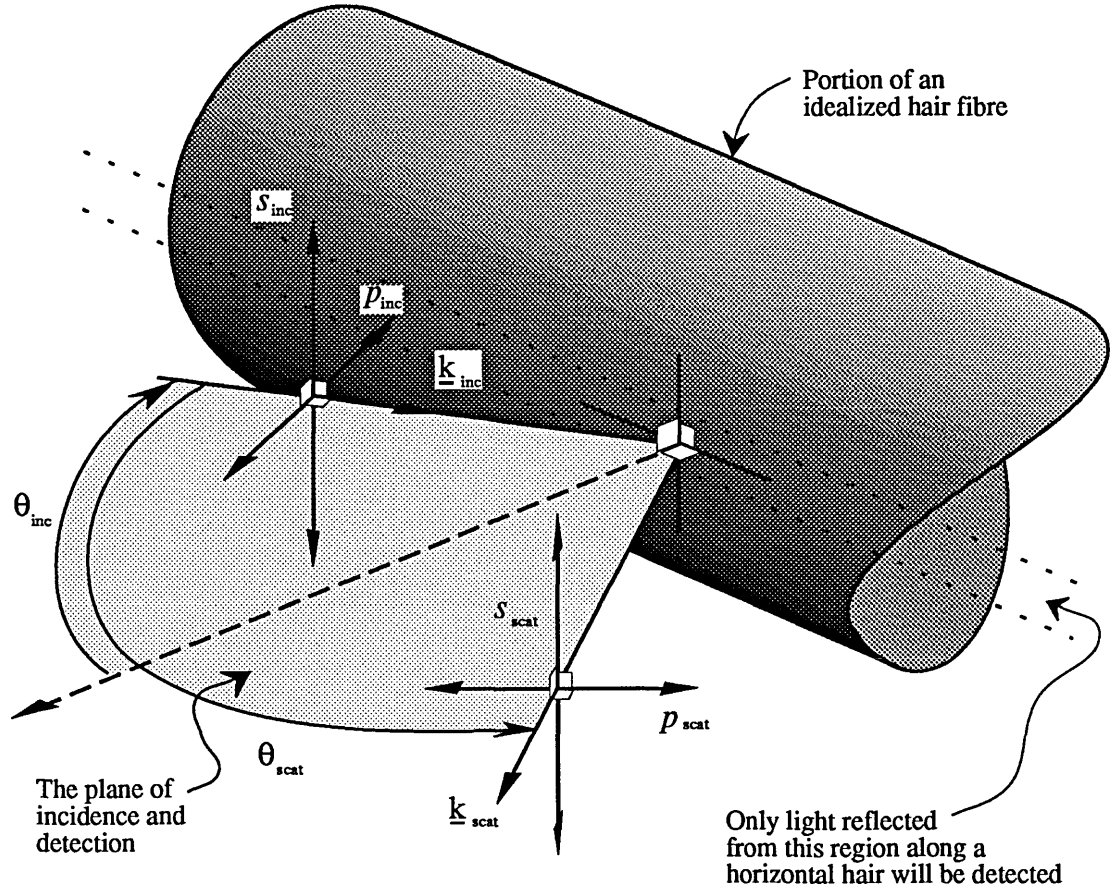


Figure 2.10: Diagram showing polarization notation with respect to a single hair fibre arranged horizontally with respect to the plane of incidence and detection.

It is also appropriate at this point to introduce the conventions that will be used in this thesis for measuring the angles of incidence and scatter. Generally, the angles of incidence and scatter would be measured in appropriate directions

with respect to the normal to the surface of the scattering object at the point of incidence. Where the normal may be accurately determined this has been done. All the scattering measurements taken on both rigs for hairs (single and planar arrays) arranged vertically to the plane of incidence have used this convention. Also, the measurements characterizing the response of the goniophotometer are presented in the same way. In these cases, the forward scatter direction is always indicated by positive angles and the backward scattering direction by negative angles. However, for examining hairs arranged horizontally, the irregular inclination of the overlapping cuticle cells introduces an uncertainty in determining a normal to the surface. It is still possible to determine a normal to the fibre axis but, as shown by the results in section 3.3.1, this may vary by several degrees from the average surface normal. Therefore, although all the angles of incidence are stated with respect to the nominal fibre axis normal, it was decided that it would be more reliable and avoid confusion if the scattering angles were measured with respect to the incident beam whose position can be accurately known. Using this convention of measuring the scattering angles for a mirror surface at a 30° incident angle, the specular peak would occur at a scattering angle of 60° .

2.8 The Response of the Goniophotometer

The final stages in the design and construction of many systems are calibration procedures such as testing their response to a standard set of stimuli. The detector response R_{det} of the goniophotometer is proportional to the radiated intensity $\langle I_n \rangle$ scattered over an effective solid angle $\Delta\Omega'_{det}$ as given in equation 2.10, but $\Delta\Omega'_{det}$ includes the weighting function $W(\theta_{scat}, \phi_{scat})$ and so has an implicit angular dependence, i.e. it may vary with θ_{scat} as the detector rotates. Thus, each scattering-rig must be characterized to determine the angular response of the effective solid angle of its detector. The goniophotometer may be characterized by calculating the weighting function from the geometric arrangement of the apparatus — this is usually quite a complex procedure; a simpler alternative method is to make a comparison between the light-scattering properties of a sample which may be predicted theoretically and the results obtained from the same sample using the goniophotometer. The next problem arises from the selection of a suitable sample, as its scattering properties must have a simple angular dependence which can be deduced. Two obvious candidates for such a problem are:—

- a perfect specularly reflecting surface (e.g. a perfect mirror) — that is, light is reflected in the specular direction only,

or

- a perfect diffusely scattering surface which reflects light according to Lambert's law[†] — that is, equally in all directions.

If the former surface were tested on a scattering-rig it would produce a peak of width equal to the angular resolution of the detection system; it would also only test the response of the detector over a restricted range of angles. In contrast, a Lambertian surface is a more thorough test of the goniophotometer since it scatters light in all directions, allowing the detector response to be tested over a wider range of angles. The problem then reduces to finding a substance which, when formed into a surface, will behave as a Lambertian scatterer. Suitable materials are usually composed of small particles, which means that multiple-scattering processes would dominate when light is scattered from its bulk volume. The sample would also need to have very high reflectances over the region of the spectrum of interest — in this case the visible.

There are a number of different surfaces that form a good approximation to an ideal Lambertian scatterer, and these include: titanium oxide, magnesium carbonate, and magnesium oxide. Traditionally, it was magnesium oxide which, although fragile in surface form, was adopted as a reflectance standard in the fields of colorimetry and photometry [67]. It was prepared by allowing the smoke produced from a burning strip of magnesium to be deposited on a clean, polished silver substrate. More recently a new substance, barium sulphate, has been used as a reflectance standard. It comes in a powder form (supplied by Eastman Kodak) and must be compressed carefully to form a surface; during compression it is important to avoid putting a 'shine' on the surface which can alter its scattering properties. Over the visible spectrum a barium sulphate surface maintains a reflectance of greater than 98%, making it an ideal choice for testing the goniophotometer.

[†]Lambert's law states that if a perfect diffusely scattering surface is illuminated by collimated light then the intensity I at an angle θ to the normal to the surface is given by:-

$$I(\theta) = I(0) \cos \theta .$$

Generally, the normalized radiometric intensity (with respect to incident power) scattered by a surface may be expressed in terms of the bidirectional reflectance function as

$$\langle I_n \rangle = \langle f_r \rangle \cos \theta_{scat} .$$

By definition, the bidirectional reflectance distribution function f_r of an ideal Lambertian surface is constant. Thus, the normalized radiometric intensity distribution from a Lambertian surface may be calculated to be

$$\langle I_n \rangle = \frac{1}{\pi} \cos \theta_{scat} ,$$

where $1/\pi$ is the normalization constant calculated from the integral of the bidirectional reflectance distribution function over the total hemisphere above the surface as follows:-

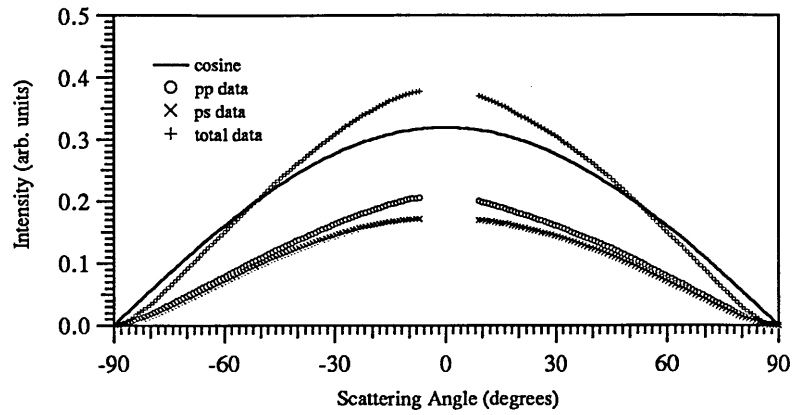
$$\int_{-\pi/2}^{\pi/2} d\phi \int_0^\pi f_r \cos \theta \sin \theta d\theta = 1$$

Therefore, if a detector produces a perfect cosine response, its effective solid angle $\Delta\Omega'_{det}$ must be independent of the angle of scatter and no modification to the data taken with this apparatus will be necessary.

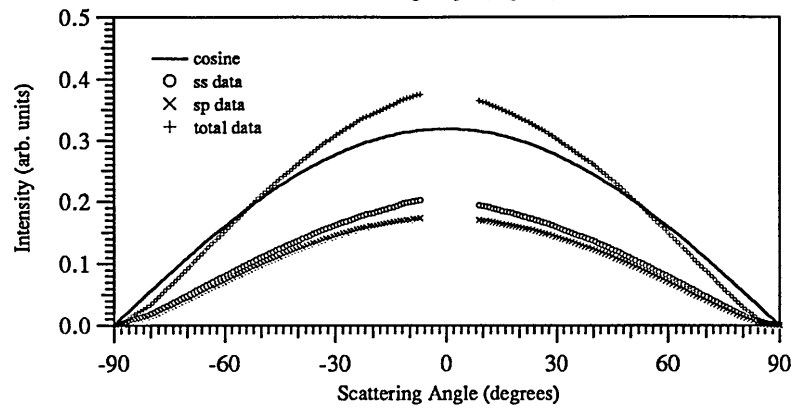
To check if the data taken using the goniophotometer would require modification, scans from -90° to 90° were made on a barium sulphate surface. Both illumination set-ups (laser at 0.633nm and 'white' light) were tested at three angles of incidence (0° , 30° , and 45°) and for both orthogonal linear polarizations (p and s). The results (normalized radiometric intensity) are presented graphically in figures 2.11, 2.12, and 2.13. These three particular incidence angles were selected as they are the ones most often used for experiments on hair. For each incident polarization the co- and cross-polarized data have been added incoherently to produce the total light scattered, and it is this curve which is then compared with the response of an ideal Lambertian diffuser. The missing data points correspond to the angles where the detector was blocking the incident beam. The scattering properties of the barium sulphate surface as measured by the goniophotometer were found to deviate only slightly from ideal; the deviation may have been due either to the surface not being a perfect Lambertian scatterer or to the effective detection solid angle of the goniophotometer varying with angle. The presence of an enhanced backscatter peak, as reported by Sant [68], proves that the properties of barium sulphate do not correspond exactly to those of an ideal Lambertian diffuser. In view of this fact it was decided that the experimental data collected by the goniophotometer

would be treated as though the detector response were independent of angle, i.e. no modifications would be made.

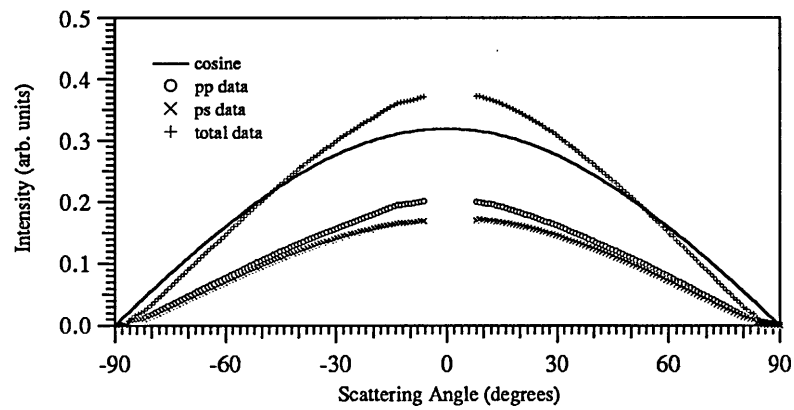
(a)
Helium-neon laser
 $\lambda = 0.633 \text{ nm}$
Light incident at 0°
p-polarized



(b)
Helium-neon laser
 $\lambda = 0.633 \text{ nm}$
Light incident at 0°
s-polarized



(c)
Quartz halogen lamp
Light incident at 0°
p-polarized



(d)
Quartz halogen lamp
Light incident at 0°
s-polarized

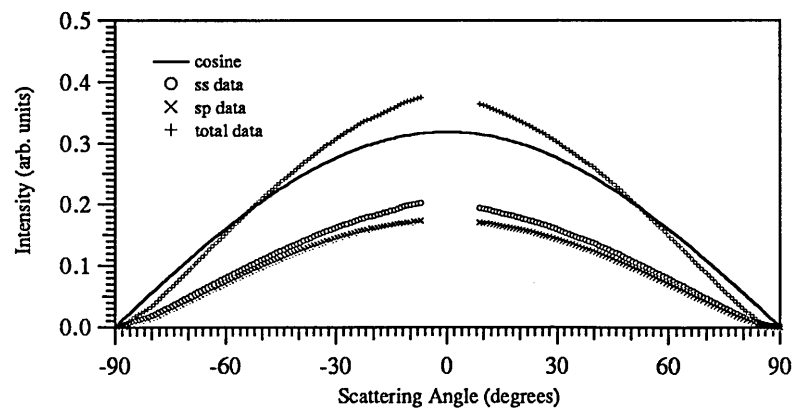
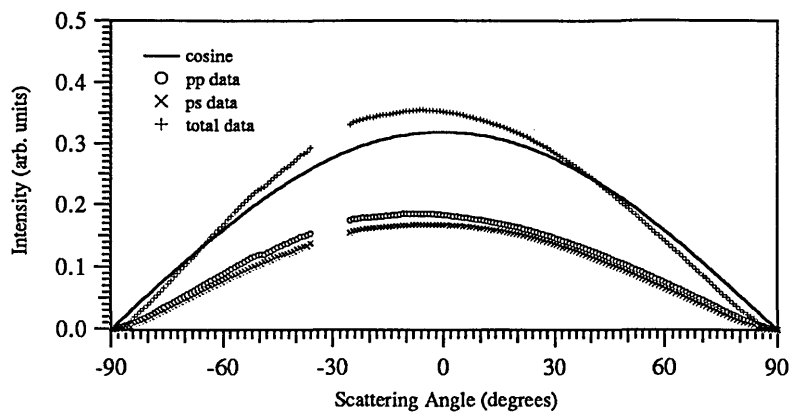
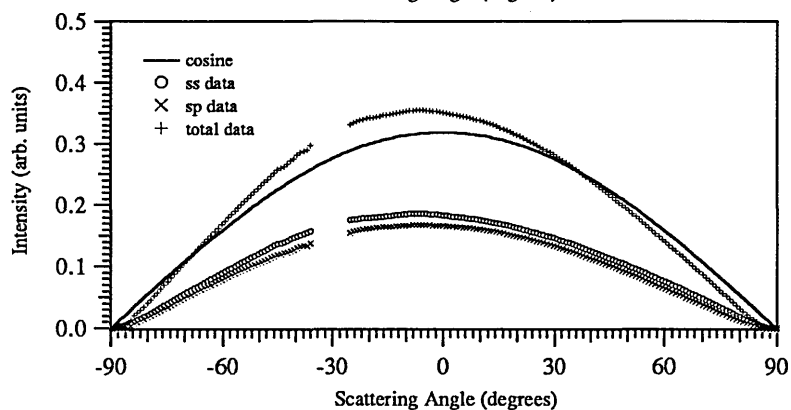


Figure 2.11: Light-scattering envelopes from a flat barium sulphate surface. The response of an ideal Lambertian scatterer is represented on each graph by a solid line which is labelled cosine.

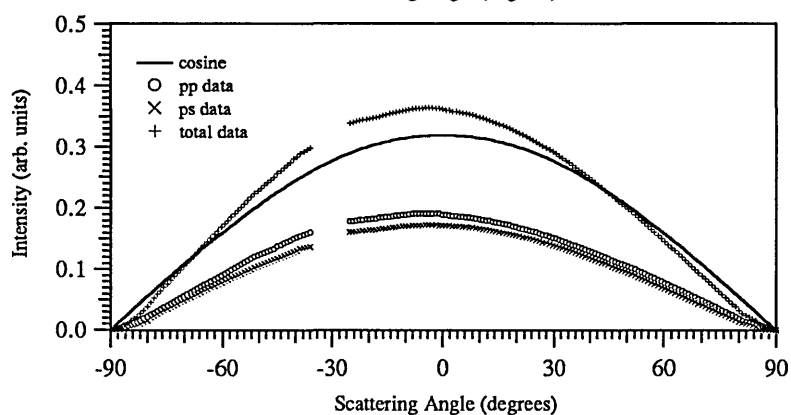
(a)
Helium-neon laser
 $\lambda = 0.633 \text{ nm}$
Light incident at 30°
p-polarized



(b)
Helium-neon laser
 $\lambda = 0.633 \text{ nm}$
Light incident at 30°
s-polarized



(c)
Quartz halogen lamp
Light incident at 30°
p-polarized



(d)
Quartz halogen lamp
Light incident at 30°
s-polarized

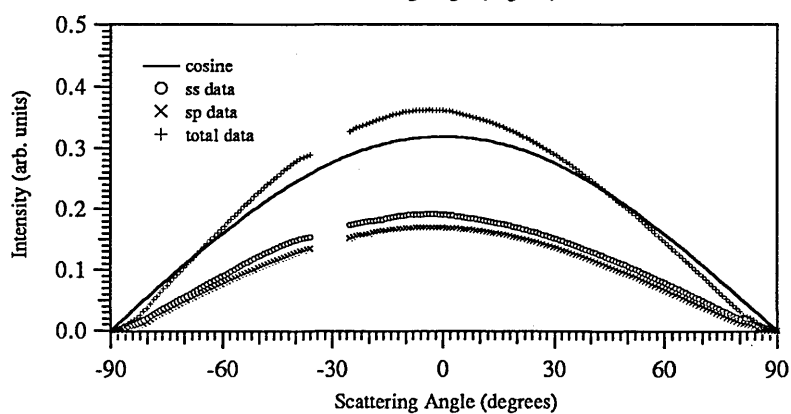
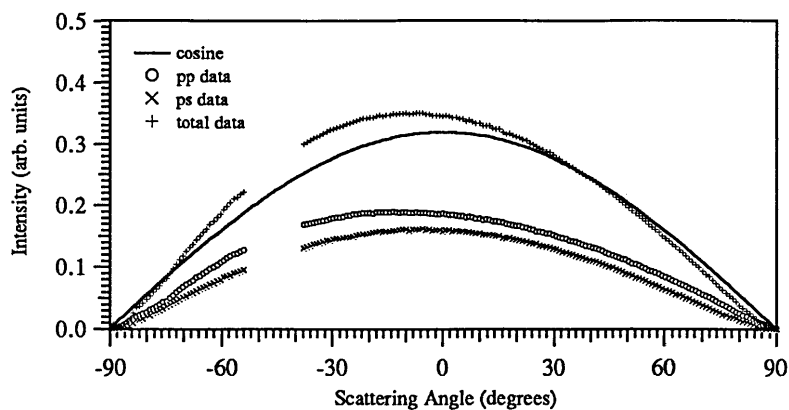
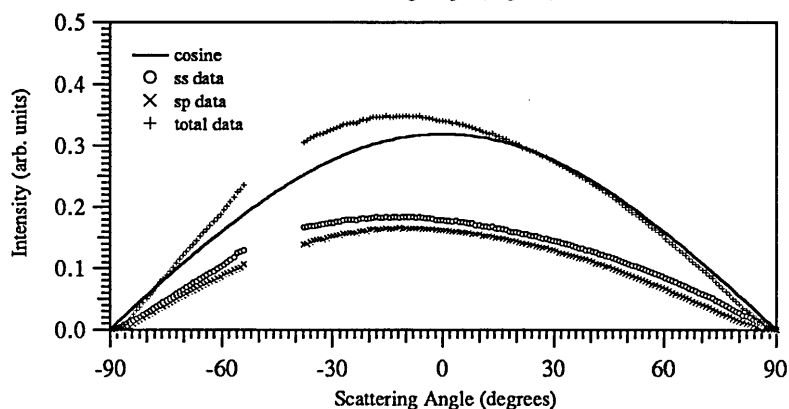


Figure 2.12: Light-scattering envelopes from a flat barium sulphate surface. The response of an ideal Lambertian scatterer is represented on each graph by a solid line which is labelled cosine.

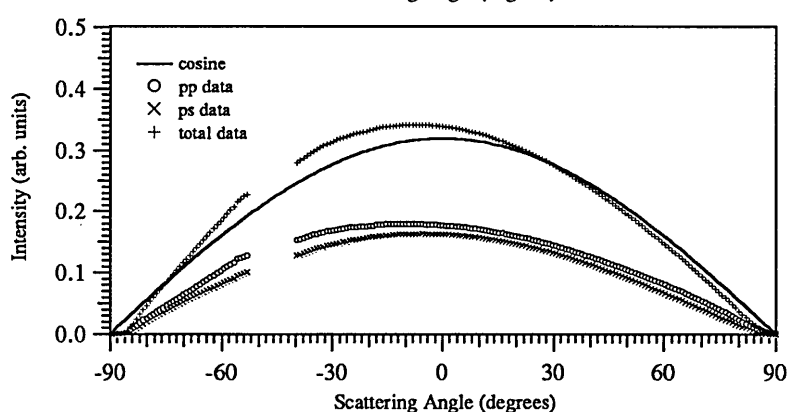
(a)
Helium-neon laser
 $\lambda = 0.633 \text{ nm}$
Light incident at 45°
p-polarized



(b)
Helium-neon laser
 $\lambda = 0.633 \text{ nm}$
Light incident at 45°
s-polarized



(c)
Quartz halogen lamp
Light incident at 45°
p-polarized



(d)
Quartz halogen lamp
Light incident at 45°
s-polarized

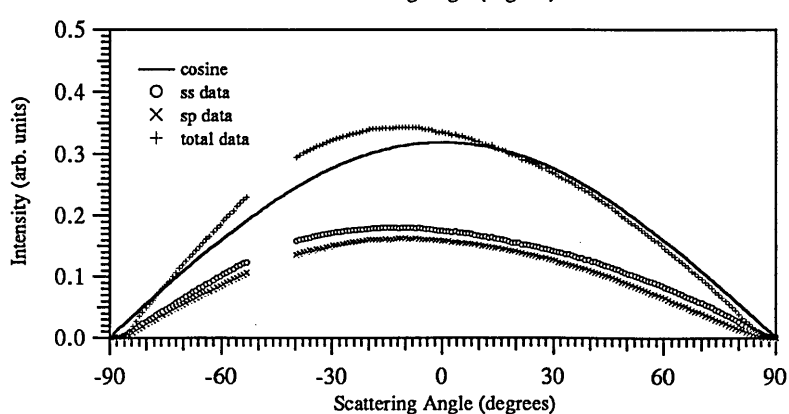


Figure 2.13: Light-scattering envelopes from a flat barium sulphate surface. The response of an ideal Lambertian scatterer is represented on each graph by a solid line which is labelled cosine.

Chapter 3

Experimental Results: Individual Hairs

3.1 Introduction

This chapter contains a summary of the results from light-scattering experiments on individual hair fibres, with the majority carried out using the same set of hair samples. The samples were selected to cover a wide range of characteristic features, which vary between hair types.

Variations in the cross-sectional shape and fibre curvature of human scalp hair have been found to be genetically controlled [6, pages 176–179]. Thus, classifying certain properties of hair according to racial origin is useful for describing typical variations in these features. Table 3.1 summarizes the primary characteristics of scalp hair from the three major races.

Table 3.1: Main racial characteristics of hair

Race	Colour	Curvature	Thickness	Cross-sectional shape
Caucasoid	Blond to dark brown	Straight to <i>wavy</i>	<i>Fine</i> to medium	Almost circular to <i>elliptical</i>
Negroid	<i>Brown-black</i> to black	Wavy to <i>woolly</i>	Medium to <i>coarse</i>	Slightly elliptical to <i>irregular elliptical</i>
Mongoloid	Dark brown to <i>brown-black</i>	<i>Straight</i> to wavy	Medium to <i>coarse</i>	<i>Almost circular</i> to slightly elliptical

Note: the description in italics describes the most common variation within the group.

From this table, for the purposes of these investigations a basis group of the following six hair types was chosen — these were: Oriental-black, Caucasian-black, Caucasian-brown, Caucasian-red, Caucasian-blond, and Caucasian-white. The choice of this group was dictated by the availability of hair of both sufficient quantity and

adequate length, and also by the wide range of colours naturally occurring for Caucasian hair.

The work in this chapter has been organized according to the choice of illuminating source and the orientation of the hair with respect to the plane of incidence, as defined in chapter two, section 2.1. The experiments on individual hairs were designed to increase the current level of understanding of the light-scattering properties of human hair, and, where appropriate, these investigations were paralleled with visual observations made on a subjective basis. The effects of variations in the natural pigmentation, surface condition, and orientation of hairs on the angular distribution of the scattered light were studied. The shape of the curves of scattered intensity versus angle will frequently be referred to as the light-scattered envelope.

When light is incident on the front face of a hair it is scattered — it may be reflected (specularly or diffusely), refracted (transmitted into the hair), or diffracted. If the hair is almost transparent, some of the transmitted light may strike the hair's surface from the inside, where a fraction will be reflected and remain inside the hair, whilst the remainder leaves the hair and adds to the total light-scattered envelope. Of the light remaining inside the hair, at each encounter with the surface of the hair a portion of this light is reflected and the rest escapes; thus, some of the light may be internally reflected several times before retransmission. The degree of pigmentation of a hair and the linear polarization state of the light have been used as tools to distinguish between the components which combine to form the total light-scattered envelope, and also to assess their relative contributions. In some sections — for a more detailed analysis of the results — the reader will be referred to chapter four, where geometric optics has been used in simple models of individual hairs to explain the observed phenomena.

During the coherent light (laser) experiments on hairs, the opportunity was taken to modify the experimental arrangement to investigate the variations in diameter along a fixed length of hair. The diameter was determined from the far-field diffraction pattern formed by each individual hair, several of which had been gold-coated.

3.2 Laser Illumination

This section describes experiments on hairs which have been illuminated using a source of coherent monochromatic light — a laser. It is subdivided into three sections: the first and second deal with goniophotometric measurements, and the third

examines the diffraction patterns produced by individual hairs. Note: as the equipment and method used in the third section were not dealt with in chapter two, they will be briefly mentioned at the beginning of this section.

3.2.1 Single Hair Orientated Horizontally

When a hair is orientated to lie horizontally in the plane of incidence, as discussed in chapter two, section 2.2, and a detector is rotated in this plane, it is possible, by choosing the appropriate angular range, to scan the intensity distribution of the light directly reflected by the uneven surface of the hair. Full 360° scans around hairs in this orientation have shown that (ignoring the unavoidable detection of the undeviated portion of the incident beam), in both scanning directions away from the direction of specular reflection, the intensity level of the scattered light slowly (over a range of $\pm 30^\circ$) decreases to negligible levels. Therefore the scan ranges used for this type of investigation were generally restricted to within $\pm 45^\circ$ of the direction of maximum reflection.

All the investigations on individual hairs mounted horizontally were carried out using the dedicated goniophotometer designed specifically for these measurements. (Note: on this rig the scattering angle was measured with respect to the incident beam.) The hairs were investigated at three illuminating wavelengths (458nm, 514nm, and 633nm), although only the results for 633nm are reported in this section. The graph in figure 3.1 shows a typical scan from an individual brown hair illuminated with a helium-neon laser at 633nm. Despite the adaptations to the goniophotometer to minimize the fundamental problem of speckle noise for individual hairs (see chapter two, section 2.2.2), the traces obtained remained spiky, especially in comparison to those obtained later using quartz halogen illumination. Many hair samples were examined to find out whether any differences resulted from using laser illumination instead of white light. Since none was discovered, and as the speckle noise problem makes interpretation of the data difficult, particularly in the region of the specular peak*, it was decided to use the data obtained with the quartz halogen lamp as the illuminating source to present most of the analysis of light-scattering results for individual hairs arranged in this orientation. More extensive analysis of data obtained using laser illumination has been undertaken for parallel arrays of hair orientated horizontally (refer to chapter five, section 5.2.1), as it was possible

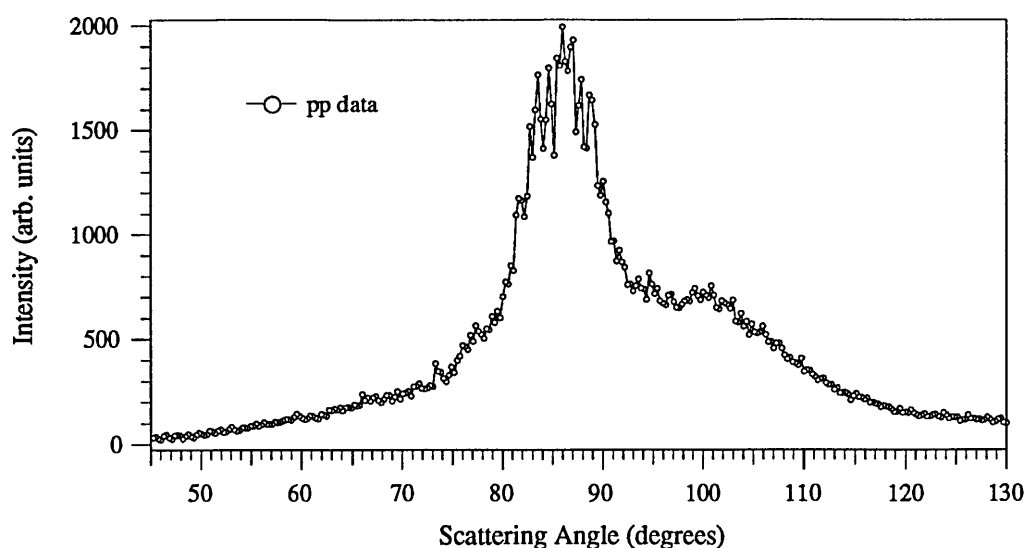


Figure 3.1: Goniophotometric curve of brown hair, light incident at an angle of 45° to the fibre axis. Note: the *pp data* legend represents light incident polarized parallel to the plane of incidence and light detected after passing through a polarizing filter with its transmission axis parallel to the same plane.

to use a sufficiently large area of illumination leading to small speckles.

3.2.2 Single Hair Orientated Vertically

In this section light scattering by individual hairs orientated vertically (see case 2, figure 2.2) is considered. In this orientation a hair, being long compared with its diameter, may be most appropriately thought of as an infinitely long, right-circular cylinder, although it is known that Caucasian hairs often have elliptical cross-sections. Light normally incident on such a smooth cylindrical structure will be scattered into a plane as shown in figure 3.2. Human hairs have an outer layer of cuticle cells which are inclined at a slight angle to the fibre axis, so the light is not scattered into a plane but rather forms the shape of a conical surface in space. This is equivalent to light incident at non-normal angles of incidence (θ_1 and θ_2) in figure 3.2. Since the scale angle is usually small (typically $\approx 3^\circ$), the half-angle of the cone of scattered light will be $90^\circ - 3^\circ$ measured to the fibre axis, as illustrated in figure 3.2. Note: if the cross-section of a hair is circular then the conical surface of scattered light will also have a circular cross-section (perpendicular to the fibre axis), and similarly if a hair has an elliptical cross-section then the cross-section of

*The light specularly reflected by a hair forms a peak of finite angular width due to the uneven nature of the hair's surface. A further explanation of this specular peak is given in section 3.3.1.

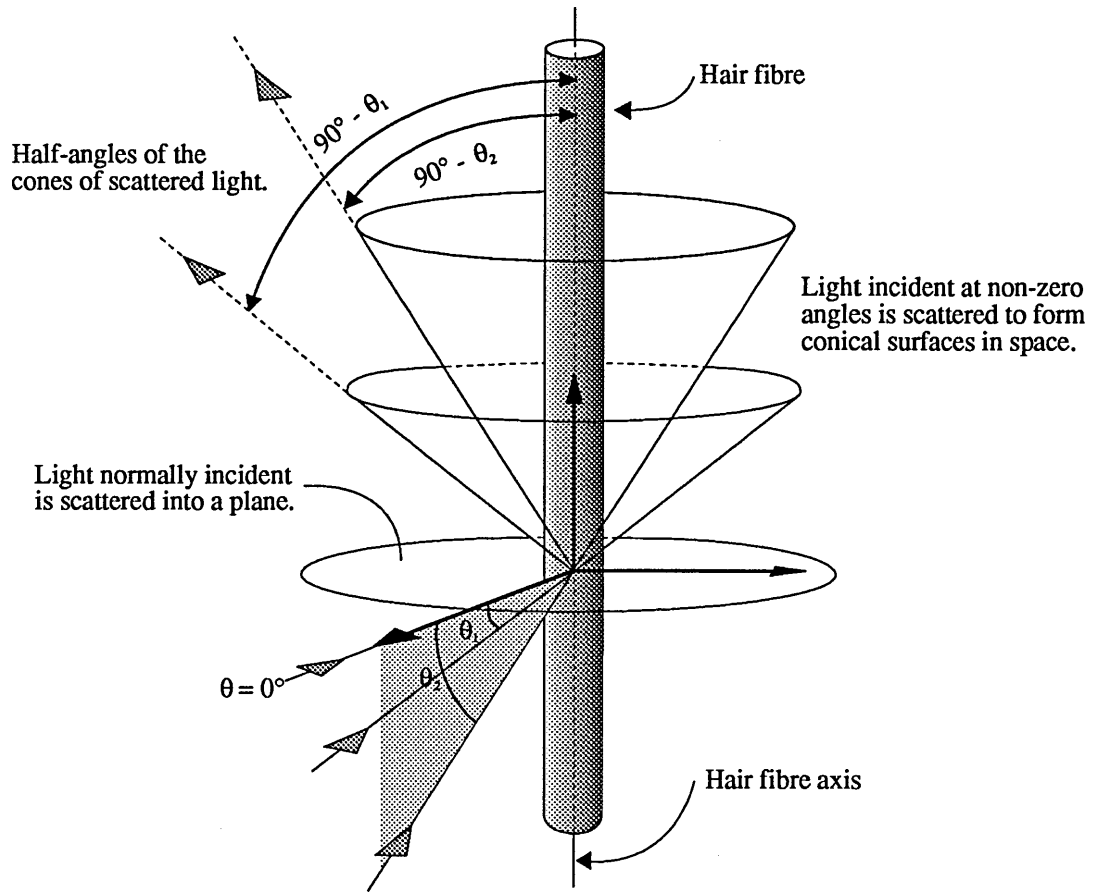


Figure 3.2: Light scattered by an infinite cylinder. Rays of light are shown incident at three angles 0° , θ_1 , and θ_2 where $\theta_2 > \theta_1 > 0^\circ$.

the conical surface will be altered likewise.

Experimentally an individual hair from each sample of the basis group was investigated using the scatterometer described in section 2.2.2 which minimized the loss of data points in the backscatter direction. Each hair was orientated vertically with its root end upwards and was illuminated with a linearly polarized laser (He-Ne) source at a wavelength of 633nm. Scans were taken over a range of angles from -90° to $+90^\circ$ measured with respect to the incident beam, i.e. over the half-plane of backward scattering.

As previously stated, the cross-sectional shape of Caucasian hairs may vary from almost perfectly circular to irregularly elliptical. When mounting a hair vertically the orientation of its cross-section, with respect to the incident beam geometry, was initially arbitrary. By rotating the hair through a known angle, about its own vertical axis, the effects of the cross-section's orientation on the distribution of the scattered light could be studied.

A summary of the results obtained for three Caucasian hairs (black, red, and

white) is presented in figures 3.3, 3.4, and 3.5. These graphs contain curves rep-

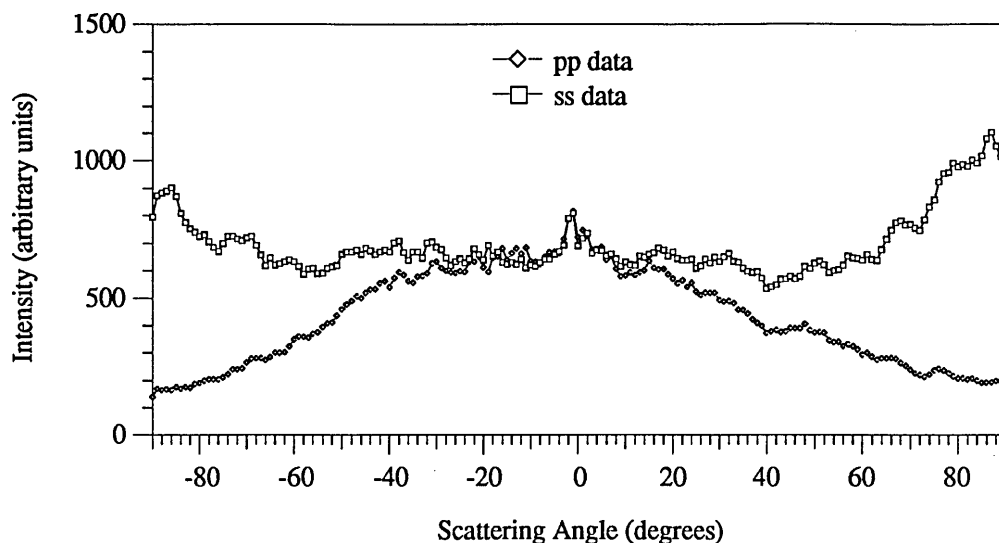


Figure 3.3: Light-scattering envelopes produced by a black hair orientated vertically.

The *pp data* legend represents light inc. polarized parallel to plane of inc. & detected after passing through a polarizing filter with its transmission axis parallel to the same plane. Similarly for the *ss data* legend, except the light incident is polarized *perpendicular* to the plane of incidence and the detected light is also perpendicularly polarized.

resenting co-polarized results only, as the intensities of the cross-polarization scans were found to be negligible in comparison.

It was discovered that the measurements from dark-coloured hairs (Oriental black, Caucasian black, and Caucasian brown) produced markedly different light-scattering distributions compared to those obtained for the light-coloured hairs (Caucasian red, Caucasian blond, and Caucasian white). Obviously this disparity in the results is linked to the transparency of a hair which in turn depends on its capacity for absorbing internally light scattered. The hairs which appear dark contain high densities of eumelanin pigment granules inside their shafts; this pigment, as reported in section 1.2.6, absorbs wavelengths of light in the visible band of the electromagnetic spectrum. It would therefore be a logical assumption that the light-scattering envelope produced by a dark hair will be dominated by the light reflected at the front air/cuticle interface. In transparent hairs the possibility exists that light which has undergone one or more internal reflections may be retransmitted through the front face of the hair to add to the total light-scattering envelope in the backward scattering half-plane. A ray following one possible path through the circular cross-section of a hair is presented in figure 3.6(a).

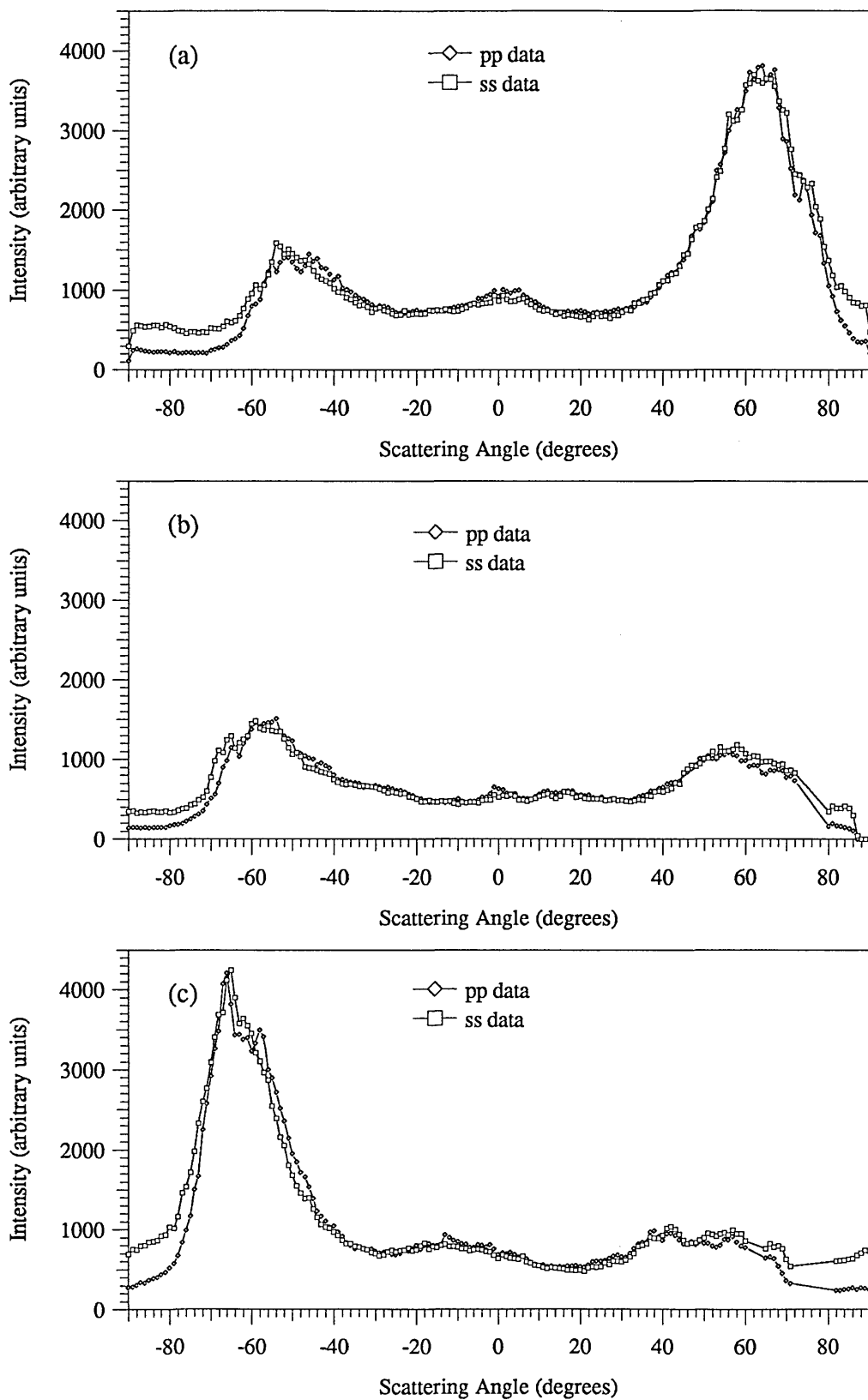


Figure 3.4: Light-scattering envelopes produced by a red hair arranged vertically to the plane of detection and orientated with its cross-section at three positions to the incident beam: (a) as arbitrarily mounted, (b) after rotation through 15° , and (c) after rotation through a further 15° .

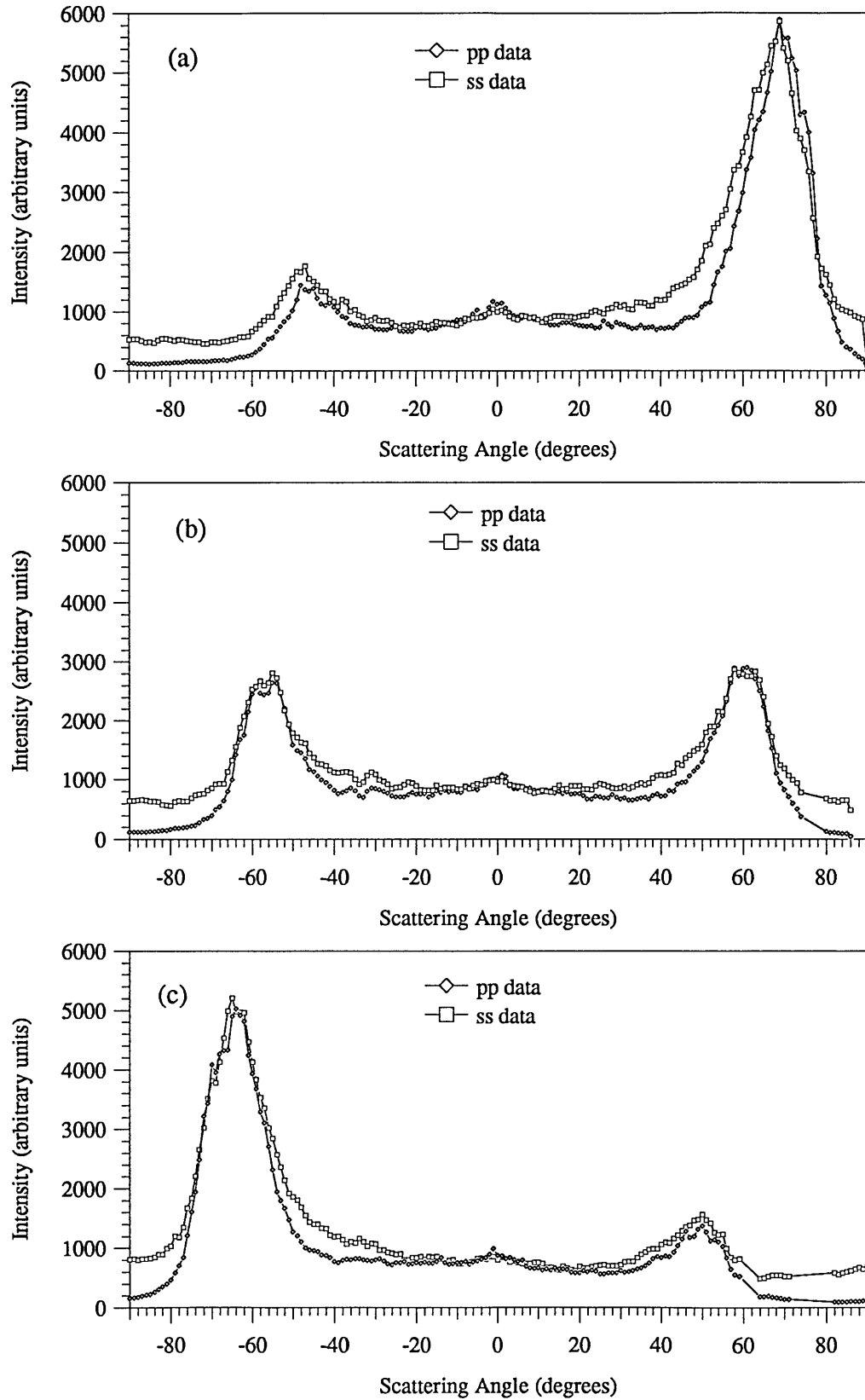


Figure 3.5: Light-scattering envelopes produced by a white hair arranged vertically to the plane of detection and orientated with its cross-section at three positions to the incident beam: (a) as arbitrarily mounted, (b) after rotation through 15°, and (c) after rotation through a further 15°.

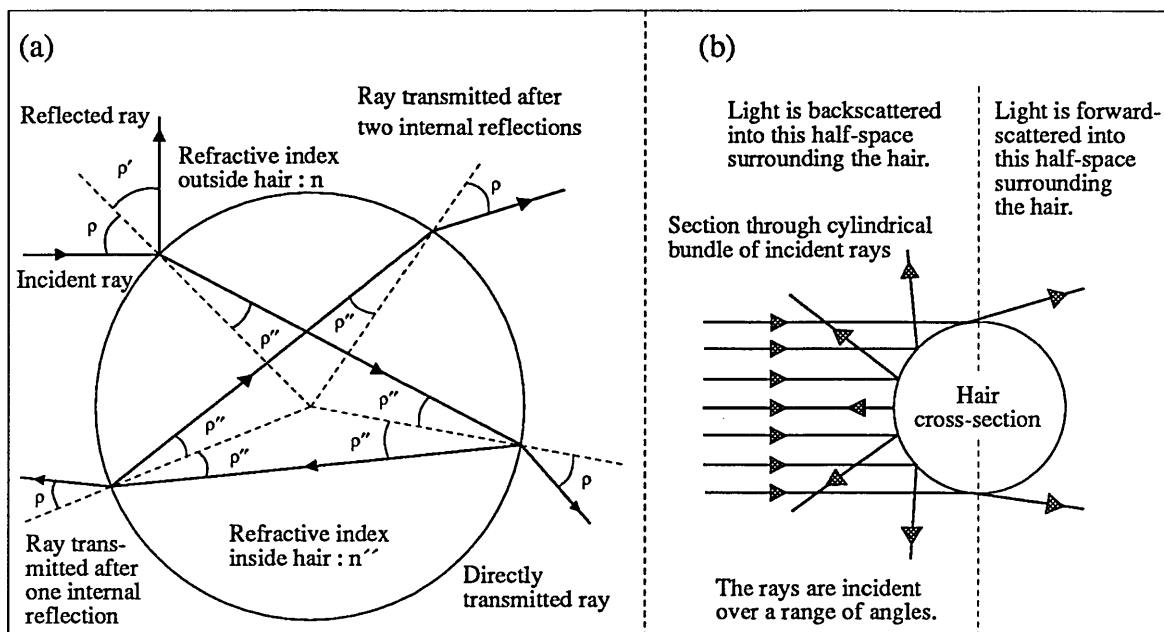


Figure 3.6: (a) Diagram showing path of one ray, incident at angle ρ and refracted at angle ρ'' , up to and including two internal reflections before transmission. (b) Light incident on hair's circular cross-section showing scattering half-spaces and range of scattering angles.

The graph in figure 3.3, for an individual black hair, shows that the light-scattering distributions generated by dark hairs vary according to the linear polarization state (s - and p -) of the incident light. The shape of the light-scattering envelopes may be explained in terms of the curved surface of the hair and the polarization state of the incident light. For hairs orientated vertically the angle of incidence of the light is dependent on the position at which it intercepts the hair's surface. If the illuminating beam is considered in terms of a cylindrical bundle of parallel rays then, at each position across the diameter perpendicular to the fibre axis of the hair, the angle of incidence between a ray and the hair surface will be different because of the hair's curvature. This concept is illustrated in figure 3.6(b), where it is clear that each ray is incident at an angle dependent on its displacement from the ray which denotes the middle of the bundle.

Although the surface of a hair appears rough in electromicrographs, many of the pits and cracks are *smaller* than the wavelength of the illuminating light so it is useful, when interpreting these results to first order, to consider hair as having an optically smooth surface. For such a dielectric surface the amount of light reflected from it will depend on the refractive index of the material, the local angle of incidence, and the polarization state (s or p in this case) of the incident light. These

quantities are related by the Fresnel formulae for the amplitude of reflected and transmitted light. The Fresnel equations for determining the amplitude reflection coefficients (r_s and r_p) of light incident at a boundary between two media of differing refractive index are [11]:

$$r_s = \frac{n \cos \rho - n'' \cos \rho''}{n \cos \rho + n'' \cos \rho''} \quad (3.1)$$

and

$$r_p = \frac{n'' \cos \rho - n \cos \rho''}{n \cos \rho'' + n'' \cos \rho} \quad (3.2)$$

where n is the refractive index in the incident medium, ρ is the local angle of incidence, ρ'' is the angle of refraction, and n'' is the refractive index of the medium into which the light is transmitted. An equivalent set of equations exists for transmission which will be introduced later in chapter four. The intensity reflection coefficients (R_s and R_p) are then simply related to the amplitude reflection coefficients, as follows:

$$R_p = |r_p|^2 \quad \text{and} \quad R_s = |r_s|^2 \quad . \quad (3.3)$$

An average value for the refractive index of a sample of whole hairs has been reported to be 1.548 at a wavelength of 589.3nm [57], and has been measured (as described in chapter four, section 4.2.1) to be 1.545 ± 0.005 with a tungsten lamp and a narrow band (20nm) interference filter at a wavelength of 549nm. Using the latter value, the Fresnel intensity reflection coefficients for s - and p -polarized incident light as a function of the angle of incidence may be calculated at an air/dielectric boundary, and these results are presented graphically in figure 3.7. The relative amounts of light incident (polarized s - or p -) that are reflected at this boundary may be determined by reading off the value of the intensity reflection coefficient from the graph at the appropriate angle and multiplying it by the intensity (I_0) of the incident light.

In figure 3.3, for the black hair, the data points of the s - and p -polarization scattering curves immediately surrounding 0° were observed to be of approximately the same value. This result is in agreement with the values of intensity reflection coefficients for both polarization states near normal incidence. This feature of both polarization curves almost touching in the backscatter direction was found to occur for all the hairs investigated, whatever their degree of transparency.

Away from normal incidence the value of the ss data curve for the black hair sample was found to increase gradually in intensity, the gradient becoming steeper

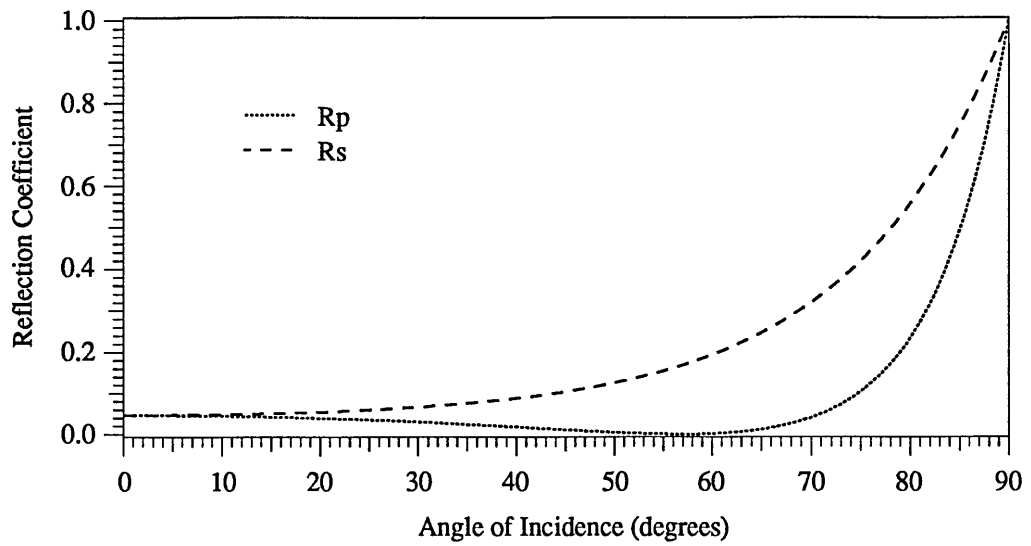


Figure 3.7: A graph presenting the Fresnel intensity reflection coefficients calculated at an air/dielectric boundary (for a dielectric material of refractive index 1.545) plotted against angle of incidence. Note: for presentation purposes the abscissa has been offset a small amount below zero.

at higher scattering angles. This can be directly explained in terms of the change in value of the s-polarization reflection coefficient, R_s , with increasing angle of incidence. Initially it increases in value slowly and then as the angle become larger the increase becomes rapid. As depicted in the diagram in figure 3.6(b), light incident at small angles to the normal to the hair's surface is reflected into small scattering angles, whilst light incident at large angles is reflected into large scattering angles (as measured with respect to the ray representing the centre of the incident bundle of rays).

Similarly, the intensity of the *pp data* curve follows the variations in value of the p-polarization intensity coefficient R_p . Initially, at small angles R_p decreases in magnitude with increasing angle of incidence until at one particular angle it reaches zero. This occurs when the angles of reflection and refraction add to equal 90° and corresponds to an angle of incidence known as the Brewster angle ρ_B , which is related to the ratio of the refractive indices of the media at the boundary by

$$\tan(\rho_B) = \frac{n''}{n} . \quad (3.4)$$

For a hair fibre (refractive index $n'' = 1.545$) in air (refractive index $n \approx 1$) this produces a Brewster angle of 57.1° , which corresponds to a scattering angle of 114.2° on the abscissa of the graph in figure 3.3. This feature of the Fresnel equations for p-polarized light explains why the *pp data* curve steadily decreases in value away from

normal incidence. Further investigation into whether it reached zero outside the scan range (restricted to $\pm 90^\circ$ here, as the supporting frame obscured the detector from the scattered light at higher angles) is described in section 3.2.2. The dips in value for the points at the extreme ends of the *ss data* curve were also caused by the supporting frames. If this purely geometric artifact had not been present then the *ss data* curve would have continued to increase in value, as is observed from the results in section 3.3.2. Changing the orientation of the dark hairs' cross-sections to the incident beam was found to modify the intensity of the light scattered without altering its distribution, as the amount of intersected beam varied.

Immediately noticeable for the transparent hairs was the emergence of areas of high intensity which appeared to the observer as a pair of bright spots, one on each side of the incident beam lying on the conical surface. As each hair was rotated about its long axis the spots were found to alter their angular position and their intensities relative to each other but they always remained in the backscattering half-space. Since these bright spots of light are not produced by dark hair and were found to be formed in the half-space of backward scatter (as indicated in figure 3.6 (b)), they were attributed to the component of light internally reflected at least once before retransmission.

As the light-scattering distribution for transparent hair was found to vary considerably with the orientation of the hair's cross-section to the incident beam, three sets of data were taken for each hair orientated vertically: the first as the hair was arbitrarily mounted; the second after it had been rotated through 15° with respect to the first; and the third after it had been rotated through 30° with respect to the first. However, it was just a coincidence that, for both these hairs (figures 3.4 and 3.5), symmetrical peaks occurred after rotation by 15° . Indeed, a blond hair (results not presented here) produced symmetrical peaks after rotation through 30° from its original mounting position. Note: the gaps in the data (particularly evident after rotation through 30° , figures 3.4(c) and 3.5(c)) correspond to the obstruction of the scattered light by the posts supporting the hair mount and were unavoidable.

Since many Caucasian hairs possess an approximately elliptical cross-section, it is thought that the change in angular position of these peaks is linked to the orientation of this ellipse to the incident beam. A fuller explanation of what these peaks are, how they are formed, and why they vary in angular position and intensity as a hair is rotated about its own axis, is given in chapter four, section 4.3.5,

where an optical model of a single hair orientated to the incident beam in this configuration is developed.

For these lighter-coloured hairs, the *s*- and *p*-polarization curves as shown in figures 3.4 and 3.5, were found to be very similar except at high scattering angles ($> 80^\circ$), where the intensity of the *p*-polarization curve was consistently lower in value than the *s*-polarization curve. This was attributed to the effects of the Fresnel intensity reflection coefficient, R_p , decreasing towards zero as the incidence angle approaches the Brewster angle condition on the amount of *p*-polarized light reflected by the hair. This would reduce the contribution of the front-face reflected light to the total light-scattering envelope for this polarization in comparison to that for the *s*-polarization state, which would steadily increase with increasing incidence angle.

Comparing the shape of the peaks in the graphs in figures 3.4 and 3.5 it was found that they were broader and less intense for the red hair than for the white. Red hairs contain high concentrations of phæmelanin pigment granules in comparison to white hairs, which are characterized by an absence of pigment granules in their shafts. Phæmelanin pigment absorbs light at the blue end of the visible spectrum and scatters it at the red; therefore, as this experiment was conducted with light at a wavelength of 633nm (i.e. in the red region of the spectrum), the light transmitted into the red hair would have encountered pigment granules and been scattered. As a consequence, light passing through the red hair tended to become spread over a wider angular range than the light transmitted through the white hair, and so, at this wavelength, the red hair produced a wider, less intense, peak than the white hair. At a shorter wavelength of 458nm (in the blue region of the spectrum) the red hair was found to produce a light-scattering envelope similar to that of the dark fibres, as the phæmelanin pigment absorbs light of this wavelength.

3.2.3 Diffraction Patterns Formed by Lengths of Hair

Human scalp hair grows at the rate of approximately 0.3mm per day, and at this rapid growth rate the hair follicle has a high protein requirement but only a low protein priority in the body (this activity not being essential to sustaining life). In some cases, to maintain diameter and conserve resources, a medulla is formed in the centre of the hair, in others a reduction in hair diameter occurs. Thus, changes in hair diameter are thought to reflect the general health and diet of its owner [4, pages 51–55].

The diameter of any cylindrical structure is related to its stiffness; for instance, the bending and torsional stiffness of cylindrical shapes increases with the fourth power of their diameter [69]. For hairs, when considered in the context of the appearance of a full head of hair, this relationship will have an effect on their manageability with regard to styling and hold. It is also useful to have a measure of the diameter of a hair since it will determine how much of the incident beam the hair actually intercepts.

In previous experiments using a diffraction method to measure the diameter of hair fibres (see section 1.3.4), the hairs have been illuminated with an unexpanded laser beam. This means that at any one time the diffraction pattern from only a short length (1 or 2mm) of hair can be examined. To determine variations along a substantial length of fibre, many measurements at small intervals would need to be made. With this limitation in mind, a method was developed whereby individual hairs (ordinary and gold-coated) were mounted and illuminated, as shown in figure 3.8, using an argon ion laser operating at wavelength 514nm. The arrangement of

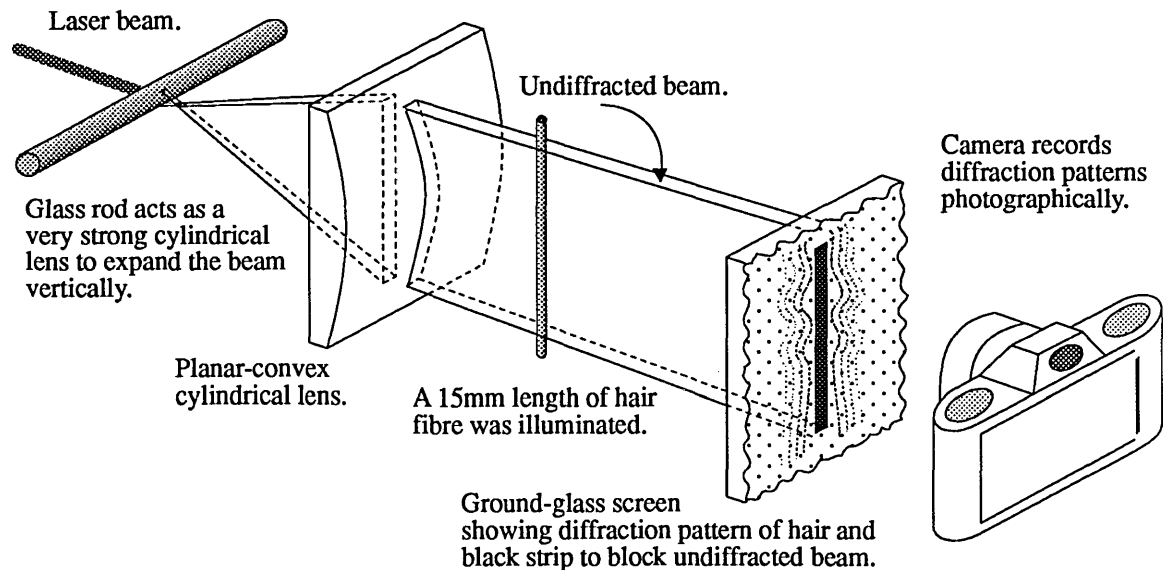


Figure 3.8: Set-up of equipment; wavelength of incident light 514nm.

cylindrical lenses allowed the beam to be relatively undeviated in the plane perpendicular to the long axis of the hair and spread out in the orthogonal plane to illuminate a 15mm length of hair. Observing the far-field diffraction pattern formed by a length of hair, any changes in hair diameter are immediately identifiable. The magnification factor in the non-diffracting plane was calculated to be 2.7 ± 0.2 . Each far-field diffraction pattern was recorded photographically, a summary of represen-

tative patterns is given in figure 3.9.

Bearing in mind the comments discussed in chapter one, section 1.3.4 (concerning the limitations of applying Fraunhofer diffraction theory to transparent dielectric fibres), the average minimum and maximum diameters were calculated using a modified version of equation 1.4 (measuring over 12 orders of the diffraction pattern for obtaining the inter-order separation with greater accuracy). The form of equation 1.4 becomes:

$$d = \frac{m\lambda}{\sin \theta_m} \quad (3.5)$$

where d is the diameter of the fibre, λ is the wavelength of the illuminating source, m is the number of minima, and θ_m is the angular position of the m^{th} minimum. For small angles of θ_m , $\sin \theta_m = a/l$ where a is the distance across the diffraction pattern out to the m^{th} minimum and l is the distance (typically of the order of metres) measured from the hair to the ground-glass diffuser.

Table 3.2: Diameters of a selection of coated and uncoated hairs as calculated from their diffraction patterns

Hair Type and Condition	Minimum Diameter d_{min} in μm	Maximum Diameter d_{max} in μm	d_{min} to d_{max} Δ_{mm} in mm
G-c Black	78.3 ± 0.6	88.3 ± 0.9	4.5 ± 0.5
G-c Brown	80.1 ± 1.5	89.1 ± 1.2	3.0 ± 0.4
G-c Red	76.1 ± 1.3	89.1 ± 1.2	11.2 ± 0.9
G-c Blond	90.6 ± 0.8	104.8 ± 0.9	9.4 ± 0.8
G-c Black (Dyed)	95.8 ± 0.8	97.5 ± 1.0	13.1 ± 1.1
G-c Red (V.Curly)	81.4 ± 0.9	107.5 ± 1.2	1.9 ± 0.4
Oriental	109.5 ± 1.0	110.3 ± 0.9	6.0 ± 0.6
Black	88.2 ± 0.7	99.9 ± 0.9	6.0 ± 0.6
Brown	56.9 ± 0.5	72.3 ± 0.7	7.5 ± 0.7
Red	85.5 ± 0.7	94.9 ± 0.7	5.2 ± 0.5
Blond	76.2 ± 0.8	86.1 ± 0.8	3.4 ± 0.5
White	70.8 ± 0.6	86.8 ± 0.8	9.4 ± 0.8
Damaged (Permed)	52.0 ± 0.3	55.1 ± 0.5	9.4 ± 0.8
Damaged (V.Curly)	49.8 ± 0.4	71.3 ± 0.5	11.0 ± 0.9
Nylon	151.1 ± 0.7	151.1 ± 0.7	—

key: G-c represents gold-coated.

Table 3.2 summarizes the minimum and maximum diameters of six gold-coated hairs and seven uncoated hairs, and a nylon fibre (obtainable for any haberdashery store). It also gives the distance, Δ_{mm} , between these two positions along the shaft

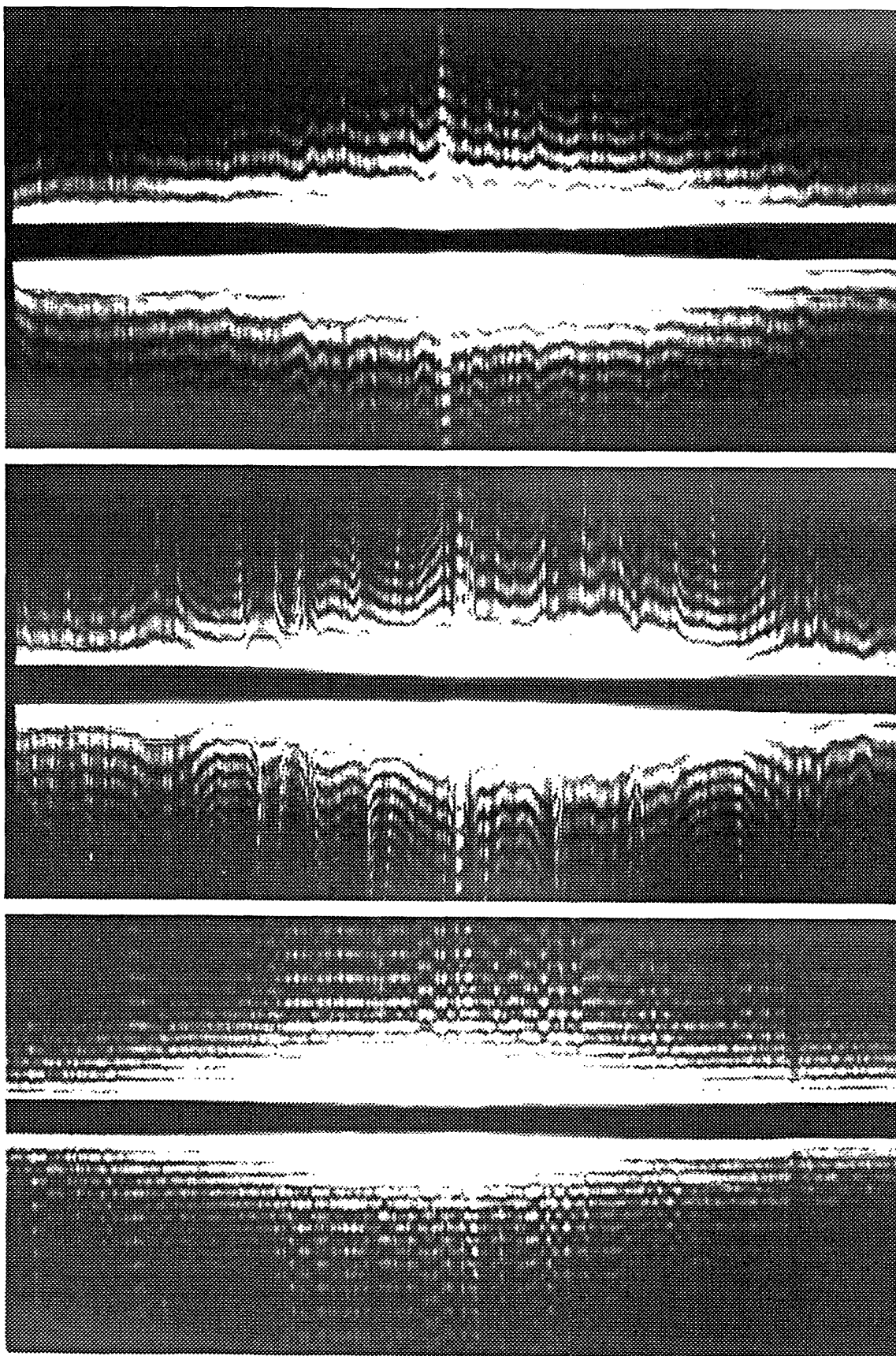


Figure 3.9: Diffraction patterns produced by three fibres orientated vertically; wavelength of incident light 514nm. The upper pattern corresponds to a straight gold-coated hair, the middle pattern to a curly gold-coated hair, and the lower pattern to a nylon fibre.

of the hair fibre. The variations in diameter correspond to the gross change along the hair fibre rather than that over the shorter lengths ($10\mu\text{m}$) of the individual cuticle cells.

As these calculations are based on formulae derived for the diffraction of light by a single slit, the measurements for the hairs which were not gold-coated will be in error. This is because it is possible for light to be transmitted through these hairs, and this light will add to the optical diffraction pattern formed by the profile of the hair. This error will be least for the dark hairs and greatest for the transparent, and will depend on the refractive index of the fibre. However, as it will be a systematic error for a given hair, both the maximum and minimum diameters will be in error by the same amount and so a comparison of diameters is still meaningful.

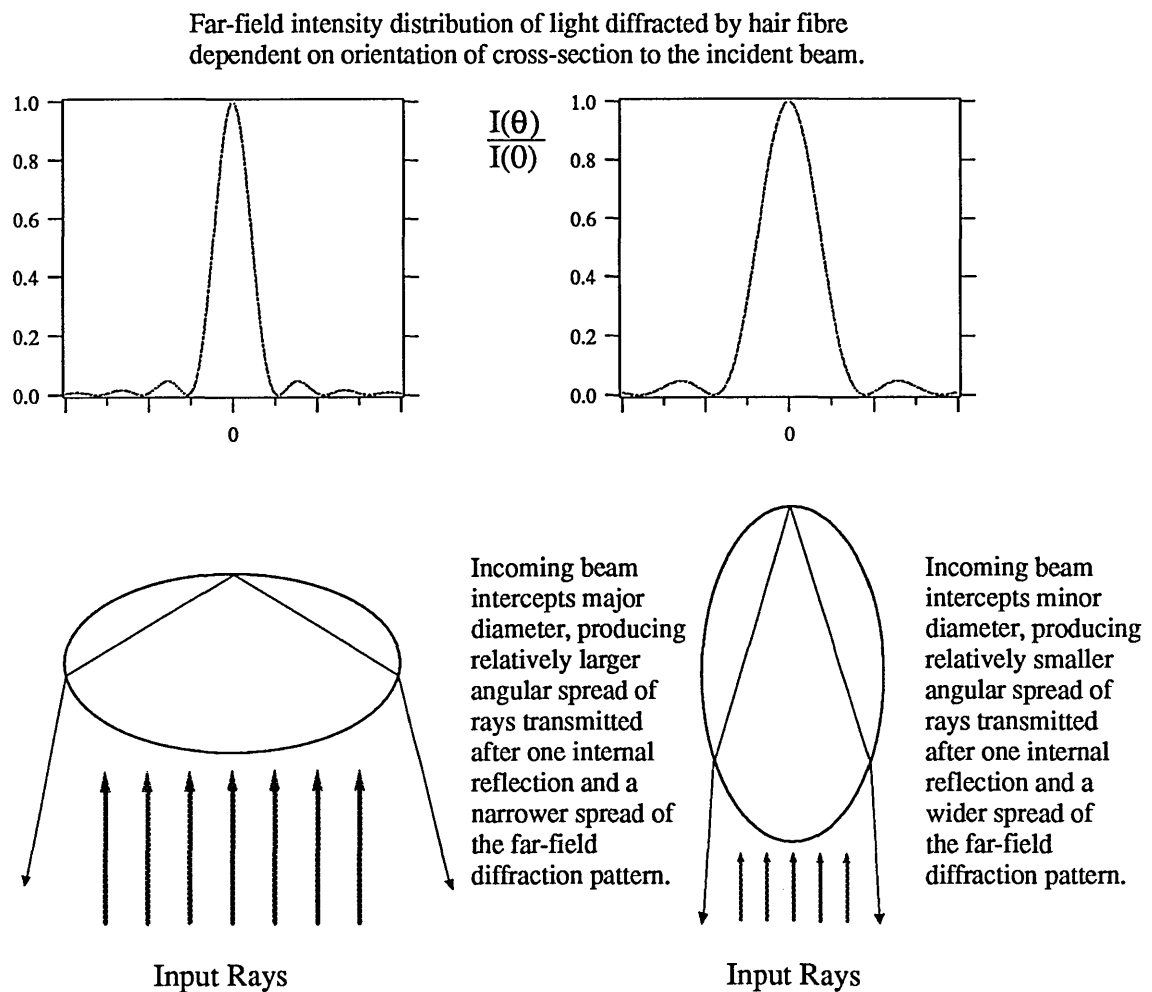


Figure 3.10: Diagram illustrating the inverse relationship between the hair diameter and the distribution of light in the far-field diffraction pattern.

All hairs vary slightly in diameter during growth but the largest variations in diameter were found to be for the curly hairs. As these hairs tend to have cross-sections which are elliptically shaped rather than the more circular cross-sections associated with straight hairs, it is possible that it is the orientation of the elliptical cross-section to the incident beam which is creating the apparently large changes in fibre diameter for curly hairs.

Figure 3.10 illustrates a schematic view of the two extreme cases of orientation of an elliptical cross-section with respect to an incident beam and the differences in the corresponding diffraction patterns which are formed. As the weighted hairs were suspended freely, it is not thought that the hairs were twisted during the experiment; if they were not, then the elliptical cross-section of a hair must gradually rotate along the length of the fibre. Indeed, it may be this rotation of a hair's cross-section which, in part, makes some hairs naturally curly. This idea is substantiated by the results for the Oriental hair fibre, which was known to have an almost circular cross-section (being very straight), and was found to vary by less than one micron in diameter along a 6mm length of hair.

These measurements also showed that damaged hairs suffer a reduction in diameter. The permed hair was taken from a sample of the brown hair which was treated with a permanent waving solution and then combed vigorously for 15 minutes (with a nylon comb). The other damaged group of hairs selected from the red sample was merely subjected to the mechanical damage of the combing process over a period of 30 minutes. The reduction in diameter has been interpreted in terms of a loss of cuticle layers (each typically $0.5\mu\text{m}$ thick) which were weakened by the chemical treatments and removed by the frictional action of the comb.

This method of determining the diameter of hairs could also be extended to an array of hairs — provided they were not touching — to obtain an average diameter of the sample over the length of hair illuminated. This technique would certainly enhance the speed with which measurements could be taken to determine changes in fibre diameter in before-and-after-treatment experiments.

3.3 Quartz Halogen Illumination

The following experiments were carried out with a quartz halogen filament lamp as the source; thus, they will loosely be referred to as 'white' light experiments although it is fully realized that this source by no means represents the full visible spectrum

or even imitates sunlight. This section is subdivided into two main sections which depend on the orientation of the hair to the incident beam, and all the scattered light measurements were taken using the dedicated goniophotometer described in chapter two.

3.3.1 Single Hair Orientated Horizontally

A single hair from each of the basis samples was studied and a variety of experiments carried out with the individual hairs orientated to lie within the planes of incidence and detection (which are defined in this set-up as the same plane). In general, the analysis has consisted of characterizing the light-scattering envelope produced by a hair in terms of features directly measurable from the graphs; in particular, in some of the experiments a contrast gloss measurement has been determined for the hairs. In each case this parameter has been calculated using equation 1.8 in chapter one, section 1.3.5, and spot values for S and D over a fixed solid angle of detection dependent on the angular resolution of the equipment. In this chapter the emphasis has been placed on understanding the light-scattering properties of hair rather than characterizing its appearance in terms of gloss, therefore a more comprehensive treatment of gloss has been left to chapter five, where parallel arrays of hair have been examined. Note: some of the results in this section may also be found in two papers published by the author references [70, 71].

Effect of Fibre Colouring on Scattering

A strand from each of the six untreated hairs of different naturally occurring colours was examined and measurements were taken along its length at ~ 3 mm intervals. Figure 3.11 shows typical data collected at the root end of three hairs (black, brown, and white) with unpolarized white light. On the graph the scattering angle is measured with respect to the incident beam direction. So, following this convention, for light incident at 45° to the fibre axis (as in this experiment) direct specular reflection from a flat surface would be expected to occur at a scattering angle of 90° along the abscissa of the graph.

There are three points of special interest to be noted about these results. The first is the angular position of the specular peak, the second is its wide angular spread, and the third is the asymmetry of the light-scattering envelope for transparent fibres. The details of each feature together with qualitative explanations are dealt with in

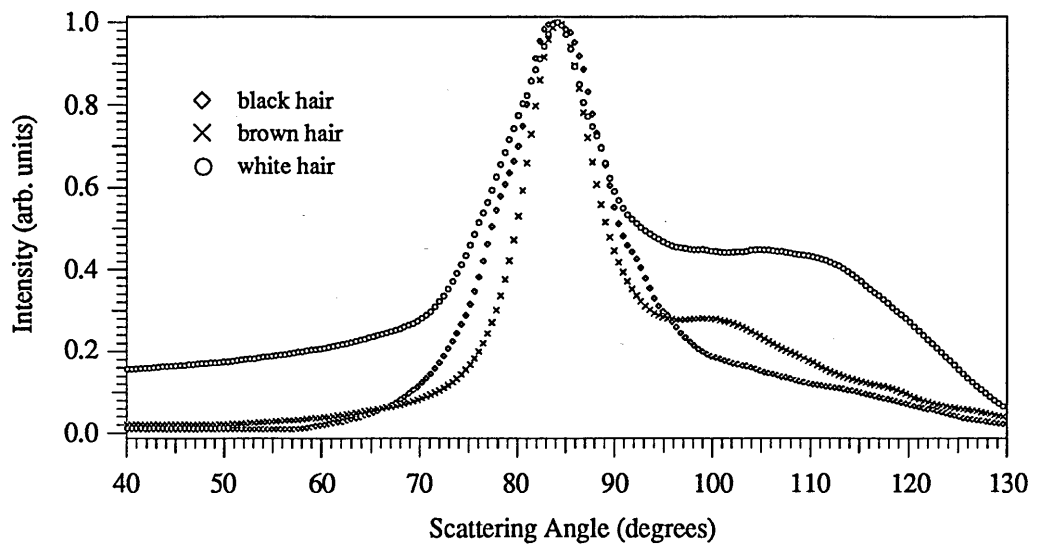


Figure 3.11: Goniophotometric data from three individual hairs. Each data set has been normalized to have a peak intensity of unity for the purposes of comparison.

turn.

If a single hair could be considered to be a smooth, opaque, uniform cylinder then the ‘specularly’ reflected light would be observed, at twice the angle of incidence (corresponding to 90° on the graph in figure 3.11), as a peak of angular width equal to the angular resolution of the illumination/detection system (less than 1°). However, for the brown hair, for instance, the specular peak occurs at 84° and is considerably widened to a full width of about 8° at half its maximum intensity. This shift in the specular peak occurs because the fibre surface is composed of scales (cuticle cells) inclined to the fibre axis. By applying simple geometric considerations, as illustrated by the diagram in figure 3.12, it can be seen that the true surface normal is shifted by the average scale angle α . Thus the reflected light is deviated through an angle of $2\theta - 2\alpha$ where θ is the angle of incidence measured with respect to the normal to the fibre axis — the angular position of the specular peak is shifted by an amount 2α . For the brown hair the average scale angle over the length ($\sim 3\text{mm}$) of fibre illuminated was calculated to be $\approx 3^\circ$.

The second feature is the unexpectedly wide angular spread of the specularly reflected light. The black, brown, and white hairs were measured to have full widths at half maximum intensity (FWHM) of 10° , 8° , and 16° respectively. Clearly, the transparency of the hair has some connection with this width but it is not the only factor involved, as even the dark hairs have FWHM many times greater than that which would be produced by a smooth cylinder.

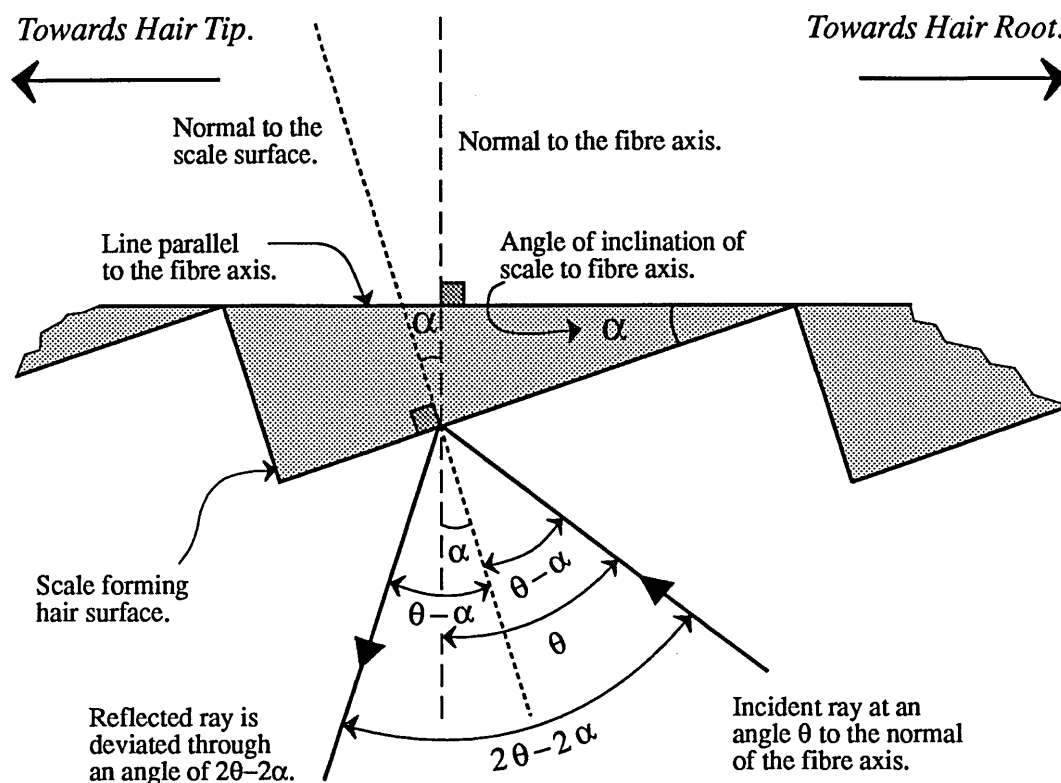


Figure 3.12: Schematic arrangement of the hair cuticle illustrating the effect of the scale angle.

In figures 1.3 and 3.12 the cuticle cells are represented as fixed in shape and orientation, overlapping regularly. Examination of hairs under a scanning electron microscope reveals that, even for a relatively undamaged hair, this is not the case. In reality, the surface of a hair therefore consists of many irregularly shaped, overlapping cells each orientated to the fibre axis at its own individual angle. Thus, when light is incident on the hair, the direction in which it is reflected will depend on the exact inclination of that particular portion of the surface to the fibre axis. The overall result produces a broad specular peak.

Electron micrographs of the black and brown hairs have exposed differences in their surface architecture. The brown hair appeared to be composed of shallowly inclined cuticle cells with large intervals between scale margins. In comparison the surface of the black hair appeared much rougher, as typical scale margin intervals were short and the cells were more irregularly inclined to the fibre axis. These observations might explain the relatively narrower FWHM of the brown hair compared to the black. This idea was further investigated by taking Talystep profiles from each hair and calculating the range of scale angles present. These results are described

in chapter four, section 4.3.6 where they are used in the development of an optical model of a single hair.

The curves in figure 3.11 also indicate that there is a relationship between the transparency of a hair and the asymmetry in the intensity distribution of the scattered light about the specular peak. To determine if this asymmetry is due to a component of light that is internally scattered by a hair, polarization experiments were undertaken and they are described in the next subsection.

Polarization Experiments

In this experiment the incident light was linearly polarized (*s* or *p*) by passing it through a polarizer before striking the hair, and a similar polarizer was placed in front of the detector to form an analyser. The axes of these polarizers could be orientated at any angle to allow transmission of the desired polarization. The results for six hair colours and types are presented in figures 3.14, 3.15, and 3.16. In each figure there are two pairs of graphs, each pair referring to one hair fibre. One graph in each pair corresponds to *p*-polarized light incident and the other to *s*-polarized light incident. The three curves on each graph correspond to the collection of *p*-polarized only, *s*-polarized only, and their incoherent sum (represented by the *total data* legend). Although these data sets have not been normalized they were all recorded under the same experimental conditions and are therefore comparable.

From these curves it can be seen that the intensity of light detected for *p*-polarized illumination is much smaller than that detected for *s*-polarized. As for section 3.2.2, this may be explained if one considers the Fresnel intensity reflection coefficients for *s*- and *p*-polarizations between air and a hair of refractive index 1.545. Represented graphically in figure 3.7, they may be used to determine the relative amounts of polarized light that are reflected or transmitted at this boundary by reading off values from the graph at the appropriate angle. For instance, they predict that, for a 45° angle of incidence, approximately 10% of the *s*-polarized light is reflected compared with approximately 1% of *p*-polarized light. However, the experimental results exhibit a ratio of 5 : 1, rather than 10 : 1; this is because the average scale angle for these hairs is 3° , which means that the angle of incidence measured with respect to the normal to the hair *surface* is approximately 42° . At this angle the ratio between the two coefficients is approximately 5 : 1.

From figures 3.14, 3.15, and 3.16 it can be seen that the presence of a secondary

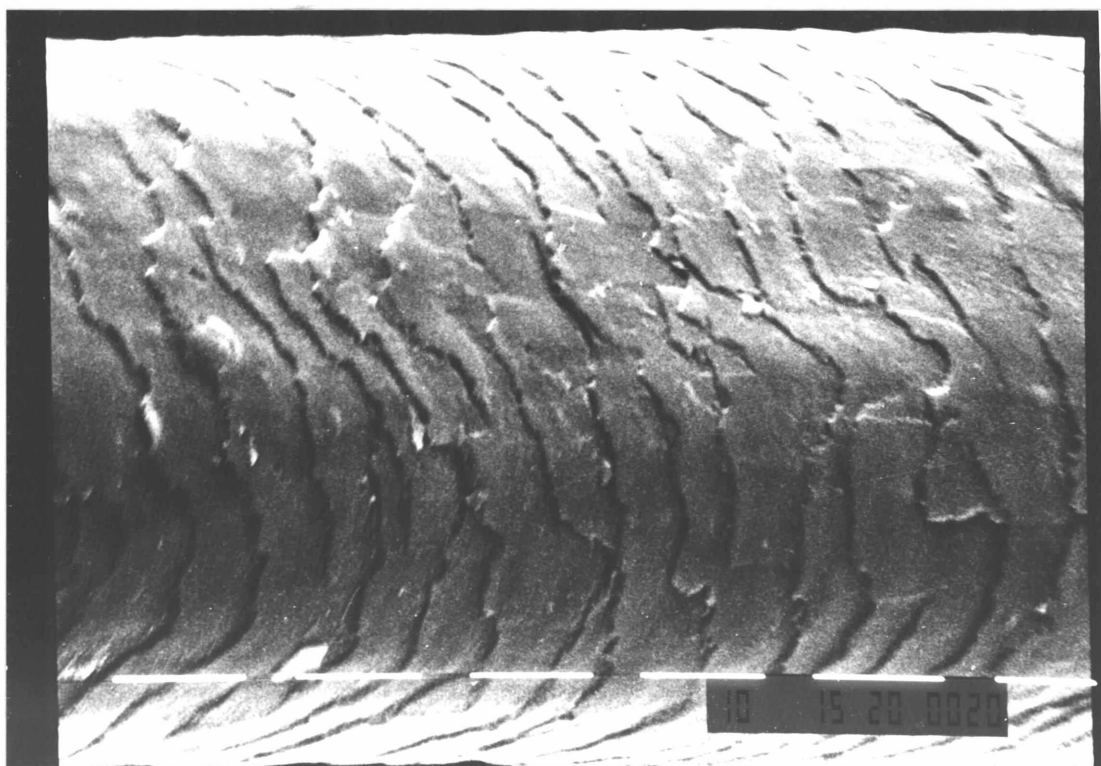
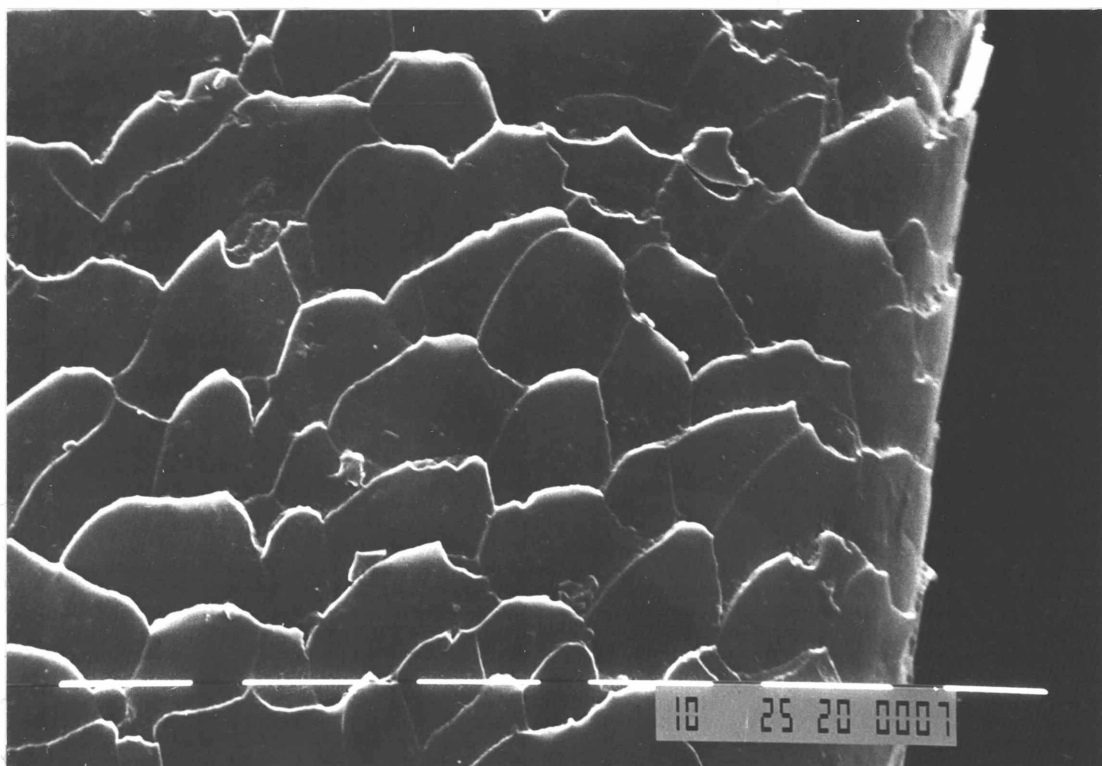


Figure 3.13: Scanning electron micrographs of hairs taken from the basis samples. Upper photograph is of a black hair, magnification 1500 $\times$, such that the length of each dashed white line is 10 μm . Lower photograph is of a brown hair, taken on the same magnification scale.

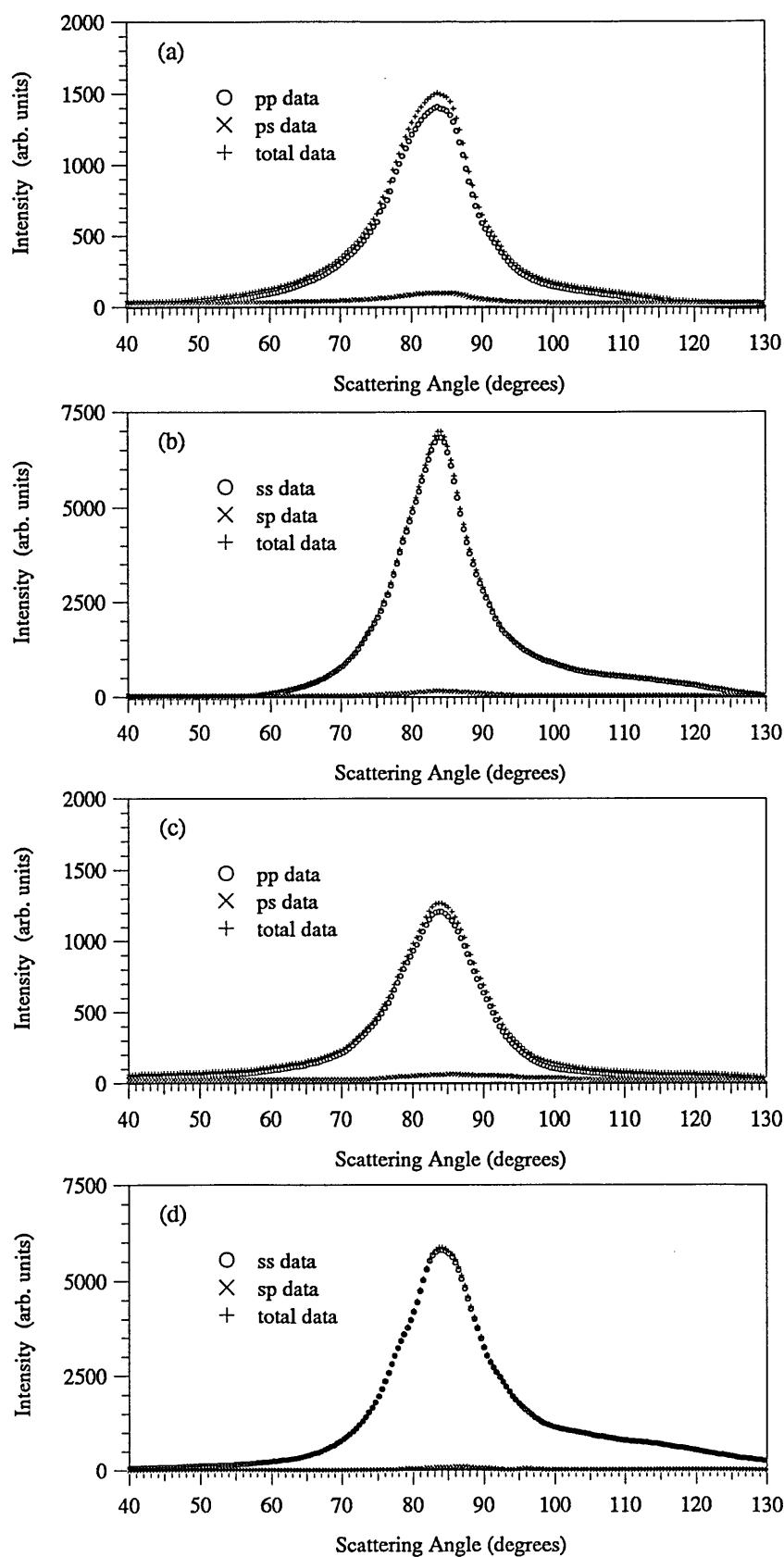


Figure 3.14: (a) Oriental hair — p -polarized light incident, (b) Oriental hair — s -polarized light incident, (c) black hair — p -polarized light incident, and (d) black hair — s -polarized light incident

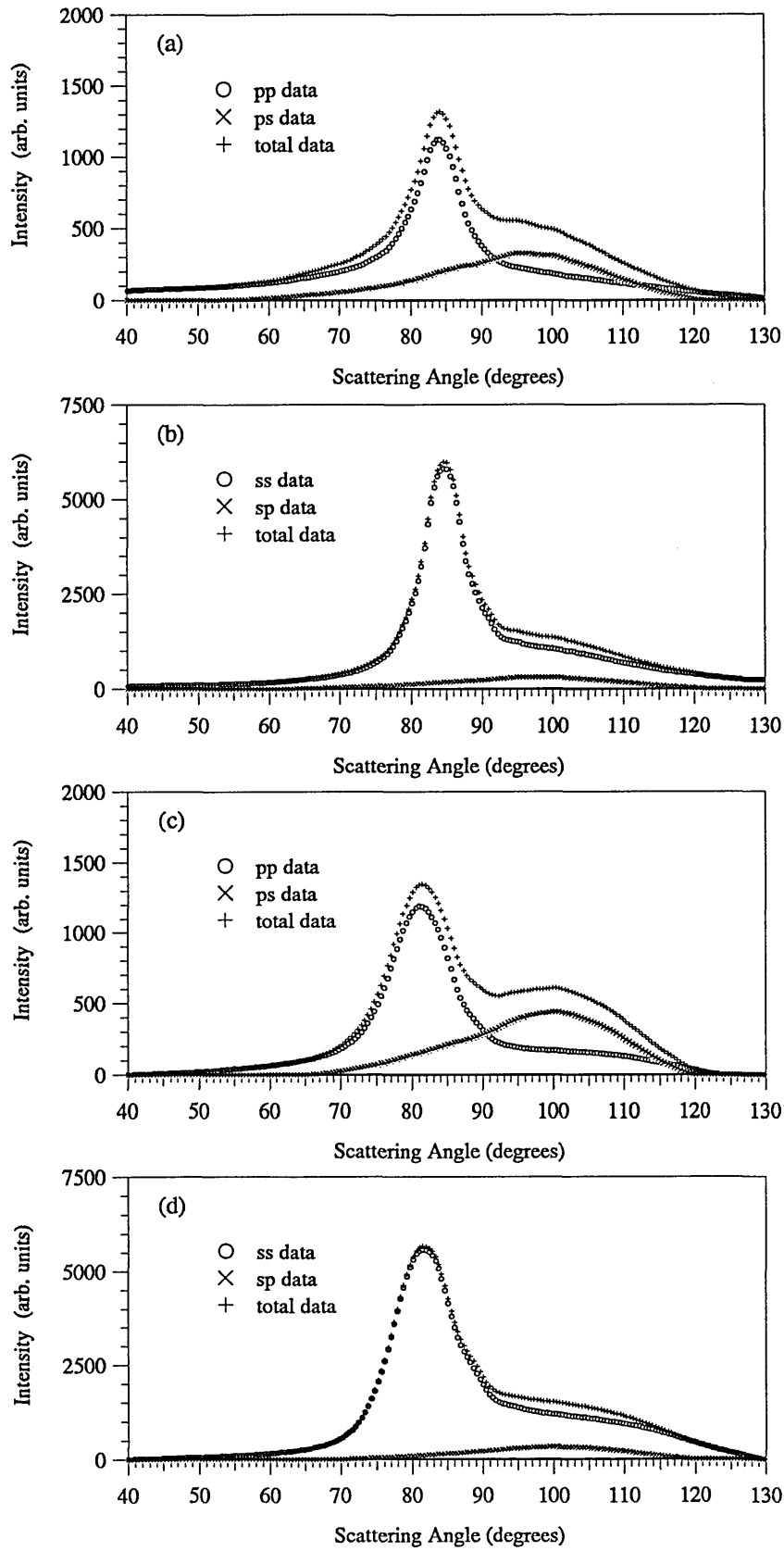


Figure 3.15: (a) brown hair — p -polarized light incident, (b) brown hair — s -polarized light incident, (c) red hair — p -polarized light incident, and (d) red hair — s -polarized light incident

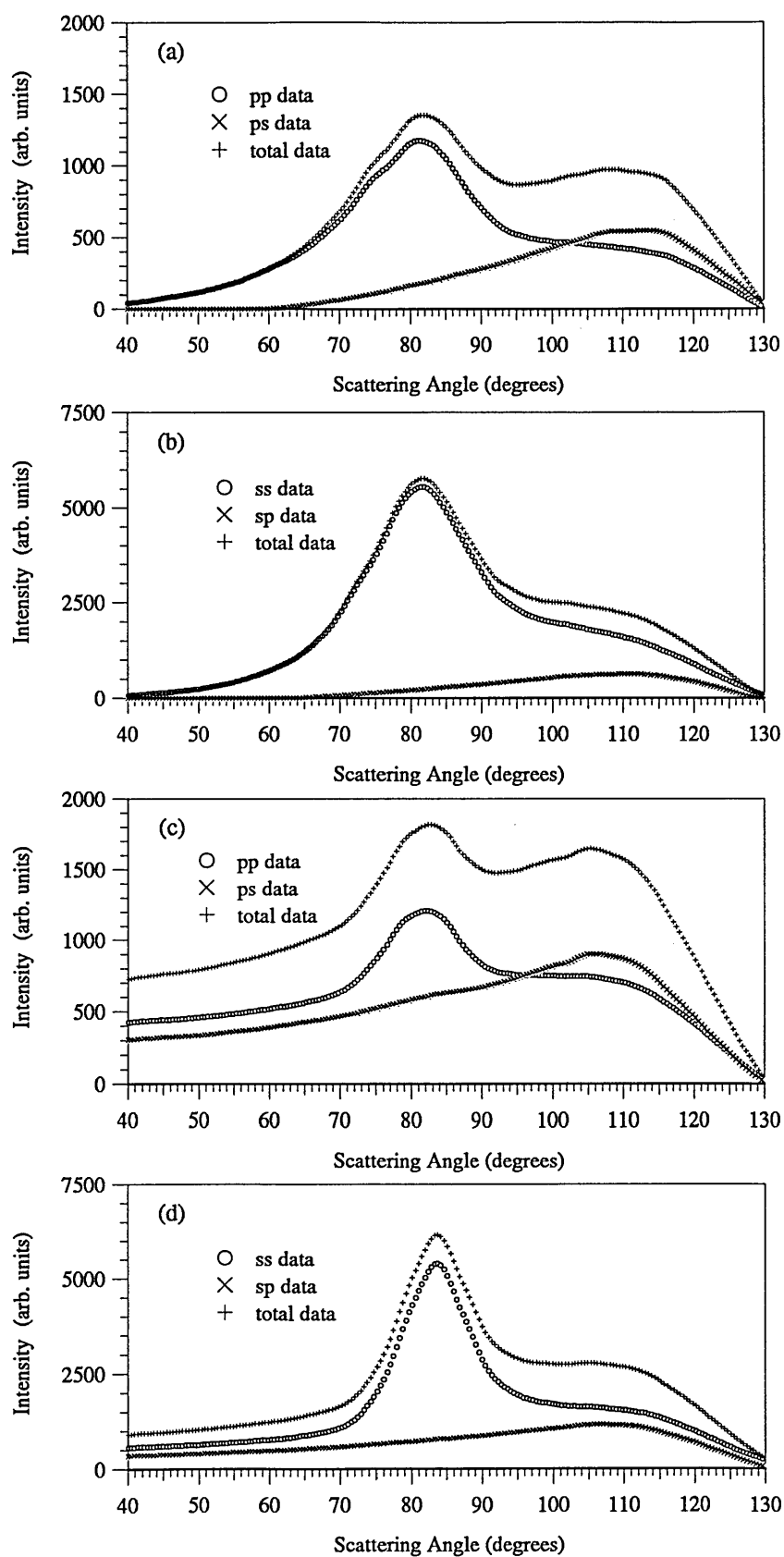


Figure 3.16: (a) blond hair — p -polarized light incident, (b) blond hair — s -polarized light incident, (c) white hair — p -polarized light incident, and (d) white hair — s -polarized light incident

peak is indeed associated with the fibre transparency, as the second peak is absent or very small for darker hairs. It was also found that for both incident polarizations the greater portion of the light which contributes to the specular peak is co-polarized (i.e. polarized in the same direction as the incident light), whereas the secondary peak is significantly composed of cross-polarized light.

This may be explained by considering what happens when light is incident on a hair fibre. Several scattering processes can occur — at the front air/fibre interface, light may be scattered into the surrounding medium (specularly and diffusely reflected) or into the hair itself (transmitted). If the surface is flat and the plane of incidence is perpendicular to this flat surface, light incident with *s*- or *p*-polarization will be directly reflected without a change in polarization, but if the surface is curved (e.g., like a hair fibre, where the plane of incidence can not be perpendicular to the entire surface) a change in the state of polarization is to be expected. However, the majority of the reflected light that is detected by the goniophotometer comes from a narrow strip along the middle of the fibre which can be considered to be locally flat (refer to figure 2.10 in chapter two, section 2.7). It is this co-polarized light which forms the majority of the specular peak.

At the front surface it is possible for light to undergo multiple scattering events. These occur if the incident light encounters pits or cracks in the cuticle. The diffuse scattering will change the polarization of the light, but the results for darker hairs (where the majority of light which enters the hair is absorbed by the high density of pigment granules in the cortex) show that there is very little cross-polarized light generated by scattering at the front surface when a hair is undamaged.

Light which is transmitted into the fibre will encounter changes in the refractive index caused by inclusions such as pigment granules and may also undergo multiple scattering (volume scattering). Hence, any light retransmitted after one or more internal reflections is likely to become, in general, elliptically polarized at some random orientation. This implies that if light of either *s*- or *p*-polarization is incident on an undamaged region of a partially transmitting fibre, the majority of the *detected* light which has its polarization altered will have entered the fibre.

As can be seen for the white, blond, red, and brown hairs, the secondary peaks are significantly composed of cross-polarized light. Thus, it may be concluded that the shape of the total light intensity distribution is dependent on the transparency of the fibre. To confirm this, it was decided to gold-coat one fibre from each sample

to prevent light entering the hair, effectively removing any contributions from the internal structure, and then repeat the measurements.

Gold-coating Fibres

The hairs were coated with a thin layer of gold (less than $0.5\mu\text{m}$) by using vacuum deposition. As, at visible wavelengths, gold is a good approximation to a perfect conductor, thin gold layers have negligible transmission; it is not possible for any light to enter a gold-coated fibre *and* return to the detector.

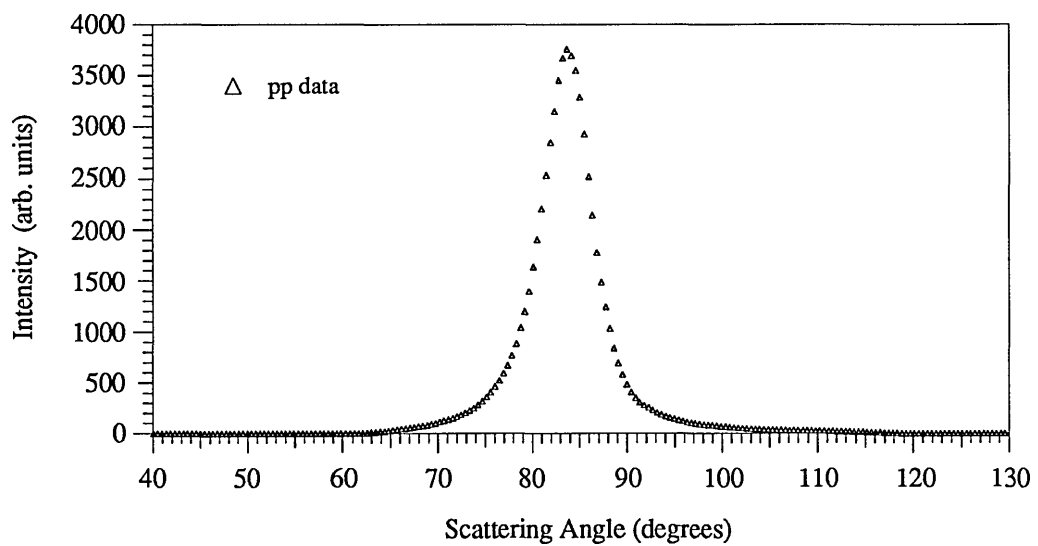


Figure 3.17: Goniophotometric scan from a gold-coated hair; *p*-polarized light incident at 45° .

Figure 3.17 shows a typical result for a white fibre which has been gold-coated. (Note that, as the detected signal is much larger in this case, the scan for this fibre was made on a reduced sensitivity setting and therefore is not directly comparable with figures 3.14, 3.15, and 3.16.) The intensity distribution of scattered light was found to be almost symmetrical about the direction of the specular reflection. Any slight asymmetries (towards higher angles) may be due to the detector seeing light scattered from the rough edges of the scales as it scans and looks along the hair from tip to root. Therefore, for such coated fibres the light scattering must be dominated by properties of the front surface.

Fibre Orientation

In all the measurements taken so far the hairs have been arranged such that the root end of the hair was to the right (RER) when observing in the propagation direction of the incident beam as illustrated in figure 3.12. However, measurements made on hairs orientated in the opposite sense (root-end-left (REL)) indicate that there are several differences between the intensity distributions of the scattered light for the two orientations. Such an experiment was performed on two individual hairs (one black and one white); in each case data were collected, using unpolarized light, at three angles of incidence. The results are summarized in figure 3.18 and table 3.3.

Table 3.3: A summary of three parameters characterizing the light-scattering envelopes produced by both orientations of the two hair fibres studied.

Hair Type	Orientation and Angle (degrees)	Specular Angle (degrees)	Specular Intensity (arbitrary units)	Av. Scale Angle α (degrees)
Black	RER at 45.0°	83.7±0.1	1836±9	3.2±0.1
	REL at 45.0°	96.3±0.1	2343±12	3.2±0.1
	REL at 38.7°	83.7±0.1	1794±9	3.2±0.1
White	RER at 45.0°	84.2±0.1	1515±7	2.9±0.1
	REL at 45.0°	95.6±0.1	1881±9	2.8±0.1
	REL at 39.2°	84.2±0.1	1495±7	2.9±0.1

Examining figures 3.18 (a) and (c) which compare the two hair orientations at the same angle of incidence, the most immediately obvious difference (as noticed by Stamm et al. [57]) is in the magnitude and angular position of the specular peak. The latter may be attributed to the effect of the cuticle cells being inclined at an angle to the fibre axis. In all the single fibre experiments the angle of incidence was taken as the angle between the normal to the fibre axis and the incoming beam, and thus did not take into account the effect of the average scale angle on the true *surface* normal. Thus, for a mean scale angle, α , the mean angle of incidence, for RER orientation, was $45^\circ - \alpha$ and for the REL orientation it was $45^\circ + \alpha$, producing a 2α difference in the actual angle of incidence between the two arrangements. A difference in angle of incidence will be accompanied by a change in the values of the Fresnel reflection coefficients at the air/dielectric boundary, which is approximately 16% for a dielectric medium with a refractive index of 1.545.

To confirm if it was merely the inclination of the cuticle scales which was causing this discrepancy, each hair was orientated (REL) at an angle which took this into

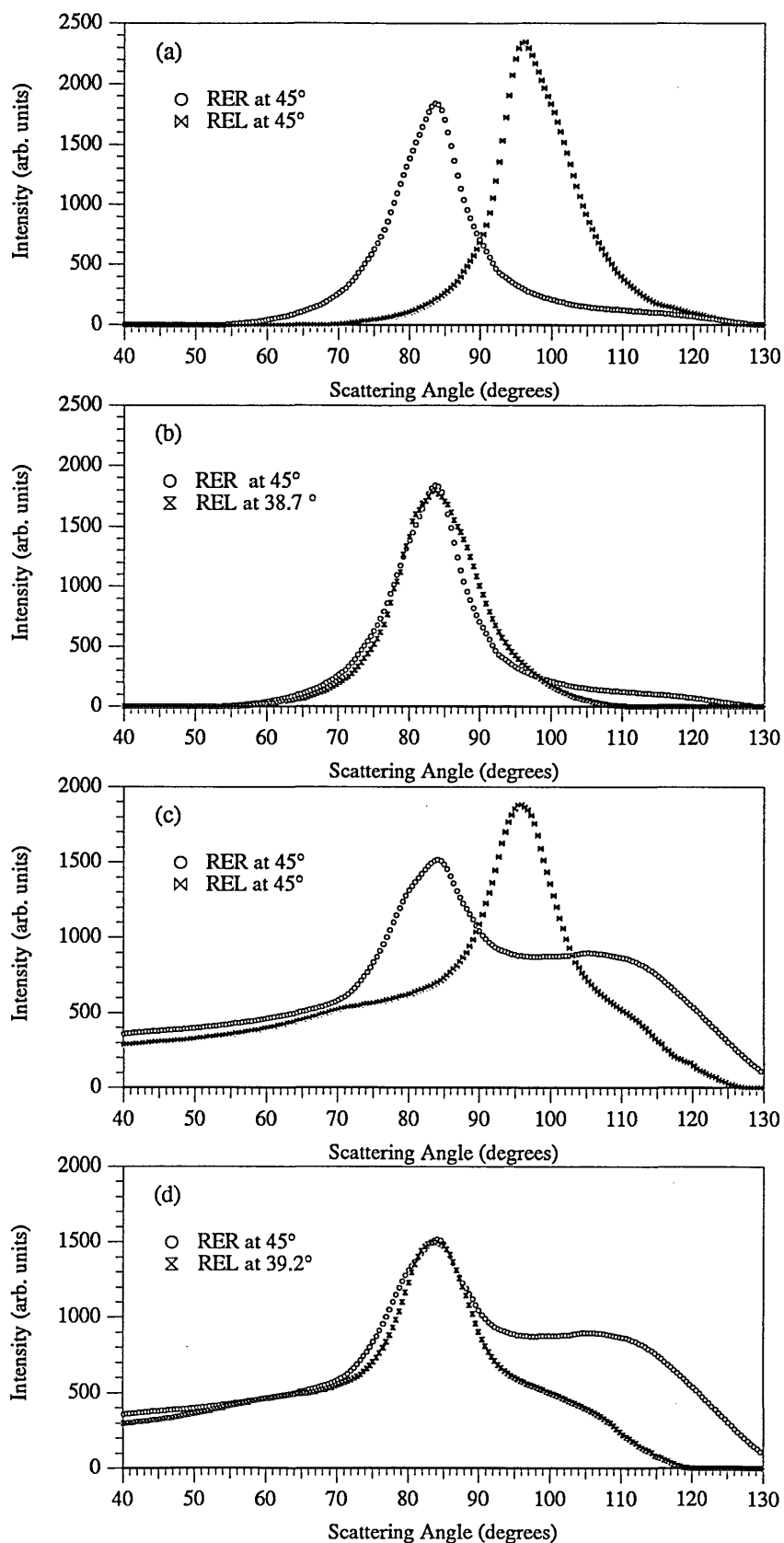


Figure 3.18: Goniophotometric scans from two hairs (the black hair results are given in (a) and (b), and those for the white hair in (c) and (d)) arranged RER at 45° and REL at 45° and at $45^\circ - 2\alpha$.

account (i.e. making the angle of incidence to the true surface normal the same as for 45° RER). As can be seen from the graphs in figures 3.18 (b) and (d), when the shift due to the average scale angle was taken into account, the peak intensities became approximately equal.

It may also be noted from the graphs, particularly for the white hair, that when the hair's orientation is reversed the secondary 'peak' does not change sides (i.e. the REL case was not simply a reversed version of the RER case). This result is consistent with the explanations given for the origin of the secondary peak. However, when compared to a graph produced by Stamm et al. [57] on page 30, summarizing an investigation into the light-scattering distributions from an array of dark brown hairs orientated first RER and then REL, it was found that in this case the secondary peak had reversed. For dark brown hair to show the presence of a large secondary peak was considered questionable, and as it had reversed sides it is thought that it was more likely to have been due to a small number of the hairs in this sample being mounted the wrong way round. Refer to chapter five, section 5.1 where a result is presented for just such a case.

Scattering as a Function of Fibre Surface Condition

In earlier discussions in this section it was mentioned that the FWHM of the specular peak may be related to the surface condition of a hair. If this is so then it may be used to monitor the effects of weathering and other surface damage along the length of a fibre. To investigate this further, goniophotometric intensity scans were taken at three positions: 5mm, 25mm, and 55mm from the root end of the six hairs which form the basis group.

At each of these positions along the hair, unpolarized light was incident at 45° to the fibre axis normal. The results, summarized in figure 3.19 and table 3.4, show that, as scans were made further away from the root end of the hair, the specular peak broadened and the total amount of light scattered into the plane of detection was observed to decrease. These effects may be explained by considering the natural weathering and grooming processes to which all hairs are exposed. Over a period of time (a typical hair growth rate is 0.3mm per day), the cuticle gradually erodes. During this process many cells become raised before breaking off, leading to an increase in the distribution of existing scale angles which, in turn, will lead to an increase in the angular spread of the light reflected by the surface, producing

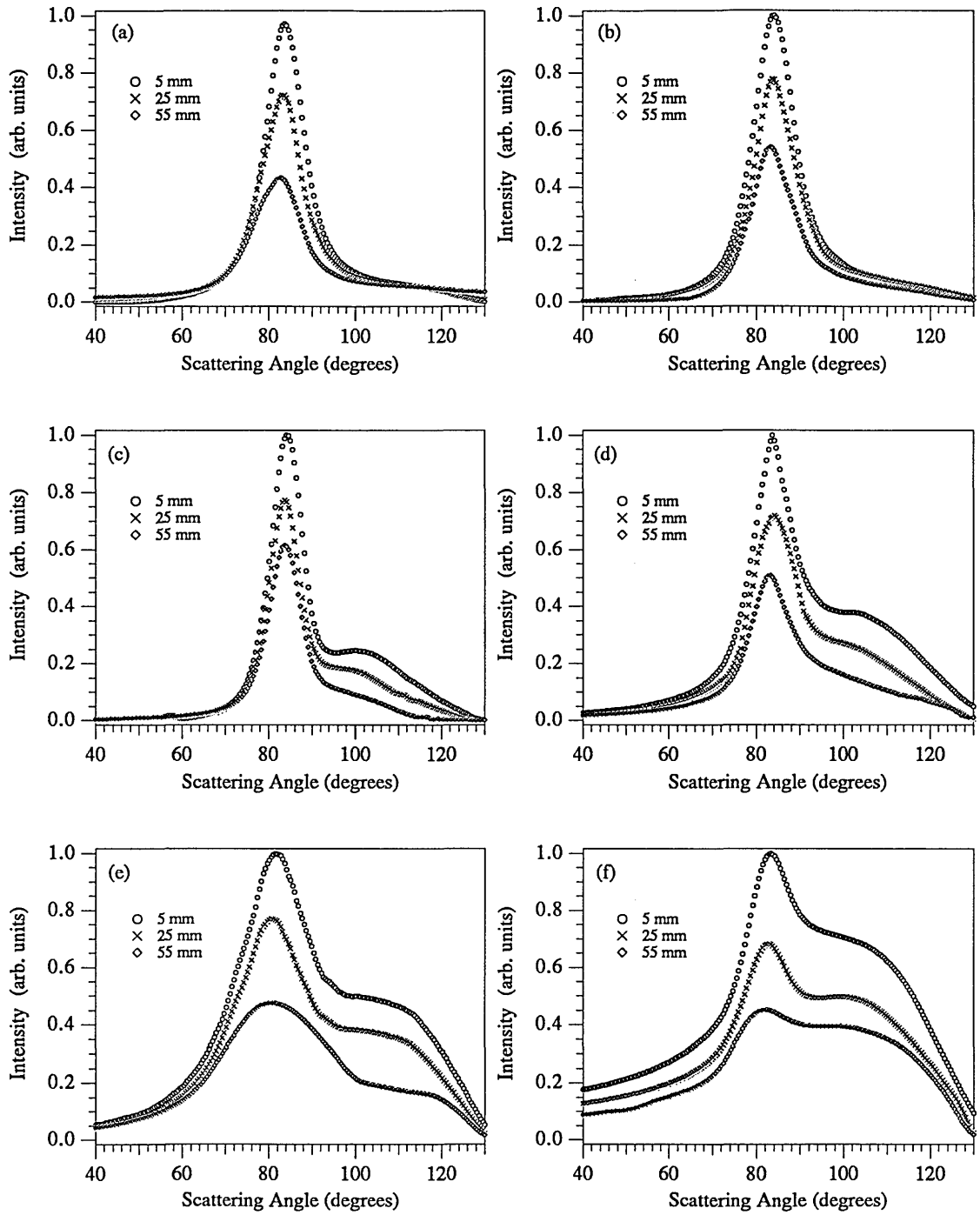


Figure 3.19: Scans from (a) an Oriental black hair, (b) a Caucasian black hair, (c) a Caucasian brown hair, (d) a Caucasian red hair, (e) a Caucasian blond hair, and (f) a Caucasian white hair, at 3 positions along each hair. Unpolarized white light was incident at 45° to the fibre axis for each measurement.

Table 3.4: Parameters characterizing goniophotometric scans at three positions on each hair.

Hair Type	Position in mm	FWHM (degrees)	Av. Scale Angle α (degrees)	Contrast Gloss G_c (no units)
Oriental	5	10.7 ± 0.1	3.2 ± 0.1	0.999 ± 0.006
	25	11.9 ± 0.1	3.4 ± 0.1	0.986 ± 0.006
	55	13.8 ± 0.1	3.6 ± 0.1	0.957 ± 0.005
Black	5	11.2 ± 0.1	2.9 ± 0.1	0.994 ± 0.006
	25	11.7 ± 0.1	3.2 ± 0.1	0.993 ± 0.006
	55	12.4 ± 0.1	3.4 ± 0.1	0.992 ± 0.006
Brown	5	8.6 ± 0.1	2.9 ± 0.1	0.994 ± 0.006
	25	9.0 ± 0.1	3.1 ± 0.1	0.992 ± 0.006
	55	9.5 ± 0.1	3.2 ± 0.1	0.990 ± 0.006
Red	5	12.5 ± 0.1	3.2 ± 0.1	0.968 ± 0.006
	25	12.9 ± 0.1	3.3 ± 0.1	0.962 ± 0.006
	55	13.5 ± 0.1	3.4 ± 0.1	0.958 ± 0.005
Blond	5	27.0 ± 0.1	4.3 ± 0.1	0.929 ± 0.005
	25	28.1 ± 0.1	4.5 ± 0.1	0.927 ± 0.005
	55	31.95 ± 0.1	4.7 ± 0.1	0.886 ± 0.005
White	5	41.5 ± 0.1	3.4 ± 0.1	0.803 ± 0.006
	25	43.2 ± 0.1	3.6 ± 0.1	0.793 ± 0.006
	55	48.4 ± 0.1	4.3 ± 0.1	0.786 ± 0.006

a broader specular peak. Under such conditions of increased surface roughness, more light is likely to undergo multiple scattering at the surface and be diffusely scattered out of the plane of incidence. This could explain the overall reduction in light detected at positions further along the hair away from the root.

It is quite difficult for the human eye to detect any significant change in visual appearance over the length of a single short strand of hair, but the visible changes in appearance of a head of long hair which has suffered considerable grooming damage are easier to discern, particularly if all the layers of cuticle cells have been eroded and the exposed, unbound cortex has split into its fibrous elements. Even a dark-coloured hair in this condition (generally known as a “split end”) appears white to an observer, as the disrupted arrangement of its internal structure scatters light in all directions (multiple scattering).

For very long hairs (greater than 20cm) this type of surface wear is common. Measurements of scale angle from a hair fibre 45cm long (given in table 3.5) show that initially the scale angle increases but eventually there is a rapid decrease. From the results for the 41–42cm zone it can be seen from the value of the scale angle

Table 3.5: Parameters characterizing goniophotometric scans at each zone along a long brown hair.

Measurement Zone on Hair	Av. Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss G_c (no units)
5-6 cm	3.0 ± 0.1	7.1 ± 0.1	0.994 ± 0.006
11-12 cm	3.3 ± 0.1	8.6 ± 0.1	0.974 ± 0.006
17-18 cm	3.6 ± 0.1	10.8 ± 0.1	0.953 ± 0.005
23-24 cm	2.8 ± 0.1	11.2 ± 0.1	0.927 ± 0.005
29-30 cm	1.5 ± 0.1	8.2 ± 0.1	0.912 ± 0.005
35-36 cm	0.9 ± 0.1	7.7 ± 0.1	0.909 ± 0.005
41-42 cm	0.0 ± 0.1	6.9 ± 0.1	0.881 ± 0.005

that the layers of cuticle cells have been removed.

Angle of Illumination

This experiment was designed to find the relationship between the contrast gloss of hair and the angle of illumination of the hair. A hair from each of the six sample groups was individually illuminated at four angles of incidence (30° , 40° , 50° , and 60°) with s-polarized white light. As before, the angles of incidence stated are those which were measured with respect to the fibre axis normal, and the scattering angle was measured with respect to the incident beam. The goniophotometric results are summarized in figures 3.20 and 3.21. Each set of data was collected using the same incident beam power and then the four sets of data per hair type were normalized[†] such that a best fit to the curve of the Fresnel reflection coefficient $R_s \times I_0$ was obtained, where I_0 is the incident intensity in this case normalized to unity. Thus each curve in a set may be compared with its companions and each set of graphs is also comparable. By normalizing the data in this manner it is possible to monitor the variation in intensity in the specular direction and determine if it is solely due to the Fresnel intensity reflection coefficient varying with increasing incident angle. Changes in other parameters, such as FWHM, scale angle, and contrast gloss, have been monitored and are summarized for each hair in tables 3.6, and 3.7.

Note: the adopted convention of representing scattering data by a plot symbol

[†]Normalization was carried out by comparing the peak intensity values of each data set with the appropriate Fresnel reflection coefficient and determining from this an average reduction ratio, i.e. the factor by which I_0 was normalized to equal unity.

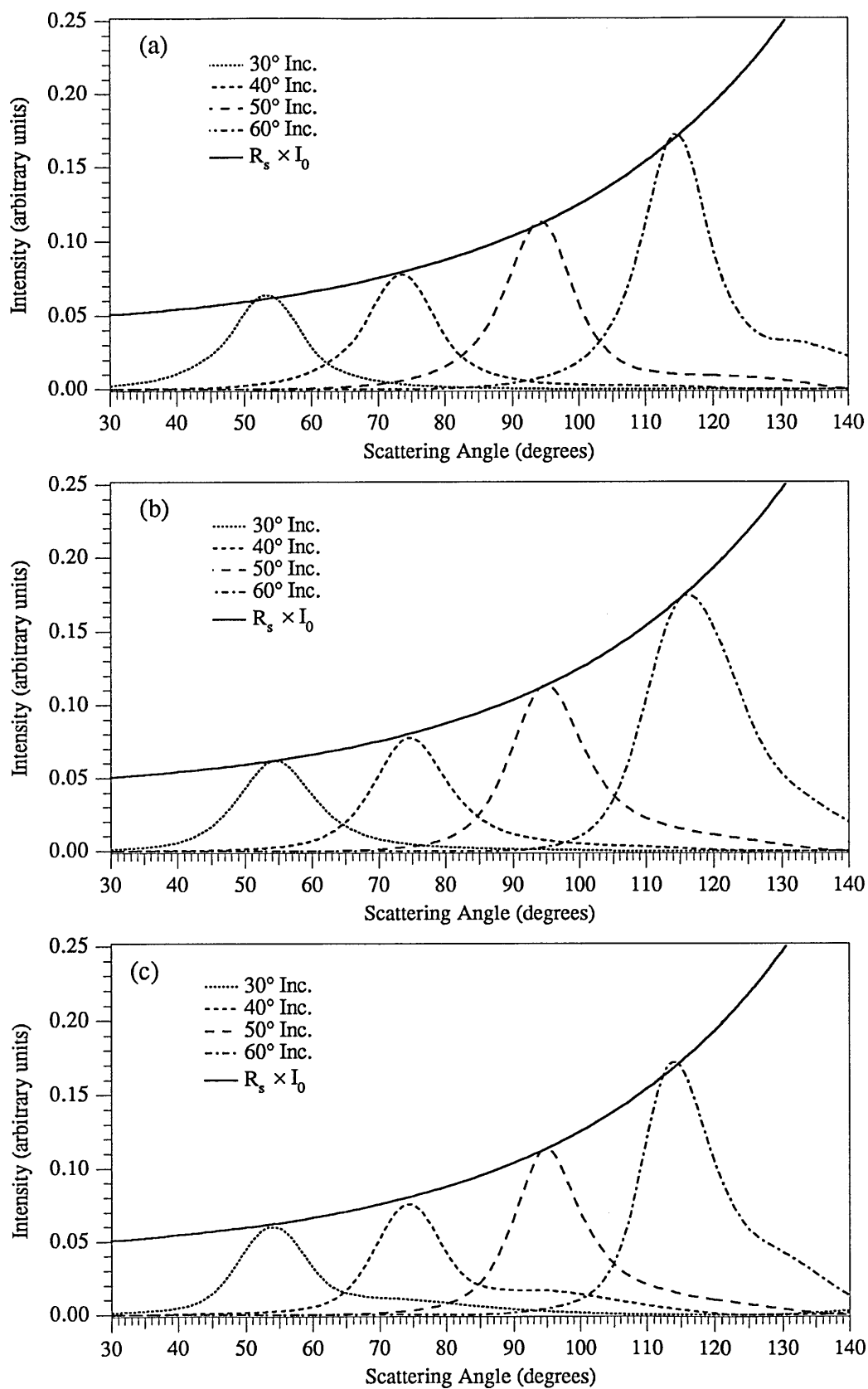


Figure 3.20: Normalized light-scattering envelopes produced by (a) an Oriental hair, (b) a black hair, and (c) a brown hair, at four angles of incidence using s-polarized light.

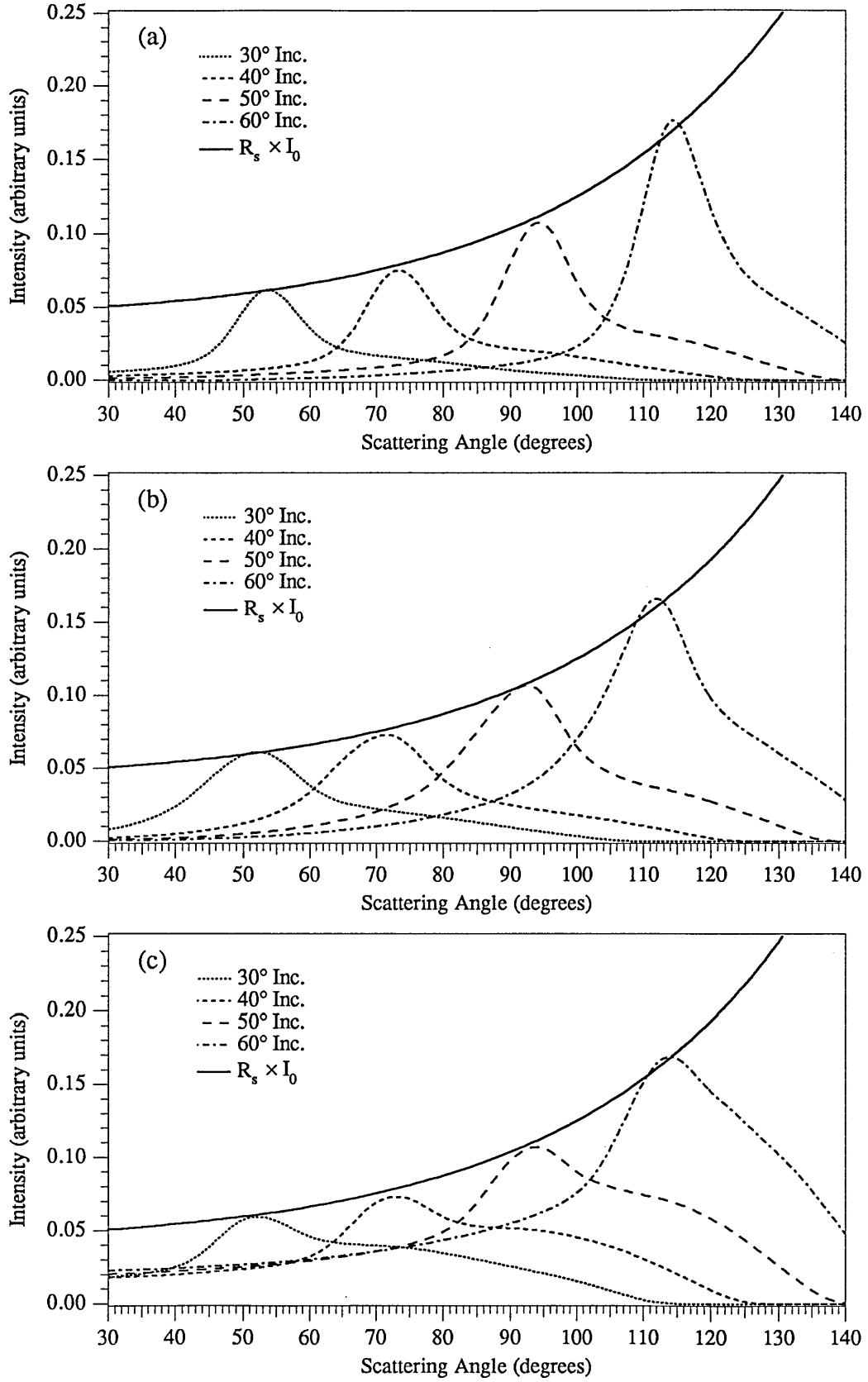


Figure 3.21: Normalized light-scattering envelopes produced by (a) a red hair, (b) a blond hair, and (c) a white hair, at four angles of incidence using s -polarized light.

Table 3.6: Summary of parameters calculated from the curves produced by individual Oriental black, Caucasian black, and Caucasian brown hairs, measured over a range of incident angles.

Incidence Angle (degrees)	Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss G_c (no units)
Oriental 30°	$3.25 \pm .5$	$11.3 \pm .5$	0.969 ± 0.006
Oriental 40°	$3.10 \pm .5$	$13.9 \pm .5$	0.995 ± 0.006
Oriental 50°	$2.75 \pm .5$	$12.3 \pm .5$	0.999 ± 0.006
Oriental 60°	$2.65 \pm .5$	$11.8 \pm .5$	1.000 ± 0.008
Black 30°	$2.75 \pm .5$	$13.4 \pm .5$	0.983 ± 0.005
Black 40°	$2.65 \pm .5$	$13.3 \pm .5$	0.997 ± 0.006
Black 50°	$2.55 \pm .5$	$13.5 \pm .5$	0.998 ± 0.006
Black 60°	$2.00 \pm .5$	$15.6 \pm .5$	1.000 ± 0.008
Brown 30°	$3.00 \pm .5$	$12.2 \pm .5$	0.977 ± 0.006
Brown 40°	$2.85 \pm .5$	$12.5 \pm .5$	0.994 ± 0.006
Brown 50°	$2.60 \pm .5$	$12.5 \pm .5$	0.997 ± 0.006
Brown 60°	$2.85 \pm .5$	$13.1 \pm .5$	1.000 ± 0.008

larger than the error associated with the point has temporarily been abandoned in order to maintain clarity of presentation. If this had not been the case the standard plot symbols as used in figure 3.11 would have been appropriate.

From the results in figures 3.20 and 3.21 it is evident that the maximum value of the specular peak closely follows the Fresnel intensity reflection coefficient R_s , calculated for an *s*-polarized beam reflected from a dielectric of refractive index 1.545.

Stamm et al. [57] observed and reported the presence, at high angles of incidence (50° or 60°), of a third peak in the light-scattering distribution from hair. This peak was always found to occur at the mirror angle of reflection and was called the ‘equal angle peak’. Examination of the results at high angles of incidence in this experiment did not reveal the presence in any of the graphs of such a peak. Of course, Stamm et al. were studying parallel arrays of hair rather than an individual hair fibre, so perhaps this is an important difference. Further comments on the presence/absence of an equal angle peak will be left until chapter five, section 5.3.1, where a report of this experiment using parallel arrays of hair is presented.

As can be seen from these tables, the contrast gloss measurement increases in value with increasing angle of incidence, indicating that, if gloss measurements are to be compared, they must not only be taken over the same solid angle of detection but also at the same angle of incidence.

Table 3.7: Summary of parameters calculated from the curves produced by individual Caucasian red, blond, and white hairs, measured over a range of incident angles.

Incidence Angle (degrees)	Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss G_c (no units)
Red 30°	$3.20 \pm .5$	$13.7 \pm .5$	0.909 ± 0.006
Red 40°	$3.30 \pm .5$	$14.0 \pm .5$	0.944 ± 0.006
Red 50°	$3.00 \pm .5$	$14.9 \pm .5$	0.968 ± 0.005
Red 60°	$2.85 \pm .5$	$14.7 \pm .5$	0.991 ± 0.005
Blond 30°	$3.90 \pm .5$	$20.4 \pm .5$	0.872 ± 0.006
Blond 40°	$4.00 \pm .5$	$21.2 \pm .5$	0.932 ± 0.006
Blond 50°	$3.30 \pm .5$	$21.2 \pm .5$	0.952 ± 0.006
Blond 60°	$3.90 \pm .5$	$20.8 \pm .5$	0.967 ± 0.005
White 30°	$3.90 \pm .5$	$43.2 \pm .5$	0.693 ± 0.005
White 40°	$3.50 \pm .5$	$44.5 \pm .5$	0.729 ± 0.005
White 50°	$3.10 \pm .5$	$40.2 \pm .5$	0.765 ± 0.006
White 60°	$3.10 \pm .5$	$31.6 \pm .5$	0.820 ± 0.006

Mechanical Hair Damage

The surface of a hair is comprised of overlapping cuticle cells which protect the inner cortex from damage. Although these outer cells consist of tough keratin they may occasionally suffer catastrophic damage in a very localized area. This can occur if a hair becomes trapped in, for instance, a hair clip and is then pulled free against the scale overlap (ie. tip to root). Such an example of localized damage was found on a mid-brown hair, approximately 5cm from the root. The graph in figure 3.22 shows two curves — one at a portion 5mm from the damaged portion in the direction of the root and the other at the damaged portion itself. As may be seen from the goniophotometric data, the damaged portion of the hair has produced a stepped curve which contains extra structure in the region of the specular peak. This probably corresponds to whole sections of scales being raised and moved. The diffuse level of scattering (at high and low scattering angles) is also considerably higher when compared to the undamaged curve. When the cells are badly damaged they may break apart, scattering small particles of debris on the surface, and so increasing the possibility of multiple light-scattering.

Under a light microscope this same portion of the hair appeared to have been squashed and flattened, the scales lifted, broken, and disordered. The spreading of the hair would have increased its dimension in one direction, and if this hair had

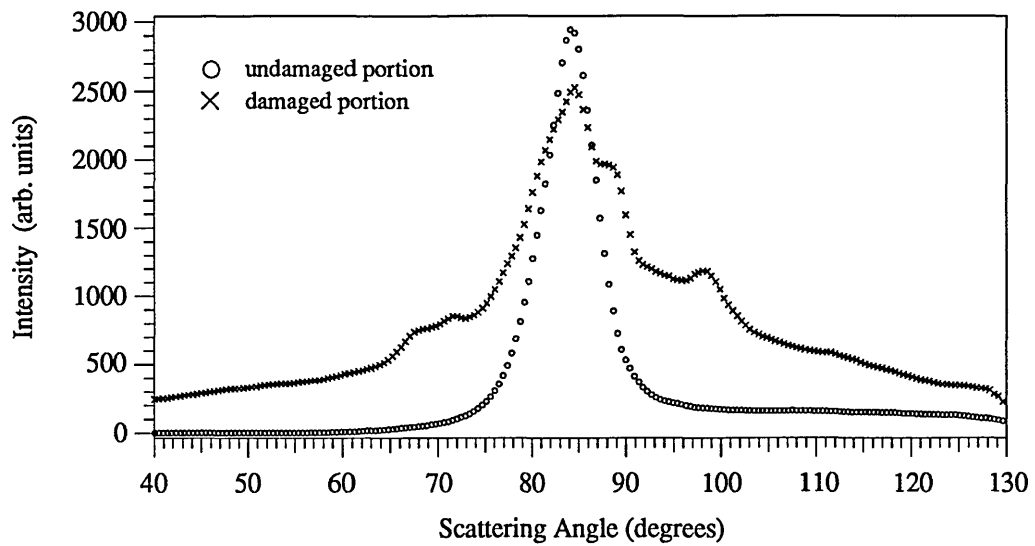


Figure 3.22: This graph compares the light-scattering envelopes produced by the same hair at two adjacent positions illuminated using unpolarized white light incident at 45° .

been orientated to present its widest face during the experiment it might explain why the total amount of light detected from the damaged region was greater than that from the undamaged region (found by comparing areas under the two curves).

The growth patterns for human hair indicate that at any one time a small percentage ($\sim 10\%$) of hairs have been exposed to weathering for a much longer period than the rest, their follicles having previously entered the dormant phase. These hairs at any given distance from the root will be more weathered than a hair which is still growing.

Because anomalies are possible in localized measurements on individual hairs it was felt that light-scattering experiments assessing the effects of cosmetic treatments on the appearance of hair would be more suited by the use of planar arrays of hair where a large surface is illuminated. Any unrepresentative contributions from an unusually, or excessively, damaged hair should be outweighed by the average response of the rest.

3.3.2 Single Hair Orientated Vertically

This experiment investigated the light-scattered envelopes produced by individual hairs orientated vertically to the plane of incidence and illuminated with the quartz halogen lamp. As before, one hair from each of the basis samples was used. The results generated with linearly polarized light by the black, blond, and white hairs

are presented in figures 3.23, 3.24, and 3.25. The results of this experiment will

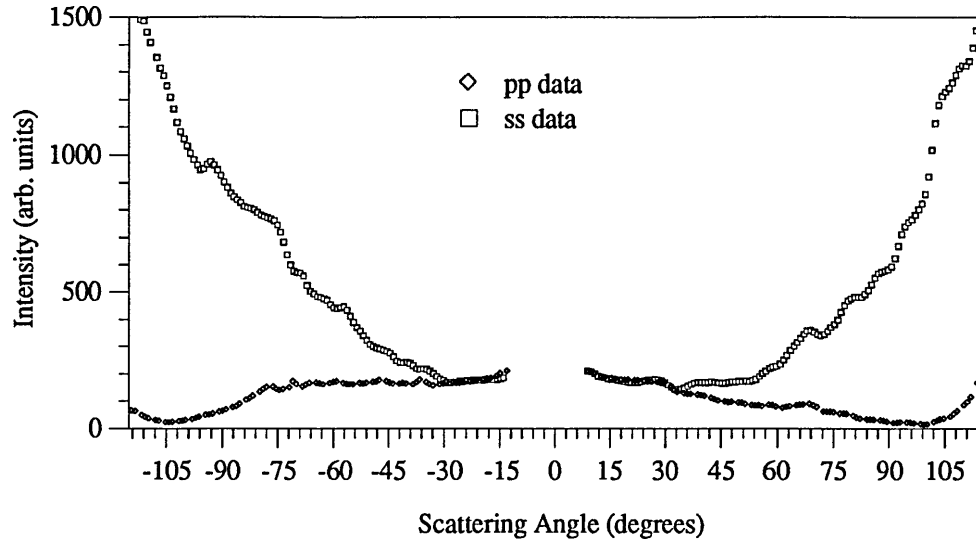


Figure 3.23: Light-scattering envelopes produced by a black hair orientated vertically; scan range of -115° to $+115^\circ$.

be compared and contrasted with those obtained in section 3.2.2, which examined individual hairs orientated vertically and illuminated with coherent monochromatic radiation. As in the coherent light experiment, each hair was rotated about its own vertical axis to determine the effects, if any, that altering the orientation of the hair's cross-section to the incident beam had on the scattered light measurements. Note: in these experiments the angle of scatter was measured with respect to the fixed incident beam, and the gap in the data points in the direction of backward scatter indicates the angles over which the detector blocked the incident beam during a scan. Although data points were lost in the direction of backscatter, the absence of supporting posts in this configuration of the dedicated goniophotometer meant that it was possible to collect data over a wider range of scan angles (-115° to $+115^\circ$) than was possible when using the scatterometer in section 3.2.2.

As before, the light-scattering envelope produced by the hairs divided into two types of results; those for the dark hairs, where the distributions are dominated by the light scattered from the front air/cuticle interface of the hair; and those for the transparent hairs, where the total envelope has more than one contribution.

Considering first the results for dark hairs and taking into account the wider scan range, it can be seen that the shapes of the *s*- and *p*- polarized curves in figure 3.23 are very similar to those obtained for a dark hair under conditions of coherent illumination (see figure 3.3). This being the case, the reader is referred

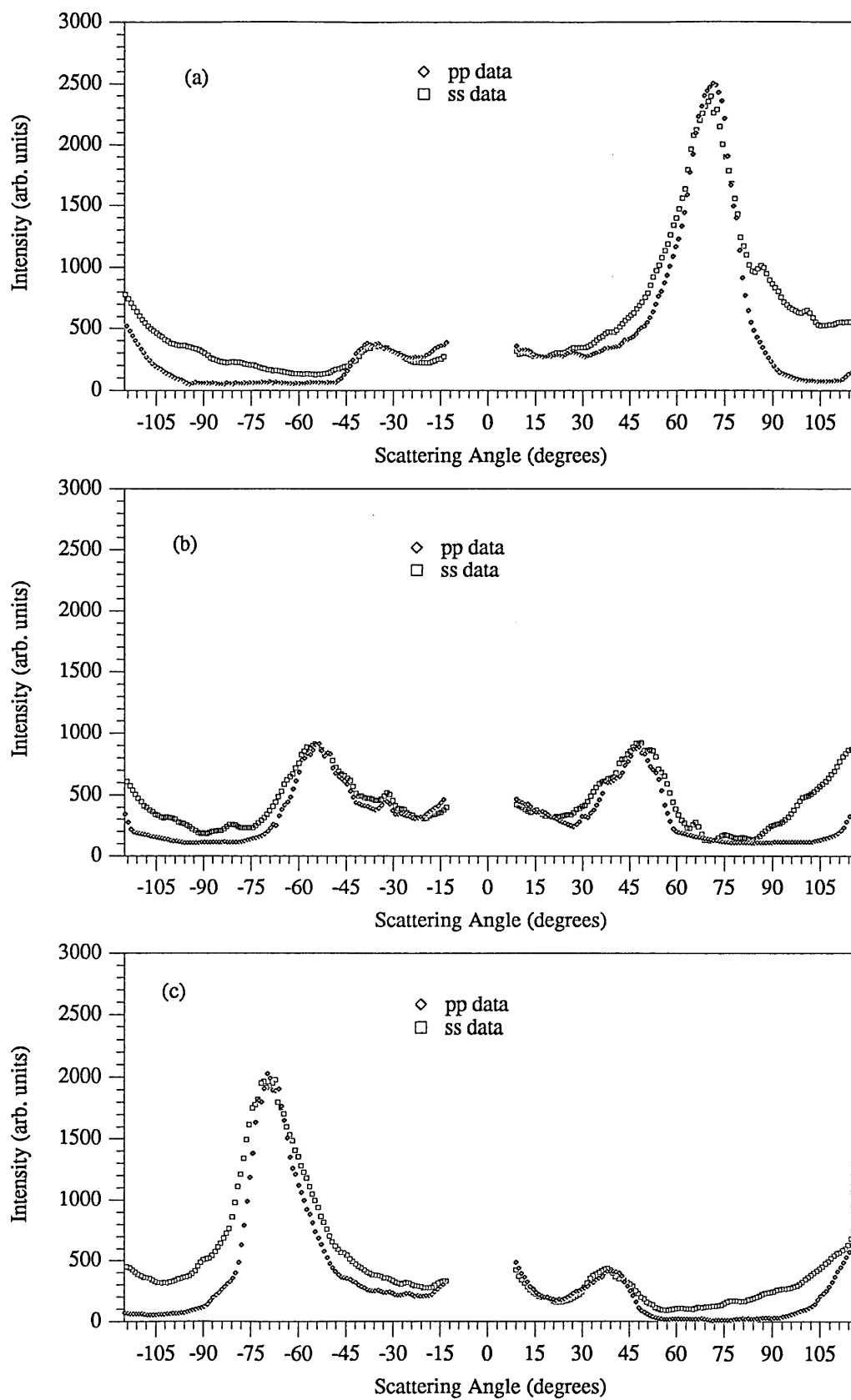


Figure 3.24: Light-scattering envelopes produced by a blond hair orientated vertically, (a) as mounted arbitrary, (b) after rotation through 15° , and (c) after rotation through a further 15° ; scan range of -115° to $+115^\circ$.

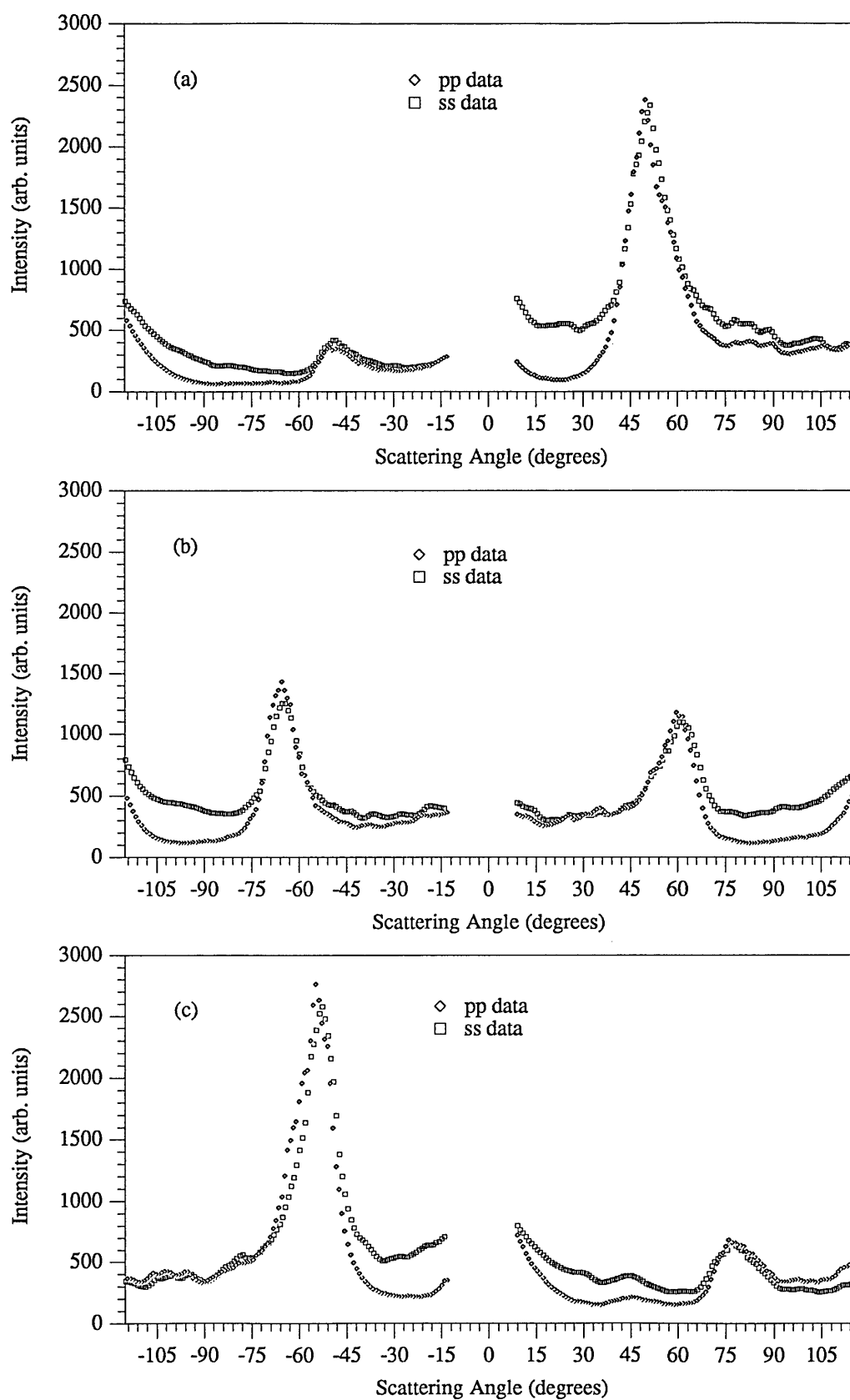


Figure 3.25: Light-scattering envelopes produced by a white hair orientated vertically, (a) as mounted arbitrary, (b) after rotation through 15° , and (c) after rotation through a further 15° ; scan range of -115° to $+115^\circ$.

to section 3.2.2, where the general shapes of these curves are explained in terms of the Fresnel reflection coefficients. Since in these experiments a wider scan range has been possible, it now includes the scattering angles at which the *pp data* curve is predicted to decrease in value to zero. Using a refractive index of 1.545 and the Brewster angle condition given in equation 3.4, it was calculated that the intensity of the *pp data* curve should equal zero at scattering angles of approximately $\pm 114^\circ$. Experimentally, the value of the *pp data* curve was not found to fall to zero at any angle but did reach minimum values at scattering angles of $\pm 101^\circ$, which corresponds to a Brewster angle $\rho_B = 50.5^\circ$ and the hair having a refractive index of 1.2. Since this value is considerably smaller than any of those produced by other methods used to determine the refractive index of hair (see chapter four, section 4.2 and is less than that of almost all other dielectric materials), it is thought that at high scattering angles ($> \pm 90^\circ$) another component of the incident light was adding to the total light detected. This would have the effect of preventing the *pp data* curve reaching zero intensity and introducing these premature minima. Another explanation may be that, although the Fresnel reflection coefficients predict the basic features of the scattering distribution, they are not entirely applicable, as the surface of an individual hair is curved and irregular.

Rotation of the dark hairs was not found to change the shape of their light-scattering envelopes but only the magnitude of the intensity relative to the first scan. When a dark hair with an elliptical cross-section is rotated about its own axis, it effectively presents a varying size of diameter to the incident beam. In one orientation the diameter would be at a maximum, intersecting a larger proportion of the beam than when it is orientated so that the minimum diameter is presented to the incident beam. As for the coherent results, rotation of the transparent hairs (white and blond) did alter the light-scattering distribution. Three results are therefore presented for each of the two hairs discussed here: the first (a) is as it was mounted (arbitrarily), the second (b) is after it was rotated by 15° with respect to the original position, and the third (c) is after it was rotated through 30° with respect to the original position. As in the coherent illumination experiments, the fact that the two data sets chosen for presentation are both rotated through units of 15° is merely a coincidence. For these white-light experiments the red fibre produced a set of results intermediate between the curves obtained for dark (black and brown) and transparent (white and blond) hairs. This was interpreted in terms of the red

phaemelanin pigment absorbing the blue and green wavelengths of the incident light and scattering the red. This did not occur for the monochromatic laser illumination work because the wavelength at which the experiment was conducted was in the red region of the visible spectrum.

Visually, bright spots of high intensity were observed to be formed around the transparent fibres in the backward scattering half-space, as illustrated in figure 3.6(b). Observed using a white-card surface these spots appeared to consist of tiny patches of coloured (mainly blue, red, and 'white') light. As these peaks can be attributed to light which has undergone at least one internal reflection before transmission, it is thought that the white light was dispersed during its passage through the hair (each component wavelength being refracted a different amount according to the refractive index of the hair at that wavelength). This effect of dispersion is commonly observed in nature as it explains the colours of the rainbow formed by water droplets illuminated with sunlight.

If the peaks in the light-scattering distribution formed by the transparent hairs were approximately symmetrically displaced on both sides of the incident beam then they appeared to be approximately equally intense (see figures 3.24(b) and 3.25(b)). Except in the direction of these peaks, the intensity of the *p*-polarized scattered light was found to be less than that of the *s*-polarized. All these results share the same explanation as the ones discussed for the coherent investigation and will also be more fully dealt with in the next chapter, where an optical model of a single hair is developed and analysed.

Chapter 4

Theoretical Model of Light Scattering by an Individual Hair

4.1 General Introduction

This chapter deals with the development of an optical model of a single hair fibre and the raytracing techniques which were applied to it. The approaches which were taken are explained, the physics behind the computational program is outlined, and any simple cases which may be derived analytically are used to check the results. In order to develop this model it was first necessary to investigate the refractive index of a whole hair to determine if each region of the hair (cuticle, cortex, and medulla) had a differing refractive index and, if so, whether it could be measured.

Along the same lines as the previous chapter, the work contained here will be divided into three sections: firstly, methods of determining the refractive index of the hair; secondly, the development of an optical model of a vertically (to the plane of incidence — see figure 2.2) arranged hair; and, thirdly, an optical model of a horizontally arranged (to lie in the plane of incidence) hair.

4.2 Determining the Refractive Index of Hair

The refractive index of a medium may generally be written as $\tilde{n} = n + im$. The real part, n , is related to the speed of propagation of electromagnetic radiation in the medium (specifically, $n = c_{vacuum}/c_{medium}$), and the imaginary part determines the attenuation of the radiation as it propagates through the medium. All substances have a complex refractive index, but in some media the imaginary component is so small that it may be ignored. For simplicity, in the following investigations it has been assumed that the keratin constituents of human hair have an entirely real

refractive index and that any attenuation of the transmitted light is due to the absorbing and scattering properties of the pigment granules included in the keratin matrix. This assumption is partially justified by the transparent appearance of pure keratin, although it is recognized that inhomogeneities inside an unpigmented hair cause scattering and attenuate the transmitted beam.

Several methods for determining the real component of the refractive index of a whole fibre have been developed. One standard technique is to immerse the fibre in a liquid of the same refractive index — the refractive index of the liquid is either known (i.e. it may come from a set of refractive index matching-oils) or it may be measured afterwards using an Abbe refractometer. Generally, the index of the liquid would be varied until it equalled that of the fibre, making the determination method a null one and a knowledge of the fibre thickness unnecessary, although it has been reported [72] that the thicker the fibre the greater the accuracy with which the index can be measured.

Another technique often used for very small objects, e.g fibre cross-sections, is to set up interference fringes across the surface of a sample and then to measure the fringe displacement across the sample which, if it is of constant thickness, will be due to changes in refractive index. This method is particularly useful for determining differences in the refractive index between the cuticle, cortex, and medulla regions of a hair.

For dielectric objects which have smooth, flat surfaces, the refractive index may be calculated by finding the Brewster angle (angle of incidence at which all the p -polarized incident light is transmitted). In application to human hair this technique has been used in an attempt to determine the refractive index of the hair's outer cuticle layer.

Finally, the transmission spectrum of melanin particles embedded in a non-absorbing matrix of potassium bromide (KBr) has been obtained in order to evaluate the degree of attenuation caused by melanin granules included in the hair's keratin matrix.

4.2.1 Becke Line Method

If a fibre is homogeneous, or heterogeneous with a homogeneous skin depth of greater than $2\mu\text{m}$, then the Becke line method may be used to find its refractive index [72] at visible wavelengths. For this method a set of matching oils and a microscope

(with its condenser removed, if possible, or the aperture restricted) are required [73]. By restricting the aperture, a narrow cone of illumination is produced which generally works best for this method, although the situation does vary according to the magnification, intensity of illumination, and nature of the object of interest. The experiments were carried out at room temperature (25°) using a Carl Zeiss Interference microscope, operating in normal transmission mode (i.e. *not* set up to produce interference fringes, etc.), with a built-in tungsten lamp for illumination. A set of Cargille Laboratories refractive index matching-oils from 1.3 to 1.8 was available in steps of 0.01. A specimen of hair was mounted on a slide and immersed in one of the oils, and then the microscope was defocused by increasing the specimen-objective distance; a bright line was seen moving towards the medium — either hair or immersion oil — of higher refractive index. Similarly, defocusing in the opposite manner (decreasing the specimen-objective distance) caused the bright line to move into the medium of lower refractive index.

When a hair was immersed in a matching oil of considerably lower refractive index ($n = 1.4$) and the focus was raised above the object, a bright band of light could be clearly seen in the hair. The larger the difference in refractive index between the object and its surrounding medium, the brighter and more distinct the Becke line appeared. Similarly, when a hair was immersed in an oil of considerably higher refractive index ($n = 1.7$) and light was focused above the object plane, a bright band of light could now be seen in the oil. The Becke line is generally attributed to reflection and refraction at the edge of the fibre, but has also been explained in terms of being the most intense fringe pattern caused by an asymmetric wave spreading from the fibre edge.

From the initial measurements it was found that the refractive index of hair lay in the region between 1.4 and 1.7; this was rapidly reduced, by immersing the hair samples in a series of oils, to a smaller range stretching between 1.53 and 1.58. Using an interference filter with a bandwidth of 20nm centred at a wavelength, λ , of 549nm, the refractive index of hair was found to be closest matched by an oil with a refractive index of 1.545. As the step size in refractive index between matching-oils was 0.005, the refractive index of hair may be stated to be 1.545 ± 0.005 , which is comparable, within the limits of experimental error, to the results of Stamm et. al. [57], who reported a refractive index for hair of 1.548 ± 0.001 at a wavelength, λ , of 589.3nm (Sodium D line).

4.2.2 Interference Shearing Microscopy

Interference shearing microscopy may be used (via the formation of fringes) to find refractive index variations across an object of constant thickness. In order to understand how this is achieved, I shall give a brief discussion on the theory of interference of electromagnetic radiation.

Light (electromagnetic radiation) has a dual nature: it may be considered as a massless particle (photon) or as a transverse wave. For the purposes of understanding the phenomenon of interference it is best to consider light in terms of its wave nature, i.e. as an oscillating movement which extends into its surroundings and causes the ambient medium to oscillate so that the movement projects into space and time. The wavelength, λ , is then the distance between two successive points in the same state of oscillation (i.e. the distance between two successive points of wave motion in the same phase).

Interference is the result of the superposition of wave motions; if two wave-trains interfere in phase then they add constructively, if they interfere exactly out of phase then they add destructively. In optics, the phase differences are obtained by causing the two waves to travel different distances from the source before recombination. This difference in distance is called the *path difference*, and the order of interference is the integral number of wavelength differences in the path lengths. In a practical situation, light from a source is split into two wave-trains by using a beam-splitter; then a path difference may be created between the two waves by arranging for one to travel a physically longer route (e.g the principle used in the Michelson interferometer), or by passing one wave through a material of a different refractive index from the surrounding medium (e.g. the principle used in the Mach-Zehnder interferometer). In the latter case, if the object (refractive index n) is compared to air and all pathlengths in air are identical then the path difference created between the two beams is $nd - d = (n - 1)d$, where d is the thickness of the object.

The type of interference microscope chosen for examining an object should depend on the size, transparency, and uniformity of the specimen. For hair cross-sections — which are small and fairly transparent — it was decided it would be most appropriate to use transmitted-light interference microscopy. The instrument used was a Carl Zeiss Peraval/Epival Interphako Interference Microscope, which in peraval mode consisted of a standard transmitted-light microscope surmounted by a Mach-Zehnder shearing interferometer. In this microscope, a single wave-train of

parallel light passes through the object; it is then split into two wave-trains, one of which passes through a combination of compensating plates and wedges, and the other through a combination of adjustable wedges (rotary for displacement of images, and a phase-shifter for fringe displacement), before recombination. The shearing procedure of this last stage produces two in-focus images of the object at the eyepiece. With suitable adjustment of the wedges it is possible to interfere the two wave-trains to create white light tilt fringes. These appear as a series of bands: a central white band, two adjacent blue-black ones, and, on the lateral sides of these, a series of coloured bands which become progressively less intense until they fade out to produce an even, white field. Interference in white light differs from that in monochromatic light in that the number of visible bands is considerably smaller, comprising of only a few orders. The central (zero order) band is colourless, since all the waves sum at this point to produce white light, while the adjacent orders appear as coloured bands, owing to the dependence of the band spacing on the wavelength. The colour makes it possible to identify a given band, so when a change in thickness and/or refractive index of the object causes a break or shift in the fringes, it is still possible to follow a chosen fringe across the whole field of view.

The traditional technique of producing cross-sections of fibres remains the microtome method [74]. In this process it is important that the embedding medium chosen should not chemically or physically alter the fibres and, to avoid compressing the hairs, its physical properties should match those of hair. Samples of brown, grey, red, and blond hairs were mounted in a cryogenic embedding medium, O.C.T. compound (note: O.C.T. compound is available from B.D.H. chemical suppliers). This is the trade name of an embedding medium that is a liquid at room temperature but solidifies to form a waxy-type substance when it has been cooled to -40°C .

Eight tresses, of approximately 25 hairs each, were fixed in a cylindrical container; liquid O.C.T. (at room temperature) was poured in and then the container was cooled in a freezer to set. A computer-controlled microtome (at SmithKline Beecham) was used to slice the hair cross-sections; sections of both $5\mu\text{m}$ and $10\mu\text{m}$ in thickness were produced. Each sample was then mounted on a microscope slide and examined under an ordinary light microscope in transmission to evaluate the success of the sectioning process. Unfortunately, it was found that the majority of the hair cross-sections were still surrounded with the O.C.T. embedding medium, even though the samples had been allowed to warm up to room temperature and

to dissipate the O.C.T. If a slide was held up to the light the residual O.C.T. could still be seen as a thin deposit across its surface. Any attempt to clean it off proved unsatisfactory, as it tended to remove the hairs as well. As its presence would affect the measurements of refractive index of the hair samples, it was decided to measure the refractive index of O.C.T. and then try to determine its distribution on the slides. In figure 4.1, a black and white photograph taken of a hair cross-section under the microscope shows that the O.C.T. tended to cling to greater depth around the cross-section, appearing as wispy strands. It was also found that the sectioning

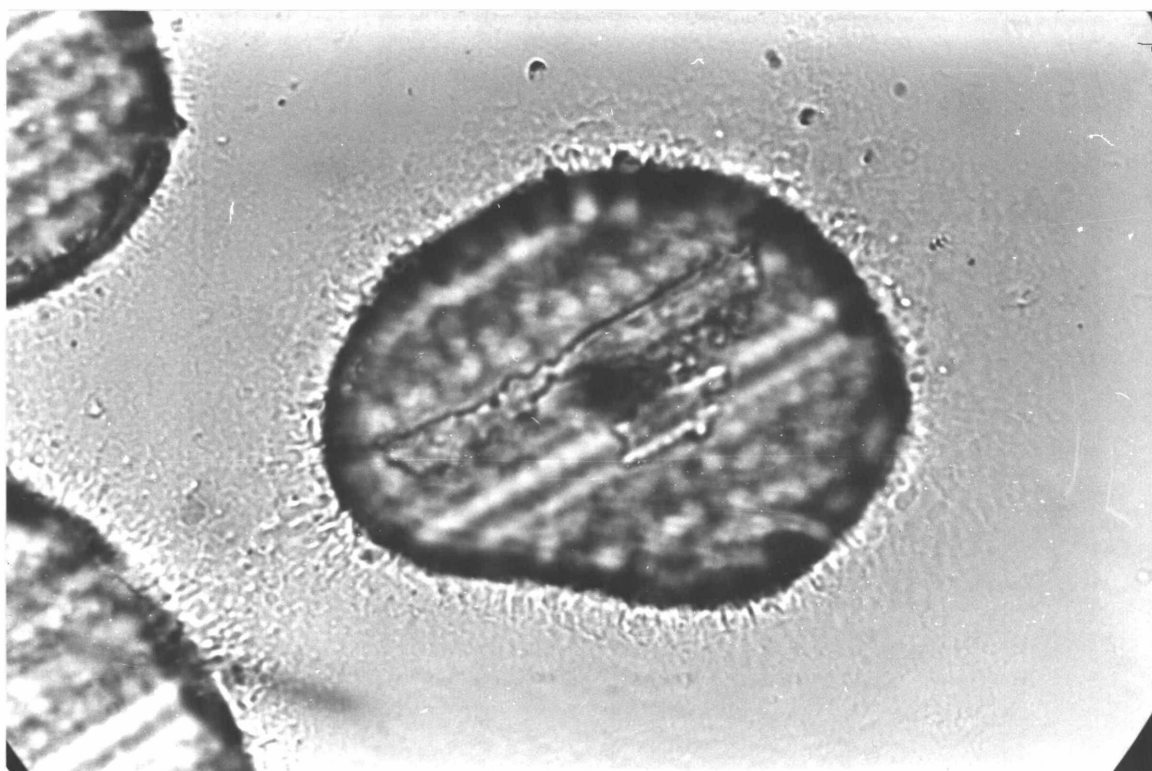


Figure 4.1: Photograph of a medullated blond hair cross-section $10\mu\text{m}$ thick illustrating the scoring effects of the sectioning process on the hair's surface and the problem of the residual presence of the O.C.T. embedding medium.

process left the cortex region of each hair with a rough surface, the direction of the cutting action of the diamond knife being clearly visible by the ridges left on the surface of the hair in figure 4.1. The natural resistance of hair to sectioning resulted in many of the hairs becoming distorted or completely fragmented, so only a few hairs in each sample were left that would be suitable for interference experiments.

The refractive index of O.C.T. was measured (see appendix 2) over a range of wavelengths and was found at 549nm (the wavelength at which it was planned to make the interference measurements) to be 1.396. From the examination of all

the hair samples it was found that the distribution of O.C.T. varied from total absence (extremely rare and usually the hair was badly fragmented, as it was not fully supported during sectioning) to having a depth of up to $10\mu\text{m}$ around the edges of a hair section, as illustrated in figure 4.2(a). However, the more common arrangement of the O.C.T. deposit seemed to be the one indicated diagrammatically in figure 4.2(b).

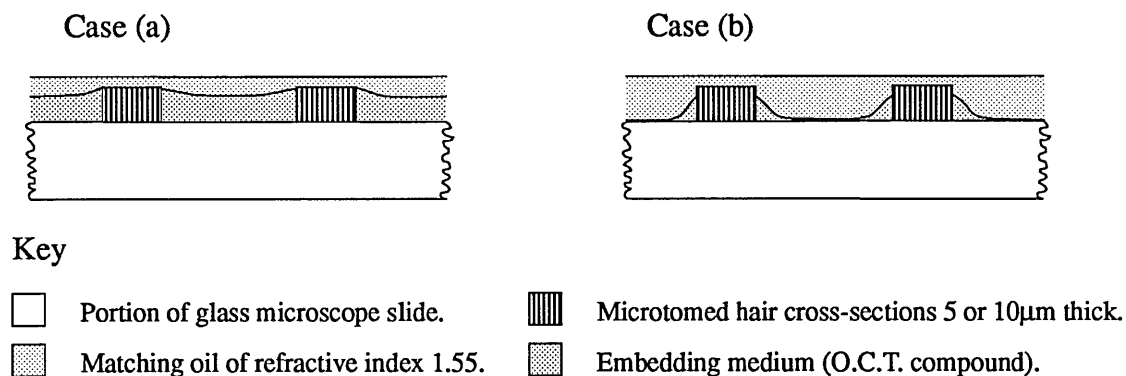


Figure 4.2: Diagram illustrating two possible cases for the arrangement of the residual embedding medium. Case (a), the embedding medium remains several microns thick between the hair sections, and, case (b), the embedding medium falls to negligible thickness between hairs and rises to an unknown depth around the sections.

The interference microscope described earlier was set up to produce white light tilt (or wedge) fringes and the hair cross-sections were examined under it. As can be seen from the colour photograph of a non-medullated circular cross-section of a brown hair in figure 4.3(a), recognizable tilt fringes were formed only outside the hair, as across the irregular, rough surface of the hair section the fringes were 'washed out'. The displacement of these fringes as they approached the hair cross-section indicated either a change in refractive index or, more likely, a change in depth of the embedding medium in this area.

To encourage tilt fringes to continue across the surface of these hair sections, the samples were immersed in an oil of refractive index 1.55 (chosen because it is thought to be close in value to the refractive index of hair) which would optically fill in the rough surface and produce a smooth layer for fringe formation. This technique proved to be successful, and an example of the result of immersing in the oil is presented in figure 4.3(b) for a medullated hair with an oval cross-section. To aid in interpreting the results in both this figure and its companion a schematic line-drawing of the photograph is included in figure 4.4 with each region of the sheared

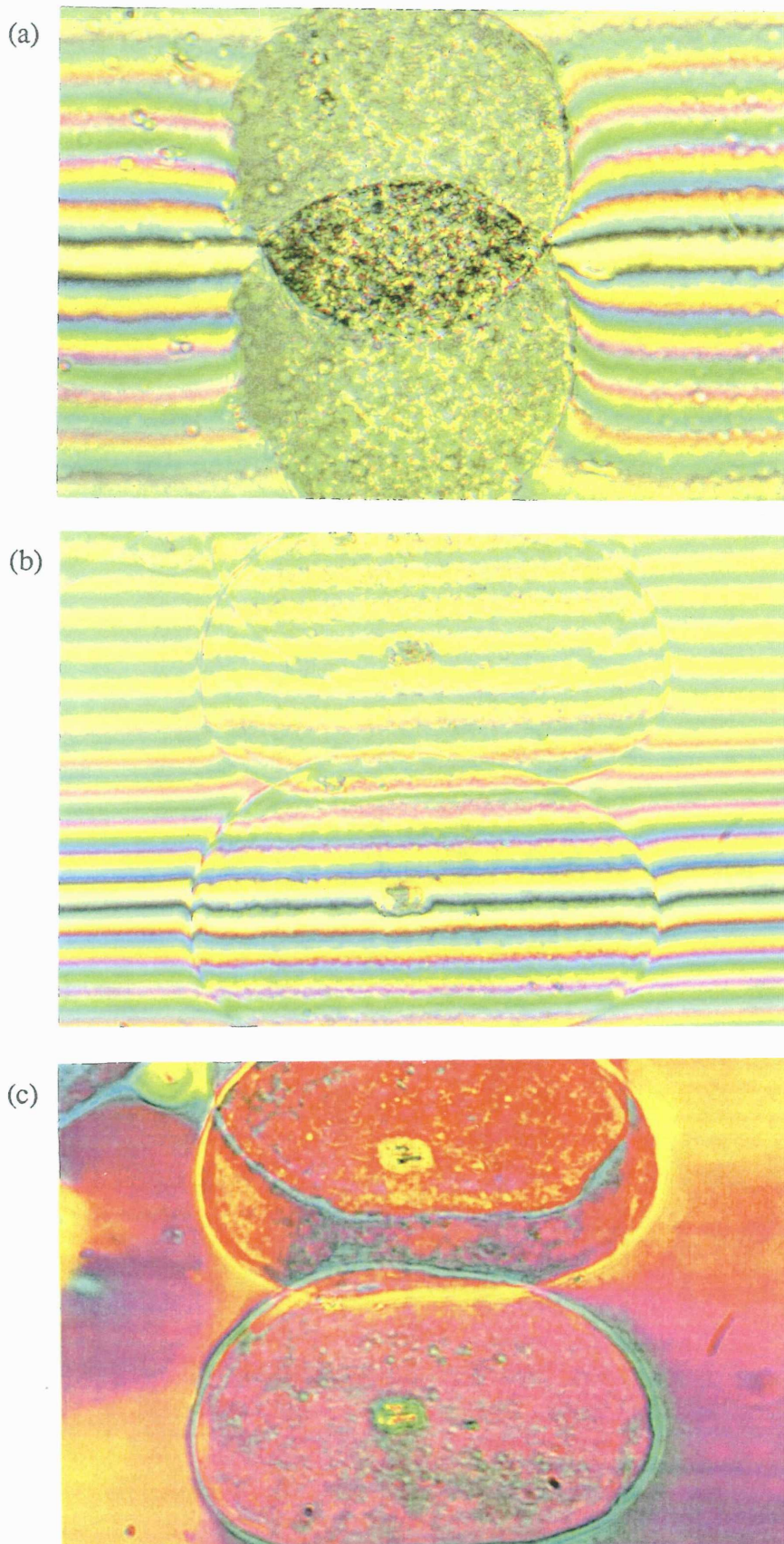


Figure 4.3: Photographs of (a) a non-medullated brown hair cross-section $10\mu m$ thick without matching oil, (b) a medullated hair with matching oil and tilt fringes and (c) the same hair with parallel fringes.

image of the medullated hair section labelled. The clarity with which the cuticle

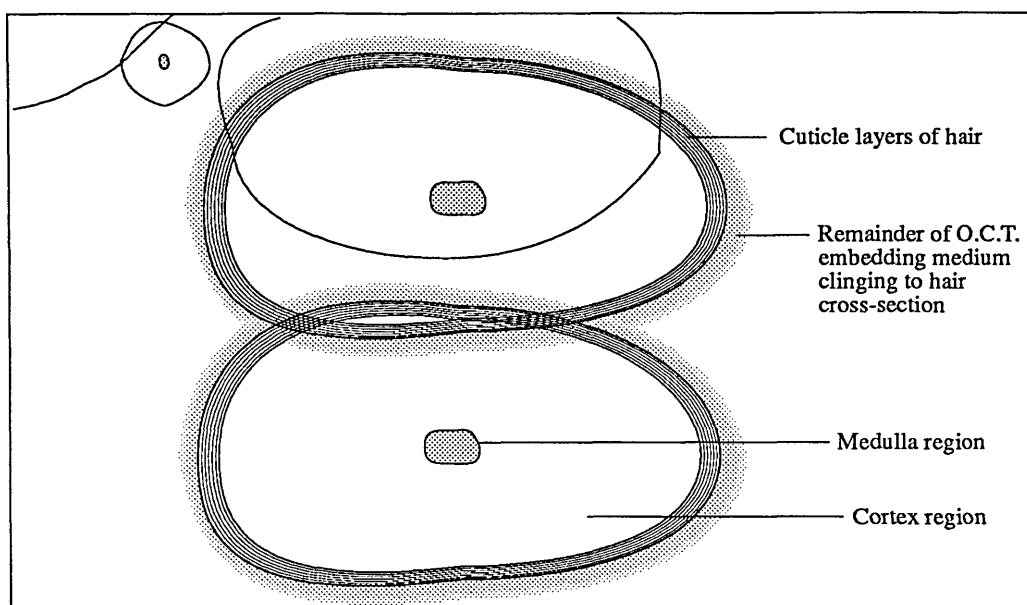


Figure 4.4: Schematic line-drawing of the medullated, oval hair cross-section shown in detail; other hair sections are shown in outline merely to aid when referring to the photographs in figures 4.3(b) and (c).

region of the hairs could be seen varied greatly between hairs, as did the amount and depth of embedding medium, but for the hair shown in the photographs in figure 4.3 it can be seen that the tilt fringes are displaced just outside the hair and then continue undeviated across the hair section, apart from in the medulla region. As the fringes are undeviated it indicates that the cortex and cuticle regions do not vary significantly in refractive index. The deflection for the medulla region was expected, as this region of the hair is filled with air pockets that give it a shorter optical path length compared to that for the other regions of the hair. The fringe shift at the edges of the hair was always in the same direction as the displacement for the medulla, indicating that the light passing through this region also experienced a shorter optical path length than light travelling through the hair or the oil. As O.C.T. compound has been measured to have a refractive index of 1.396 ($\lambda = 549\text{nm}$), which is less than that of the matching oil (refractive index of 1.55), then a fringe shift in the same direction as that for the medulla fits with the theory of a build-up of O.C.T. around the edges of the hair section.

If the wedges in the interferometric unit of the microscope are moved so that parallel fringes are formed (i.e. the white light tilt fringes are 'fluffed out') then it becomes possible to fill the field of view with one colour, i.e. a uniform field.

Observing the effect on the sheared images of the object, one will appear a slightly different colour as it is advanced or retarded in phase with respect to the other. Similarly, any regions in the object which differ in refractive index and/or thickness will show as a contrasting colour and, conversely, areas of equal phase will appear the same colour. The tilt fringes across the hair section in figure 4.3(b) were ‘fluffed out’ to produce the result given in figure 4.3(c); immediately, it can be seen that part of the medulla region appears as one colour and the remainder, together with the cortex and cuticle regions, as another. The halo around the hair indicative of the presence of the O.C.T. compound appears the same colour as the contrasting region of the medulla. Whilst in other hairs it was observed that the entire medulla region often appeared as one colour, the variations in the case illustrated here are possibly due to the infiltration of a quantity of the matching-oil into the broken medullary cells which would otherwise have been filled with air, producing differences between one area and another.

It had originally been planned from these investigations to calculate values for the refractive index of each region of the hair for the raytracing work. However, from these results it appears that the cuticle and cortex have very similar, if not identical, refractive indices, and the medulla, if present, may be considered to contain mainly air and for simplicity can be assigned a refractive index of unity. Also, because of the added complications of the uncertain variation in depth of the embedding medium and the rough surface of the hair sections, it was decided that any values of refractive index based on these results would not be as reliable as those calculated using the Becke line method.

4.2.3 Brewster Angle Method

In chapter three, section 3.2.2, it was mentioned that the Fresnel intensity reflection coefficient, R_p , dips to zero at one particular angle of incidence, which implies that at this angle all the p -polarized light incident on the dielectric medium is transmitted. This phenomenon may be explained in simple terms if we again consider light as a wave oscillating in space and time. When this incoming wave, linearly polarized with its electric vector parallel to the plane of incidence (i.e. p -polarized), is incident at an angle ρ on the dielectric it will be transmitted at angle ρ'' , according to Snell’s law

$$n \sin \rho = n'' \sin \rho'' , \quad (4.1)$$

where n and n'' are defined as the refractive indices in the incident and transmitted mediums respectively. The electric field of this transmitted wave will drive the bound electrons in the medium to oscillate, the direction of oscillation being the same direction as that of the transmitted electric field. These dipoles then radiate energy, but not in the direction of their oscillation. If the light was incident such that the angles of reflection and transmission add to equal 90° (i.e. $\rho' + \rho'' = 90^\circ$), then the field radiated by the oscillating electrons in the dielectric medium in the direction of the reflected light is zero. Thus all the light incident at this angle (known as the Brewster angle ρ_B) is transmitted. Using Snell's law and the relationships between ρ_B , ρ' , and ρ'' it is possible to derive Brewster's law:

$$\tan \rho_B = \frac{n''}{n} . \quad (4.2)$$

Stamm et al. [57] suggested that this unique condition could be used to determine the refractive index of the surface of a hair, although they do not report any measurements in either of their papers. For this technique to work, the surface of hair must obey the Fresnel equations for reflection and transmission at a boundary. The results of the experiments in sections 3.2.1 and 3.3.1 showed that the surface of a hair (orientated horizontally to lie in the plane of incidence) can be considered to be optically smooth, because the amount of light reflected by a dark hair at any given angle of incidence could be explained in terms of the Fresnel intensity reflection coefficients. Therefore, it was decided for this measurement to orientate the hair *horizontally* in the plane of incidence as drawn in case 1, figure 2.2. As the hair's curved surface will reflect the majority of the incident light out of the plane of detection, the portion of the hair which will dominate the results corresponds to a narrow strip along the middle of the hair which may be considered to be locally flat. Thus, temporarily overlooking the effects of the cuticle cells (i.e. the range of possible inclinations of these scales to the fibre axis), it would be expected that all the detected light would be, within the limits of angular spread of the beam, incident at a single angle.

The Becke line method indicated that the refractive index of hair was 1.545, which would correspond to a Brewster angle of 57.1° . Using this knowledge, a range of incident angles from 55° to 63° to the fibre axis (which approximately correspond to 52° to 60° to the hair's surface) were chosen to be investigated in this experiment. A series of measurements were made on a dark hair (selected to avoid the added complication of internally reflected components of light) over a scan range

of scattering angles from 90° to 140° . The quartz halogen source was used with the polarizer and the analyser aligned to transmit only p -polarized light. The results are given graphically in figure 4.5, and the angular position of the recorded minimum intensity for each incident angle is given in table 4.1.

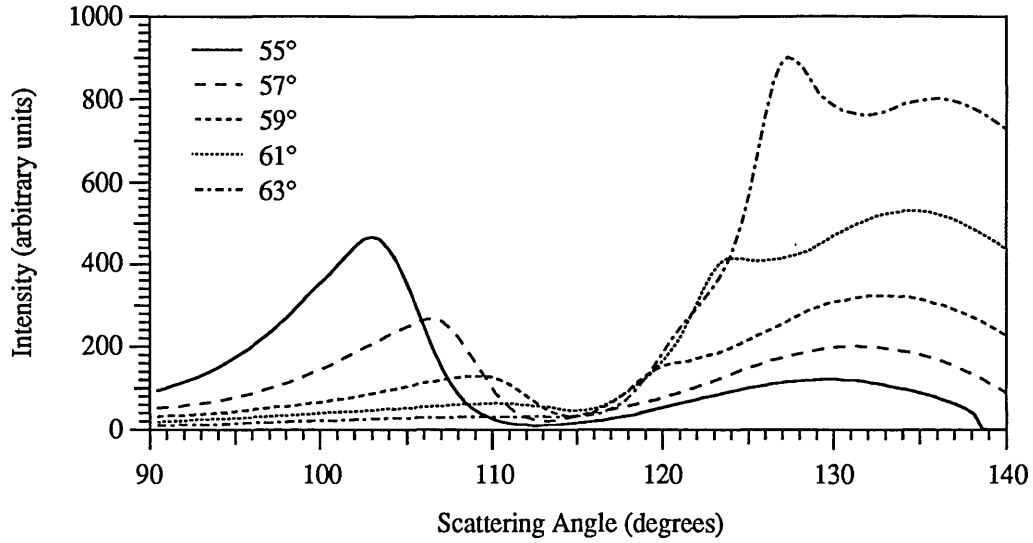


Figure 4.5: Scans of specular peak using light incident with its electric vector p -polarized parallel to the plane of incidence and detected through an analyser with its axis of transmission also orientated parallel to this plane.

Note: for clarity on the graph only half the total number of scans have been plotted and lines rather than plot symbols have been used, a convention adopted in previous sections when many data sets were illustrated in one graph.

Table 4.1: Angular position and intensity value of minima in light-scattering envelope recorded for a range of incident angles.

Angle of Incidence ρ (degrees)	Minimum Intensity I_m (arb. units)	Scattering Angle at I_m (degrees)
55.0 ± 0.1	9 ± 2	112.5 ± 0.45
56.0 ± 0.1	16 ± 2	112.95 ± 0.45
57.0 ± 0.1	20 ± 2	113.2 ± 0.45
58.0 ± 0.1	28 ± 2	114.0 ± 0.45
59.0 ± 0.1	33 ± 2	114.75 ± 0.45
60.0 ± 0.1	38 ± 2	114.75 ± 0.45
61.0 ± 0.1	45 ± 2	115.2 ± 0.45
62.0 ± 0.1	41 ± 2	115.2 ± 0.45
63.0 ± 0.1	30 ± 2	115.4 ± 0.45

As explained in chapter 3, section 3.3.1, the cuticle cells are inclined at a variety of angles to the fibre axis (note: the average scale angle for this portion of hair was

determined to be $2.76^\circ \pm 0.45^\circ$ from an *s*-polarized incident light measurement), which means that near the Brewster angle (ρ_B) there is always likely to be a portion of the surface actually orientated so that light strikes it at the Brewster angle. Thus, into the scattering angle $2\rho_B$, which corresponds to reflection of light incident at the Brewster angle, there will be an absence of reflected light when compared to the other scattering angles. As the angle of incidence is varied about the Brewster angle, so does the *number* of cuticle cells on the hair's surface which happen to be orientated so that light is incident on them at the Brewster angle. Indeed, the scattered intensity was not found to fall completely to zero at any angle, not only because the polarizer and analyser were probably not 100% efficient, but also because the surface of the hair is not smooth. With some regions of hair surface orientated slightly differently from others, those portions not exactly at the Brewster angle, but only near it, will at these low levels of detected intensity nevertheless provide a significant contribution to the total light-scattering envelope.

From the results it was found that the minimum intensity value increased with increasing angle of incidence, probably because away from the Brewster angle dip the Fresnel reflection coefficient rapidly increases for higher angles of incidence. The mean position of all the angular positions of the minima was calculated, together with its standard deviation, and was found to be $114.21^\circ \pm 0.36^\circ$; if this is taken to equal $2\rho_B$ then it corresponds to a refractive index of 1.546 ± 0.011 for the surface of this hair.

4.2.4 Effect of the Melanin Pigment

From the results in chapter three, sections 3.2 and 3.3, it can be concluded that the level of pigmentation of a hair affects the distribution of light scattered by it. For a dark (highly pigmented) hair, it was found that the majority of the light transmitted into the hair was absorbed — indicated by the absence of a secondary peak. As stated in chapter one, melanin pigments are long-chain molecules which are able to absorb light at visible wavelengths. Consequently, in this region, melanin has a complex refractive index, i.e. $\tilde{n} = n + im$.

Melanin pigment granules fall into two chemically distinct classes: eumelanin granules (black pigment), which are typically $0.6\text{--}0.8\mu\text{m}$ in size and are elongated ellipsoids in shape, and phæmelanin granules (red pigment), which are often smaller, typically $0.2\mu\text{m}$, and ovoid or spherical in shape [23]. The absorption coefficient of

eumelanin has been reported [75] to be almost constant between 400–700nm but it rises rapidly towards shorter wavelengths. Phæmelanin also absorbs more light at shorter wavelengths [24], but this trend begins earlier, in the green region (520nm) of the visible spectrum.

Of course, the manner in which the granules attenuate a transmitted beam depends on their state of aggregation. It has been found [76, 77] that large differences exist between the scattering of light by a bulk material and that by a particulate medium (i.e. collection of particles of the same material). Melanin pigment granules vary in size and distribution in human hair; they are found mainly in the cortex region of the hair, but in dark hairs they also sometimes occur in the cuticle layers [14].

From the interference microscopy investigations on thin sections of hair, the refractive index of the cortex region was observed to be reasonably uniform, but, since the hairs studied were generally those that contained low concentrations of pigment, this result did not give any information about the effects of high densities of pigment granules. To develop a comprehensive optical model of hair, the absorbing and scattering effects of the melanin granules in a keratin matrix must be taken into account.

One method of achieving this would be to determine the complex refractive index of melanin in the visible region of the spectrum and then, using one of the ‘effective medium’ theories available [76], calculate an effective refractive index for the cortex region. For instance, the Maxwell-Garnett theorem treats the region as containing small particles buried in a matrix, each with its own distinguishable refractive index, and calculates on this basis an average dielectric constant, which in turn yields an average refractive index. The main problems to this type of approach are: firstly, measuring the refractive index of melanin (not trivial — see further on) and, secondly, fulfilling the underlying assumption in effective medium theories that the included particles are in size very much smaller than the incident wavelength. As mentioned earlier, the diameters of pigment granules are comparable to the wavelengths of visible light (0.4–0.7 μ m).

Bearing these problems in mind, a sample of synthetic eumelanin (prepared by persulphate oxidation of L-tyrosine) was obtained in powder form (manufactured by Sigma chemical company) with a view to measuring its transmittance. In appearance, it was found to be similar to a set of powders called carbon blacks (soots)

which typically have a refractive index of $\tilde{n} = 1.5 + 1i$ in the visible region [77]. Measuring the refractive index of a powder is not as simple as measuring that of a bulk solid or a liquid. Before reflection and transmission data can be collected, the powder must be converted into a suitable form for experimentation.

Several methods of converting the powder to measure its refractive index have been developed [77]. The simplest and therefore the first method tried was to compress the powder in a die to form a bulk substance. This method works well if the particles pack evenly and a smooth surface is formed, but a compacted disc of melanin powder was found to form too rough a surface to carry out the transmission measurements, as scattering at its surface did not follow the Fresnel reflection formulae. A second, alternative, method is to immerse the powder in a suitable fluid to form a suspension which will obey Rayleigh scattering. This method is viable if the particles are regular in shape and smaller in size than the wavelength at which the refractive index is to be determined. Unfortunately, melanin particles are irregular ellipsoids which have typical sizes of the same order as the wavelength range of visible light. So, instead, a sample of the melanin powder was mixed with another powder which does pack evenly and was then compressed. It was always arranged for this second powder to be present in greater quantities than the melanin so that it formed a matrix around the pigment particles.

A suitable matrix powder is potassium bromide (KBr), which is essentially non-absorbing in the visible spectrum and sinters to form 1mm thick discs under reasonable pressures. It is slightly hygroscopic and precautions were taken to store it in a dry environment. When making the discs it was also important that the melanin powder was evenly dispersed throughout the sample; this was achieved by hand-mixing the two powders in a mortar and pestle using a hexane dispersant.

The percentage transmission of light through three individual KBr-melanin discs (each comprised of a different concentration of melanin) and one pure KBr disc was measured using the equipment described by Dolan in reference [77, pages 222 – 226] over the wavelength range 0.4 to $1.0\mu\text{m}$ at intervals of 0.01. By comparing the percentage transmission through these discs of KBr-melanin with the transmission through the blank KBr disc it is possible to calculate the extinction coefficient of melanin particles in a KBr matrix.

If we consider a ray of light transmitted through a slab of a homogeneous material as shown in figure 4.6, its irradiance will be attenuated exponentially due to

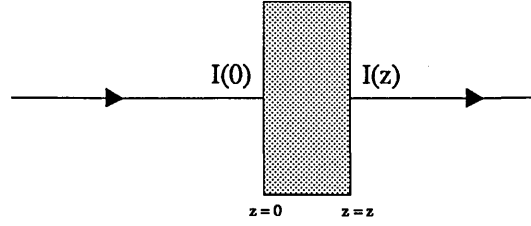


Figure 4.6: Transmission by a slab of absorbing material.

absorption and scattering such that:

$$I(z) = I_0 \exp(-\alpha z) \quad (4.3)$$

where α is the linear extinction coefficient and I_0 is the irradiance at $z = 0$. Also sometimes known as the linear attenuation coefficient, α is a measure of the ability of a medium to diffuse and absorb radiation. In an experimental situation it is difficult to measure a value of α corresponding to a single ray path in a sample, instead a volume-averaged value may be determined which corresponds to the volume of the medium through which a beam of finite area was transmitted. Thus, equation 4.3 may be rewritten in terms of the mass of particles per unit cross-sectional area (σ) and the density of particles (ρ) in the medium to give:

$$I = I_0 \exp\left(\frac{-\alpha\sigma}{\rho}\right), \quad (4.4)$$

where α becomes a volume-averaged extinction coefficient. It is now possible to apply this equation to a disc of KBr and also to a disc of KBr-melanin mixture, giving two equations which may be combined to produce a single equation in terms of the percentage transmission T , where $T = I/I_0$.

$$T_{KBr+Mel} = T_{KBr} \exp(-\alpha_m \sigma) \quad (4.5)$$

where α_m is now the extinction coefficient of melanin relative to KBr, normalized per unit mass, and has units of m^2kg^{-1} . T_{KBr} is the percentage of transmitted light through a sample of pure KBr, and $T_{KBr+Mel}$ is the percentage of light transmitted through a sample of KBr-melanin mixture.

The mass of melanin particles per unit cross-sectional area (σ) was determined for each KBr-melanin disc from its mass (m), size (πr^2), and the concentration of melanin (c), as follows:

$$\sigma = \frac{c \times m}{\pi r^2} . \quad (4.6)$$

Hence, at any given wavelength, α_m may be calculated for melanin in a KBr matrix. A selection of values calculated for α_m from the transmission data through a disc of concentration $\sigma = 0.406 \times 10^{-4} \text{gcm}^{-2}$ taken over the region of the visible spectrum is presented in table 4.2. The refractive index of melanin could then be combined with

Table 4.2: Extinction coefficient, α_m of synthetic eumelanin with respect to potassium bromide (KBr).

Wavelength λ (μm)	Extinction Coefficient α_m $\times 10^4 (\text{cm}^2 \text{g}^{-1})$
0.40 ± 0.01	3.331 ± 0.005
0.45 ± 0.01	2.776 ± 0.004
0.50 ± 0.01	2.325 ± 0.003
0.55 ± 0.01	1.910 ± 0.003
0.60 ± 0.01	1.546 ± 0.002
0.65 ± 0.01	1.245 ± 0.002
0.70 ± 0.01	0.983 ± 0.001

that measured for the cortex of transparent hairs to evaluate an effective refractive index for that region which would vary depending on the concentration of melanin in a given hair shaft. This calculation process is lengthy and includes several assumptions which may cause inaccuracies. However, it was noted that the refractive index of KBr is comparable to that measured for the keratin matrix (cortex region of hair) at visible wavelengths, see table 4.3. So, if it is assumed that optically the

Table 4.3: Refractive index values of potassium bromide (KBr) at 22°C.

Wavelength λ (μm)	Refractive Index n (no units)
0.436	1.581
0.486	1.572
0.509	1.568
0.546	1.564
0.588	1.560
0.644	1.556
0.707	1.552

Values were obtained from ‘The Infrared Handbook’ [78] section 7-70.

two embedding media are equivalent, then the separation of a refractive index for melanin and recombination with the refractive index of keratin become unnecessary steps. The quantity (the attenuation of a beam passing through a matrix of melanin

particles) actually required for the raytracing model of the hair could be determined directly. Returning to equation 4.3, the attenuation of a ray travelling a distance z in a melanin and KBr-like matrix may be calculated as:

$$I(z) = I_0 \exp(-\alpha_m \sigma_v z), \quad (4.7)$$

where $\sigma_v = \sigma/z$ and is the mass of melanin per unit total (KBr + melanin) volume. For a given hair colour (assuming only eumelanin present) σ_v is fixed, so, knowing α_m (by choosing the same wavelength as was used to collect the experimental data), it is possible to calculate the attenuation of a ray due to the distance it travels inside a hair. These results are implemented in section 4.3.6 where the effect of varying pigmentation levels is included in the optical model of a hair.

4.3 Development of an Optical Model of a Hair

4.3.1 Introduction

When developing a theoretical model that will describe the interaction of a particle with light, the first stage must be to decide on the most appropriate method of approach. In optics, this is determined by the size of the particle (d) with respect to the wavelength (λ) of the incident light. Where the particle is smaller or the same size as the wavelength ($d \leq \lambda$), wave-diffraction theory is usually necessary to predict the results accurately, but when the particle is larger than the wavelength ($d > \lambda$), geometrical optics (raytracing) is satisfactory. In the geometrical optics limit, λ tends to zero and light propagation is represented by pencil rays. For an irregularly shaped particle it is always the smallest dimension which determines the appropriate method.

A hair is a long, thin, approximately cylindrical structure, so in this case it is the diameter which must be considered. Indeed, a survey of several papers [41, 79, 80, 81] dealing with scattering of light by glass cylinders (frequently optical fibres) showed that a wave approach was taken where the diameter of the cylinder was of the same order as the incident wavelength, but as soon as the diameters increased with respect to the wavelength the approach shifted to raytracing. In the case of human hair, for average diameters around $80\mu\text{m}$ and wavelengths in the visible region ($0.4 - 0.7\mu\text{m}$), the relative sizes indicate that a raytracing approach is probably more appropriate. Of course, the hair does include features (notably, pits and cracks in

the outer cuticle layer) that fall into the scattering region where raytracing will not work, and to include these an alternative treatment would be needed.

4.3.2 Geometrical Model of Hair

For the purposes of the raytrace, it was decided to simulate the scale-like surface of the hair by a series of appropriately proportioned flat-top cones, as illustrated in figure 4.7 (not to relative scale). Initially a single conic unit was set up as shown in

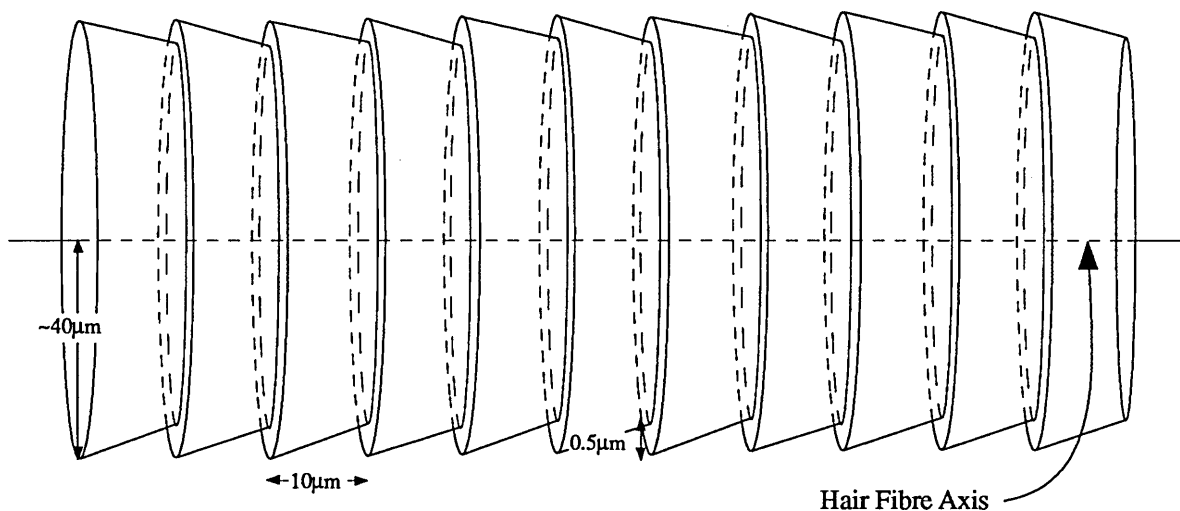


Figure 4.7: Geometrical arrangement of abutting flat-top cones proposed for raytracing from a model of a single hair fibre.

figure 4.8 with respect to the 3-dimensional reference co-ordinate axes. Thus, the equation of the surface area of a cone, given below, may be defined in terms of the height, H , and base and ‘apex’ radii of B and A respectively. By setting up the equation of a cone in this manner, the element described may be simplified to a cylinder by setting $A = B$.

$$x^2 + y^2 = \frac{z^2(A - B)^2}{H^2} + B^2 + \frac{2zB(A - B)}{H} \quad (4.8)$$

This facility was useful particularly when elliptical cross-sections were included.

4.3.3 Raytracing Theory

To explain the application of general raytracing theory to the optical model of a hair, a single ray incident on the conic surface, as shown in figure 4.9, will be considered. The incoming ray [82] is specified by its direction cosines L, M, N (cosines of the angles between $\hat{\mathbf{r}}$ and $\mathbf{i}, \mathbf{j}, \mathbf{k}$ respectively) and by its point of origin (x_0, y_0, z_0) .

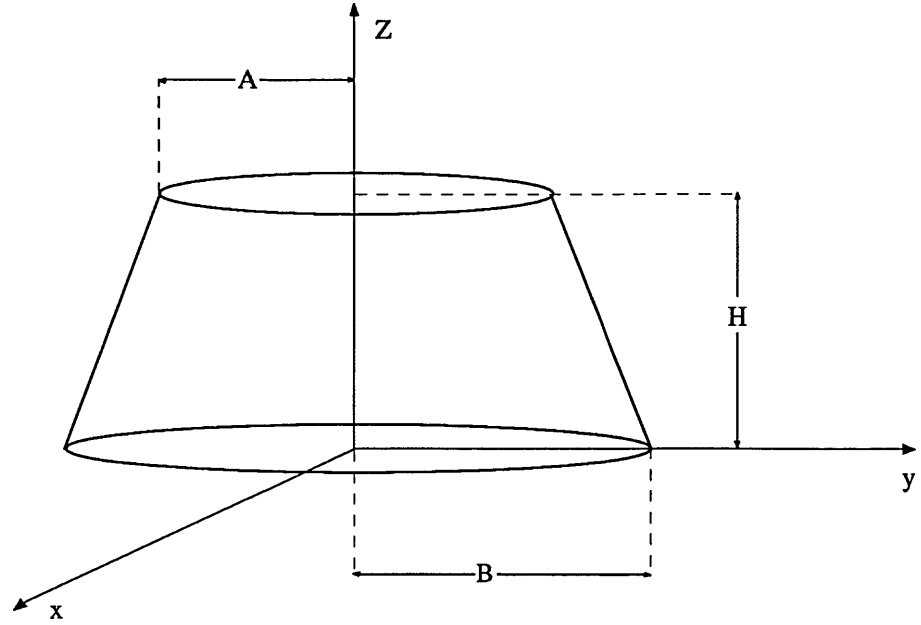


Figure 4.8: The basic conic element shown with respect to a set of three-dimensional co-ordinate system axes.

Therefore, the equation of a unit vector along the ray is:-

$$\hat{\mathbf{r}} = L\mathbf{i} + M\mathbf{j} + N\mathbf{k} = (L, M, N) . \quad (4.9)$$

The initial co-ordinates (x_0, y_0, z_0) and the direction cosines are chosen by the pro-

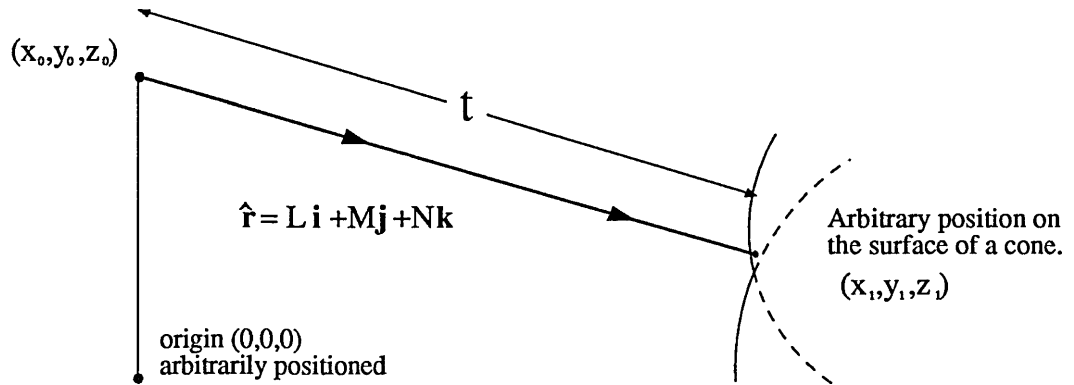


Figure 4.9: Diagram illustrating ray propagation from an arbitrary point in space to the curved surface of the conic object.

gram user and it is then possible to find the co-ordinates of intersection (x_1, y_1, z_1) of the incident ray with the cone [83]. As illustrated by the diagram in figure 4.9,

$$x_1 = x_0 + Lt \quad (4.10)$$

$$y_1 = y_0 + Mt \quad (4.11)$$

$$z_1 = z_0 + Nt \quad (4.12)$$

where t is the distance travelled along the ray in the direction of L, M, N . Substituting into equation 4.8 for x_1, y_1 , and z_1 produces a quadratic in terms of the original start co-ordinates of the ray and the distance it has travelled, t .

$$\begin{aligned} &\left(L^2 + M^2 - \frac{(A-B)^2}{H^2}N^2\right)t^2 + \left(2x_0L + 2y_0M - 2z_0N\frac{(A-B)^2}{H^2} - 2BN\frac{(A-B)}{H}\right)t \\ &+ \left(x_0^2 + y_0^2 - \frac{(A-B)^2}{H^2}z_0^2 - 2Bz_0\frac{(A-B)}{H} - B^2\right) = 0 \end{aligned} \quad (4.13)$$

Solving equation 4.13 normally generates two values of t , temporarily called t_1 and t_2 . A series of positional boundary conditions which vary as the ray is traced through the cone determine which value of t is used for the rest of the calculations. The values of t will also decide whether the ray is going to ‘escape’ from the cone, forming an *output ray*. These decisions are summarized in table 4.4.

Table 4.4: Boundary conditions for t and further actions of raytracing program.

Condition	Decision	Reason and further action
$t_1 > t_2 > 0$	t_2	Incident ray intersects cone twice, trace ray to near-side intersection
$t_2 > t_1 > 0$	t_1	
$t_1 < t_2 < 0$	Neither — it is a miss	Incident ray does not strike the conic surface, trace next ray
$t_2 < t_1 < 0$		
$t_1 > 0, t_2 = 0$	t_1	$t = 0$ is last intersection on cone, trace ray to next intersection
$t_2 > 0, t_1 = 0$	t_2	
$t_1 < 0, t_2 = 0$	Neither — escaping ray	$t = 0$ is last intersection on cone, generate output ray
$t_2 < 0, t_1 = 0$		

Using the chosen value for t , the co-ordinates on the surface of the cone may be found from equations 4.10 to 4.12. To continue the trace it is necessary to find the outward unit normal $\hat{n}_s$ to the surface at the point of intersection. In general,

$$\hat{n}_s = n_x\mathbf{i} + n_y\mathbf{j} + n_z\mathbf{k} \quad (4.14)$$

so, taking partial derivatives of the equation of the surface area of a cone, normalizing and rearranging determines n_x, n_y , and n_z :-

$$n_x = \frac{x}{\sqrt{x^2 + y^2}\sqrt{1 + \frac{(A-B)^2}{H^2}}} \quad (4.15)$$

$$n_y = \frac{y}{\sqrt{x^2 + y^2} \sqrt{1 + \frac{(A-B)^2}{H^2}}} \quad (4.16)$$

$$n_z = -\frac{\left(\frac{z(A-B)^2}{H^2} + \frac{B(A-B)}{H}\right)}{\sqrt{x^2 + y^2} \sqrt{1 + \frac{(A-B)^2}{H^2}}} \quad (4.17)$$

From the geometry in figure 4.10 it is possible to determine the angle of incidence

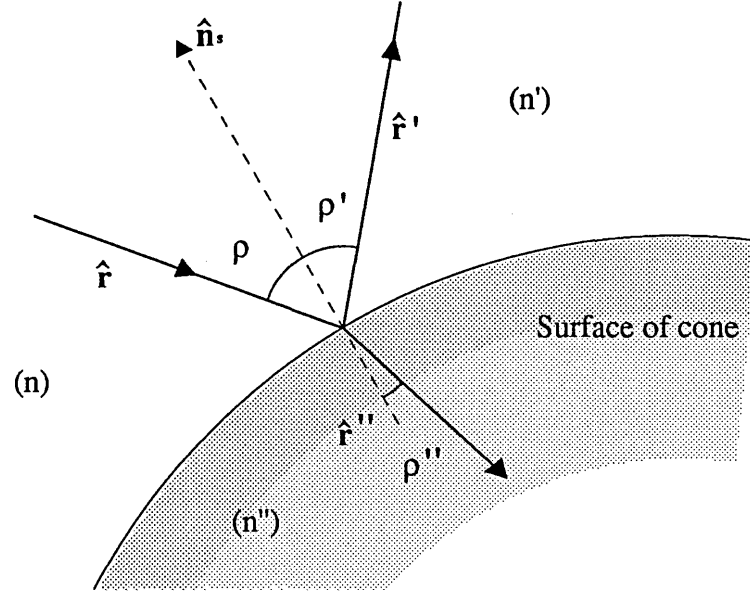


Figure 4.10: Geometry of reflection and refraction at a curved surface.

by taking the dot product of the incoming ray with the normal to the surface:–

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{n}}_s = |\hat{\mathbf{r}}| |\hat{\mathbf{n}}| \cos \rho$$

which reduces to give

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{n}}_s = \cos \rho \quad (4.18)$$

as $\hat{\mathbf{r}}$ and $\hat{\mathbf{n}}_s$ are unit vectors. However, from equations 4.9 and 4.14

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{n}}_s = Ln_x + Mn_y + Nn_z \quad (4.19)$$

so the angle of incidence, ρ , may be found. The fundamental equations of raytracing are:–

$$n' L' = nL + kn_x \quad (4.20)$$

$$n' M' = nM + kn_y \quad (4.21)$$

$$n' N' = nN + kn_z \quad (4.22)$$

where n' and n are the refractive indices in the reflected and incident regions respectively and k is defined as:-

$$k = n' \cos \rho' - n \cos \rho . \quad (4.23)$$

In the case of an air-incident reflected ray $n = 1$, and effectively $n' = -1$, so, simplifying and substituting for $\cos \rho$ and $\cos \rho'$ in equation 4.23:-

$$k = -2n(Ln_x + Mn_y + Nn_z) \quad (4.24)$$

Hence substituting back into equations 4.20 to 4.22, the new direction cosines (L', M', N') for the reflected ray may be found. Similarly, in the refracted case:-

$$n''L'' = nL + ln_x \quad (4.25)$$

$$n''M'' = nM + ln_y \quad (4.26)$$

$$n''N'' = nN + ln_z \quad (4.27)$$

where the variable l is defined as:-

$$l = n'' \cos \rho'' - n \cos \rho . \quad (4.28)$$

By invoking Snell's law, $n'' \sin \rho'' = n \sin \rho$, and a little manipulation it is possible to rewrite the angle of refraction in terms of variables we already know:-

$$\cos \rho'' = \pm \sqrt{1 - \left(\frac{n}{n''}\right)^2 (1 - \cos \rho)} \quad (4.29)$$

This allows l to be determined and also the direction cosines (L'', M'', N'') for the refracted ray to be calculated.

The process of raytracing may now begin again with the newly generated direction cosines and positional co-ordinates. This continues until the energy associated with the ray becomes so low that any contribution it may make will be negligible.

Introduction of Fresnel Coefficients

The next refinement to the basic raytracing model was the introduction of Fresnel reflection and transmission amplitude coefficients and their application at every interface. The Fresnel equations which define these coefficients are:-

$$r_s = \frac{n \cos \rho - n'' \cos \rho''}{n \cos \rho + n'' \cos \rho''} \quad (4.30)$$

$$t_s = \frac{2n \cos \rho}{n \cos \rho + n'' \cos \rho''} \quad (4.31)$$

$$r_p = \frac{n'' \cos \rho - n \cos \rho''}{n \cos \rho'' + n'' \cos \rho} \quad (4.32)$$

$$t_p = \frac{2n \cos \rho}{n \cos \rho'' + n'' \cos \rho} \quad (4.33)$$

where n , n'' , ρ , and ρ'' are defined as before (see reference [11]). The plane of incidence is defined by the direction of the incoming ray and the outward normal to the surface at the point of incidence. Note: s -polarized light has its electric vector perpendicular to the plane of incidence, and p -polarized light has its electric vector parallel to the plane of incidence. As a consequence, it is always the s component of the electric vector which is conserved across boundaries of differing refractive indices. A graph giving the angular variation of the reflection intensity coefficients for a refractive index of 1.545 (refractive index of hair) is shown in figure 3.7.

To apply the Fresnel equations you need to know the amount of polarization in the orthogonal s and p directions. For a specific incident polarization these will vary as the surface normal changes direction over the cone. During the raytrace the normal to the surface has already been calculated and thus the normal to the plane defined by $\hat{\mathbf{r}}$ and $\hat{\mathbf{n}}_s$ may be found by taking their cross product:-

$$\hat{\mathbf{n}}_i = \hat{\mathbf{r}} \wedge \hat{\mathbf{n}}_s \quad (4.34)$$

After that it is a simple matter to determine at each interface the amount of s and p -polarizations by taking the dot product of the unit vector $\hat{\mathbf{n}}_i$ and the vector describing the incident polarization.

4.3.4 Output of Data

To build an overall picture of the result of the raytrace it is convenient, to avoid tracing thousands of rays, to use a method of *integrated* raytracing. This involves tracing groups of a minimum of three rays across the region defined by the incoming beam of light. The bundles of rays chosen are such that they originate close together, their co-ordinates forming a triangle and having direction cosines that make them co-linear. Knowing the input beam intensity and the area enclosed by the three rays, it is possible to calculate the amount of energy associated with the three rays (input energy). As each set of three rays is traced through the cone this input energy is modified (due to Fresnel's equations and absorption), and then, by calculating the

area of the output triangles formed by any escaping rays generated in the trace, the output energy may be converted back into an output intensity. In this way, to a first approximation, it is possible to calculate the intensity distribution of the incident light due to interaction with the object. Note: the escaping rays are always traced a set distance from the object (typically several metres) so that the light-scattering distribution may be considered to be in the far-field.

4.3.5 Hair Vertically

As previously mentioned, a single conic unit was used as the building-brick from which the model of a hair fibre has been constructed. A 3° cone angle was chosen as this was taken to be the average scale angle for human hair. For an individual hair orientated vertically to the incident beam, it was decided as a first approximation to raytrace through one flat-topped cone with a circular cross-section. These results were compared with those that were generated by a cylinder and were found for this orientation of hair to be almost identical — the scale angle being so small. In view of this result and the wide variation in the natural cross-sectional shapes of human hair, it was decided to extend the model using cylinders to elliptical cross-sections of varying degrees of ellipticity, e , and also for a range of incident angles. All the results were calculated for the same input intensity $I_0 = 100$ (arbitrary units) and the same refractive index of 1.545.

Results of a Raytrace Through a Circular Cross-section Cone

The first set of results generated by the raytracing program was for a single (3°) cone with a circular cross-section. The light was chosen to be incident along the x -axis (as illustrated in figure 4.8) with direction cosines $[1,0,0]$. For the purposes of comparison with experimental results, two polarization states (s and p) of the incident light were considered. The results of each raytrace have been split up according to the order of interaction of the light with the object. For this raytrace, three orders of interaction have been summarized by the graphs in figure 4.11. The first graph, figure 4.11 (a), contains the component of light *directly reflected* from the front face (front-face reflection — f.f.r.), the second graph, figure 4.11 (b), contains the component of light *directly transmitted* (d.t.) through the object (i.e. transmitted at both the front and the back faces), and the third graph, figure 4.11 (c), contains the component of light *transmitted after one internal reflection* (t.a.o.i.r.). In each

case the scattering angle is measured in degrees with respect to the incident beam, which corresponds experimentally to a scan by the detector in the xy plane of figure 4.8, and may be compared to the results in chapter three, sections 3.2.2 and 3.3.2.

As the results conveniently split up into three categories, each category (or order of interaction) will be dealt with in turn.

Front-Face Reflection

It can be seen from figure 4.11(a) that the raytrace shows the distribution of scattered light from the front face to be strongly dependent on the polarization state of the incident light. At backscatter (0°) the two curves for s - and p -polarization states touch; the p -polarization state curve then dips to zero at $114.3 \pm 0.5^\circ$. This is interpreted as a consequence of the Brewster angle effect. At these scattering angles the total angle of deviation corresponds to twice the Brewster angle, hence a value for the refractive index may be calculated and used to check the validity of the raytrace.

In the case of a circular cross-section, another analytical check of the raytrace is possible. This involves deriving the general form for the distribution of the light reflected from the front face in the xy plane in figure 4.8. The diagram in figure 4.12 illustrates in cross-section a single ray displaced by a height h from the x -axis incident at an angle θ with the normal. From the geometry in this figure,

$$\sin \theta = \frac{h}{r}; \quad \sin \frac{\phi}{2} = \frac{h}{r}, \quad (4.35)$$

where r is the radius of the circle and $\phi = 2\theta$ the total angle through which the ray is deviated after reflection. By energy conservation $I(h) dh = I(\phi) d\phi$, which rearranges to give equation 4.36,

$$\frac{I(\phi)}{I(h)} = \frac{dh}{d\phi}. \quad (4.36)$$

Differentiating equation 4.35,

$$\frac{dh}{d\phi} = \frac{r}{2} \cos \frac{\phi}{2}, \quad (4.37)$$

and substituting back into equation 4.36 and rearranging produces

$$I(\phi) = I(h) \frac{r}{2} \cos \frac{\phi}{2}. \quad (4.38)$$

Integrate to find the total intensity:-

$$I_{total} = \int_{-\infty}^{\infty} I(h) dh. \quad (4.39)$$

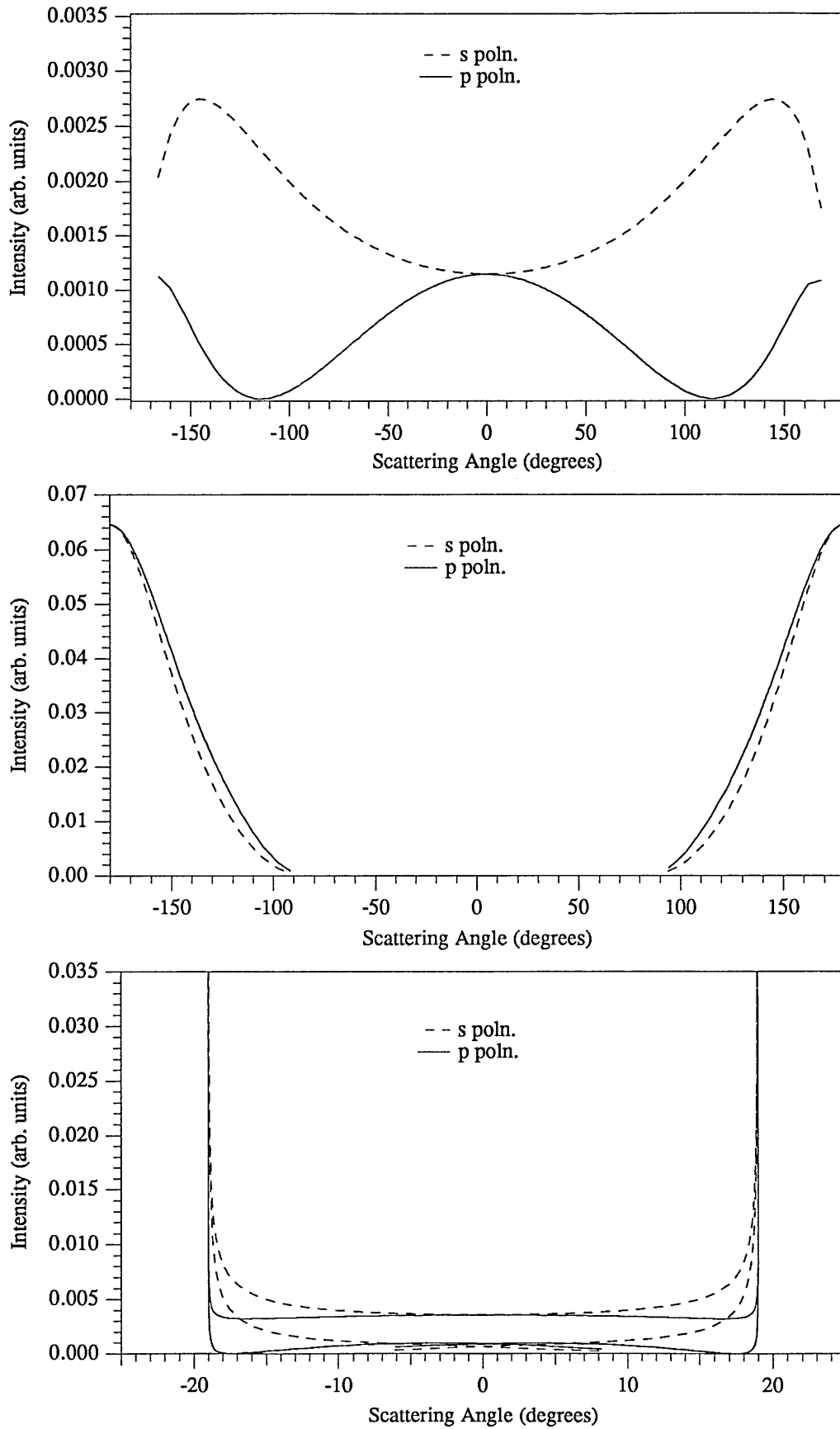


Figure 4.11: Graphs showing the results of a raytrace through a single cone with a circular cross-section. Each graph contains a component of the total light scattered: (a) front face reflected, (b) directly transmitted, and (c) transmitted after one internal reflection.

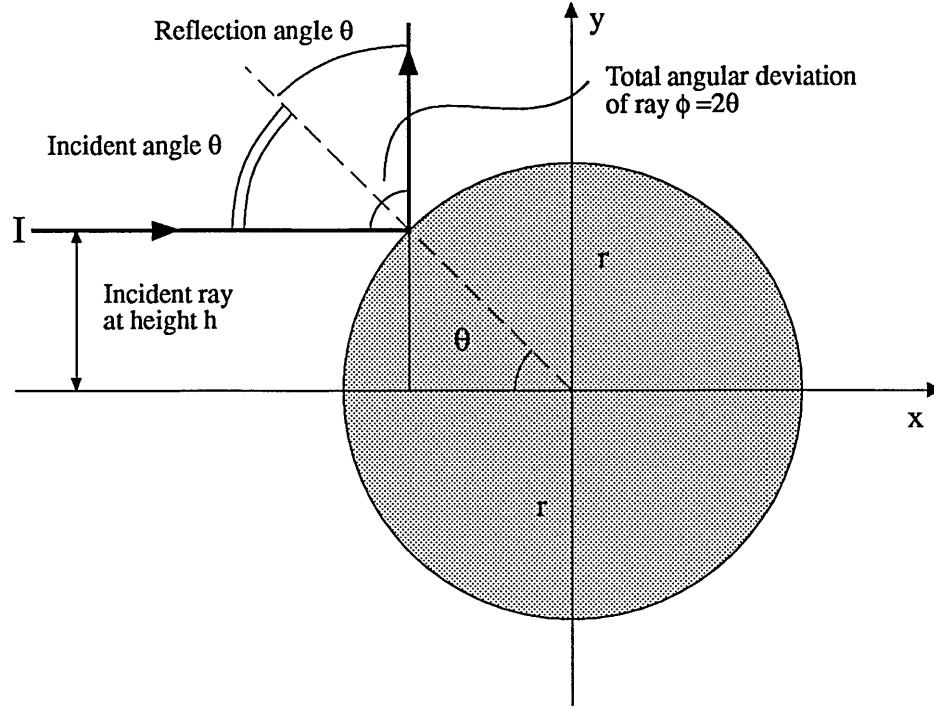


Figure 4.12: Cross-section of cone showing geometry of incident beam.

In general, the limits of the integration will be the radius of the incident beam (H),

$$I_{total} = \int_{-H}^H I(h) dh . \quad (4.40)$$

If $I(h)$ is a constant over the beam size of $2H$ then the integral reduces to $I_{total} = 2HI_0$, where I_0 is the average intensity. To find the fraction of light scattered, equation 4.38 is divided by I_{total} resulting in,

$$\frac{I(\phi)}{I_{total}} = \frac{I(h)r \cos \frac{\phi}{2}}{4HI_0} . \quad (4.41)$$

Again, replacing $I(h)$ with I_0 and cancelling gives

$$\frac{I(\phi)}{I_{total}} = \frac{r \cos \frac{\phi}{2}}{4H} . \quad (4.42)$$

However, under the conditions of the raytrace, the diameter of the hair (r) will limit the range of integration, so

$$\frac{I(\phi)}{I_{total}} = \frac{\cos \frac{\phi}{2}}{4} . \quad (4.43)$$

Clearly this function has a cosine dependence; if at each angle this function is modified by the appropriate Fresnel coefficients for s - and p -polarizations it is possible to confirm the results of the raytrace — see figure 4.13.

In terms of the experimental results, this order of interaction may be appropriately compared to the results for an individual dark hair orientated vertically to the

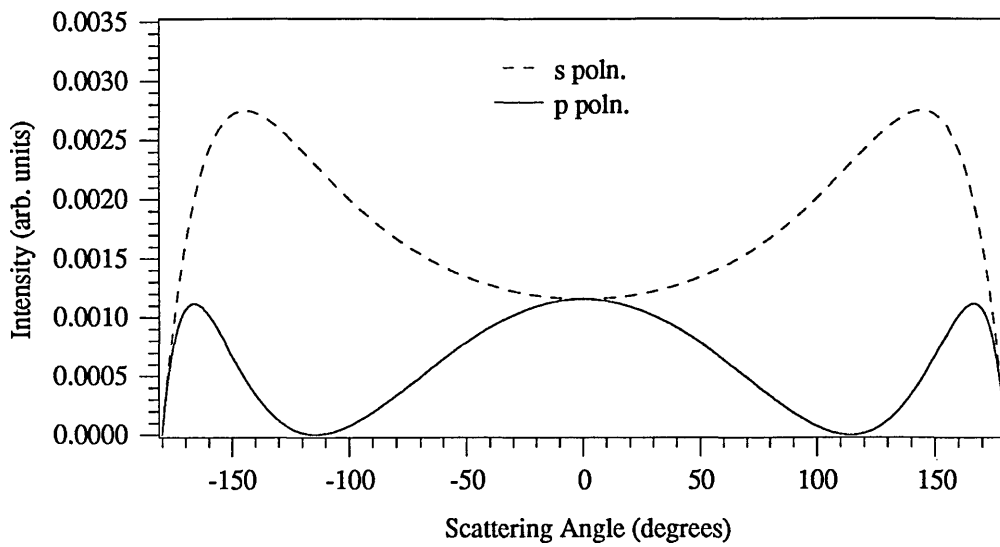


Figure 4.13: Graph summarizing the components of light reflected from the front face of a circular cross-section object as derived analytically.

plane of incidence. In this case it is likely that any light entering the hair would be absorbed by the high concentrations of pigment granules and so the total light-scattering envelope would be dominated by the front-face reflections. Comparison with the graphs in figures 4.11 (a) and 3.3 show that the raytracing results provide good agreement with the experimental, although the dip in the p -polarization curves for the experimental results occurs at lower scattering angles than is predicted either by the Brewster effect or the raytrace.

Directly Transmitted

At the front air-fibre interface, according to the Fresnel transmission coefficients, the majority of the energy associated with the light is transmitted. In the case of no internal absorption, much of the energy goes on to be directly transmitted through the fibre. From the graph in figure 4.11 (b) it can be seen that the magnitude of this component is $20\times$ greater than that of the front face reflected. Experimentally it was not possible to measure this component as it was always unavoidably mixed with the undeviated portion of the incident beam, and so no comparisons may be drawn with experimental results.

Transmitted After One Internal Reflection

Under experimental conditions, this component of the scattered light is present only for transparent hairs (white, blond, and red). As was mentioned in chapter three, the

results for transparent hairs were found to be very different from those produced by dark, opaque hairs. Transparent hairs produced peaks which varied in magnitude and angular position as the hair was rotated with respect to the incident beam. From the raytrace it was found that light which is transmitted after one internal reflection undergoes a concentrating effect exiting from the front face of the fibre over a relatively small range of angles — see figure 4.11(c). At two scattering angles ($\approx \pm 19^\circ$) the raytrace produced very large or, indeed, infinite intensities. Although the scattered intensity can be quite large it cannot be infinite at any angle, and this is where the assumptions underlying geometrical optics produce an error.

This result is similar to another in geometrical optics — namely, the prediction of an infinite intensity at the focal point of a lens, through which passes a finite amount of light. The intensity at the focus of ordinary rays is predicted to be infinite because at such places the neighbouring rays intersect and the cross-sectional area enclosed by the rays becomes zero, so when the principle of energy conservation is applied to the tube of rays it produces an infinite intensity for the field there. The solutions to such singularities (e.g. at the focus of ordinary rays) in the geometrics light field are called caustics [76].

Geometrical optics is thus limited in its use as a theory of light propagation. In the main it fails to account for certain optical phenomena which come into the category called diffraction. Basically, any deviation of light from rectilinear paths which cannot be interpreted as reflection or refraction is called diffraction. The underlying assumption behind geometrical optics is that the wavelength of the light may be allowed to tend to zero. In cases where the light-scattering medium has structures, such as edges or inhomogeneities, which vary with a scale similar to that of the incident wavelength, the geometrical optics approximation breaks down. The same limitation is encountered for surfaces whose radii of curvature are similar to, or less than, the illuminating wavelength. By diffraction theory the gap is bridged between geometrical optics and full-wave theory to explain some of these effects mentioned [84].

A similar phenomenon to that in the hair fibre is observed in water droplets, where the angles at which these singularities occur are called the rainbow angles. This problem has been explained by Descartes in terms of reflection and refraction accounting for the principle features observed [85]. However, the complete treatment of the rainbow involves a difficult diffraction problem. In both media (hair fibre

and water droplets) the refractive index of the material is wavelength-dependent, so dispersion will occur and a ‘rainbow’ or ‘prism’ effect may be seen when the object is illuminated by white light. Rainbows are amongst the most commonly documented examples of caustics. It may be anticipated that the greater the transparency of the hair fibres, the bigger this effect will be, as less absorption will occur. At the appropriate viewing angles this effect has been found to dominate the appearance of such hairs (see figures 3.4, 3.5, 3.24, and 3.25 in chapter three), as would be suggested by the relative intensities of the graphs in figures 4.11 (a) and (c).

Another check on the accuracy of the raytrace would be to calculate the ‘rainbow angles’, i.e. the angular position of the caustics may be calculated using geometrical optics. The condition for a caustic to be formed by a sphere or cone with a circular cross-section is

$$\cos \rho_i = \sqrt{\frac{n^2 - 1}{3}}, \quad (4.44)$$

where ρ_i is the angle of incidence which generates the caustic. By trigonometry, the angle into which light is transmitted after one internal reflection may be calculated to be $\theta = 2\rho_i - 4\rho_t$, as measured along the abscissa of the graph in figure 4.11 (c). (Note: from Snell’s law, $\rho_t = \sin^{-1}(\sin \rho_i / n)$.) For a refractive index of $n=1.545$, caustics are predicted to be formed when light is incident at angles of $\rho_i = \pm 47.15^\circ$ which correspond to scattering angles of $\theta = \pm 19.01^\circ$. This is in agreement with the raytrace as can be seen from the positions of the caustics on the graph in figure 4.11 (c).

In figures 3.4, 3.5, 3.24, and 3.25 the angular position of the caustic peaks was found to vary depending on the individual hair and its orientation to the incident beam. This was thought to be due to the natural variations in the shape of hair cross-sections and is investigated using an extended version of the optical model in the following sections.

Extension of Theoretical Model to Include Elliptical Cross-section

In order to check if the angular position of the caustic depended on the cross-section of the fibre, the computer program was modified to accommodate different orientations of an elliptical cross-section. This basically involved changing the equation of the surface area of the cone. Note: as the scale angle is very shallow, to first order, there was found to be very little difference between the results generated by a single conic element and a cylinder. To keep the raytrace simple it was decided to use a

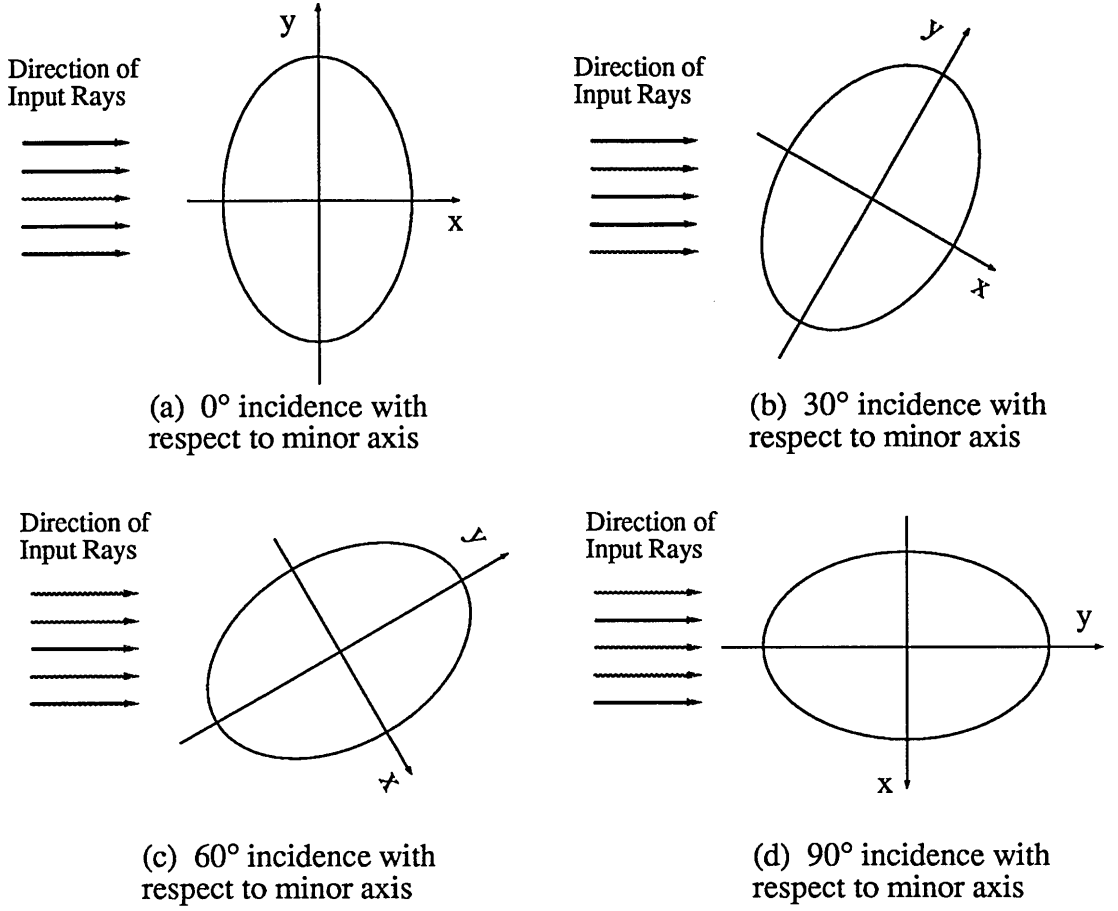


Figure 4.14: Diagram illustrating input rays at four angles of incidence on an ellipse.

cylindrical model with an elliptical cross-section. The equation of an ellipse is:

$$B^2x^2 + A^2y^2 = A^2B^2, \quad (4.45)$$

where A and B are the major and minor axes of the ellipse. With this co-ordinate system, a cylinder, unlike the cone, has no z dependence [83] and this simplifies the extension into elliptical cross-sections. The calculation then proceeds as before, solving the equation of the ellipse in terms of the raytracing parameter t [86, 11].

Initially, two cases (0° and 90°) were investigated by the program — they are included in figure 4.14. In the case of 0° incident angle, the major axis is perpendicular to the incident rays and the minor axis is parallel; this position is effectively reversed in the 90° incident angle case. The computational results for an ellipticity index of $e = 1.15$ were calculated for s - and p -polarizations, and are shown in figure 4.15. Note: the ellipticity index is defined here as the ratio of the major axis to the minor axis, i.e. it will always be greater than one for any ellipse.

In the regions where two lines exist, the total observed intensity would be the

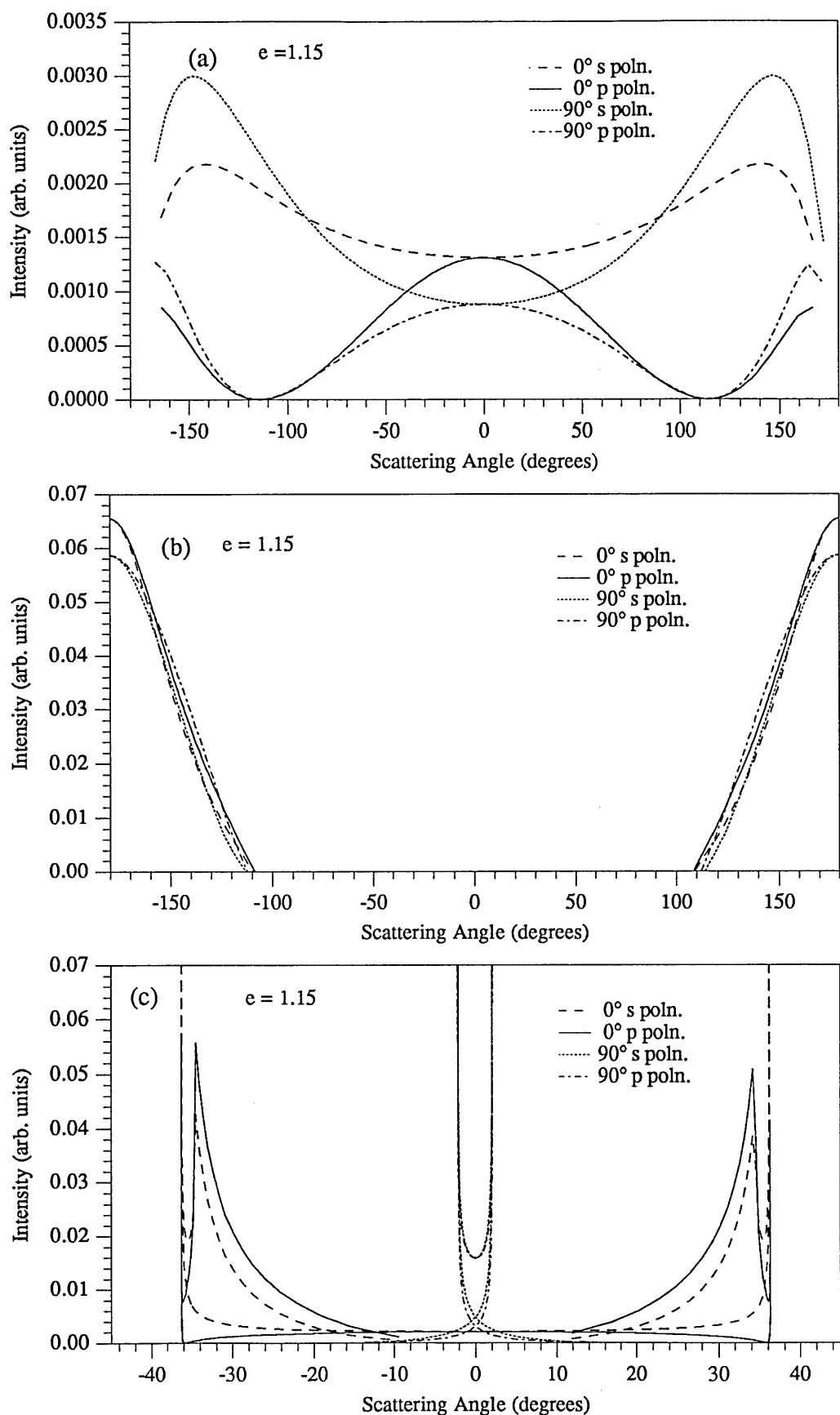


Figure 4.15: Graphs showing the results of raytraces through a cylinder with an elliptical cross-section of $e=1.15$. Each graph contains a component of the total light scattered: (a) front face reflected, (b) directly transmitted, and (c) transmitted after one internal reflection.

sum of the individual intensities at that point. It can be seen when comparing these results with those obtained for a circular cross-section, figure 4.11, that the major differences in the light-scattering distribution occur for the third component of the scattered light, i.e. that which is transmitted after one internal reflection. For this ellipse ($e = 1.15$) at 0° incidence the computer program predicts the singularities to occur at $\sim \pm 36^\circ$, whilst at 90° incidence they are predicted to occur at $\sim \pm 2.5^\circ$, compared to $\sim \pm 19^\circ$ for a circular cross-section (irrespective in this case of incident angle). These angles of incidence (0° and 90°) cover the extremes in angular displacement for an ellipse of these relative dimensions. In practice, the ellipse may have a different eccentricity or be orientated at some arbitrary angle to the incoming light, and both of these factors may alter the angular position for the formation of the caustics. Indeed, the graphs in figure 4.16 demonstrate the variation in angular position of the caustics produced by this ellipse over a range of incident angles traced for p -polarized incident light.

It can be seen from these graphs that the angular position of the caustics is dependent on the incident angle of the illuminating source, and that the displacement of the pair of caustics measured with respect to the incident beam is not symmetrical when the ellipse is orientated at angles between 0° and 90° . Examples of such incident angles (30° and 60°) with respect to an elliptical cross-section are shown diagrammatically in figure 4.14.

Asymmetry in the angular position of the pair of caustic peaks has been observed experimentally for transparent hairs — see figures 3.4, 3.5, 3.24, and 3.25 in chapter three. This may now be interpreted to have occurred when the incident angle of the illumination was at some arbitrary angle between 0° and 90° with respect to the axes of the hair's elliptical cross-section. It may also be noticed from the experimental results that the peak intensity of the caustics that form a pair are generally equal when their angular displacement from 0° is similar, but where this was not the case a discrepancy between their relative peak intensity values was also to be found. Note: in both the experimental data and the raytrace the scattering angles were measured with respect to the incident beam. Using this convention allows the raytrace data to be compared directly with the experimental data, as altering the angle of incidence with respect to a fixed elliptical cross-section (as in the raytrace) and keeping the angle of incidence fixed but rotating the elliptical cross-section (as under experimental conditions) are equivalent procedures.

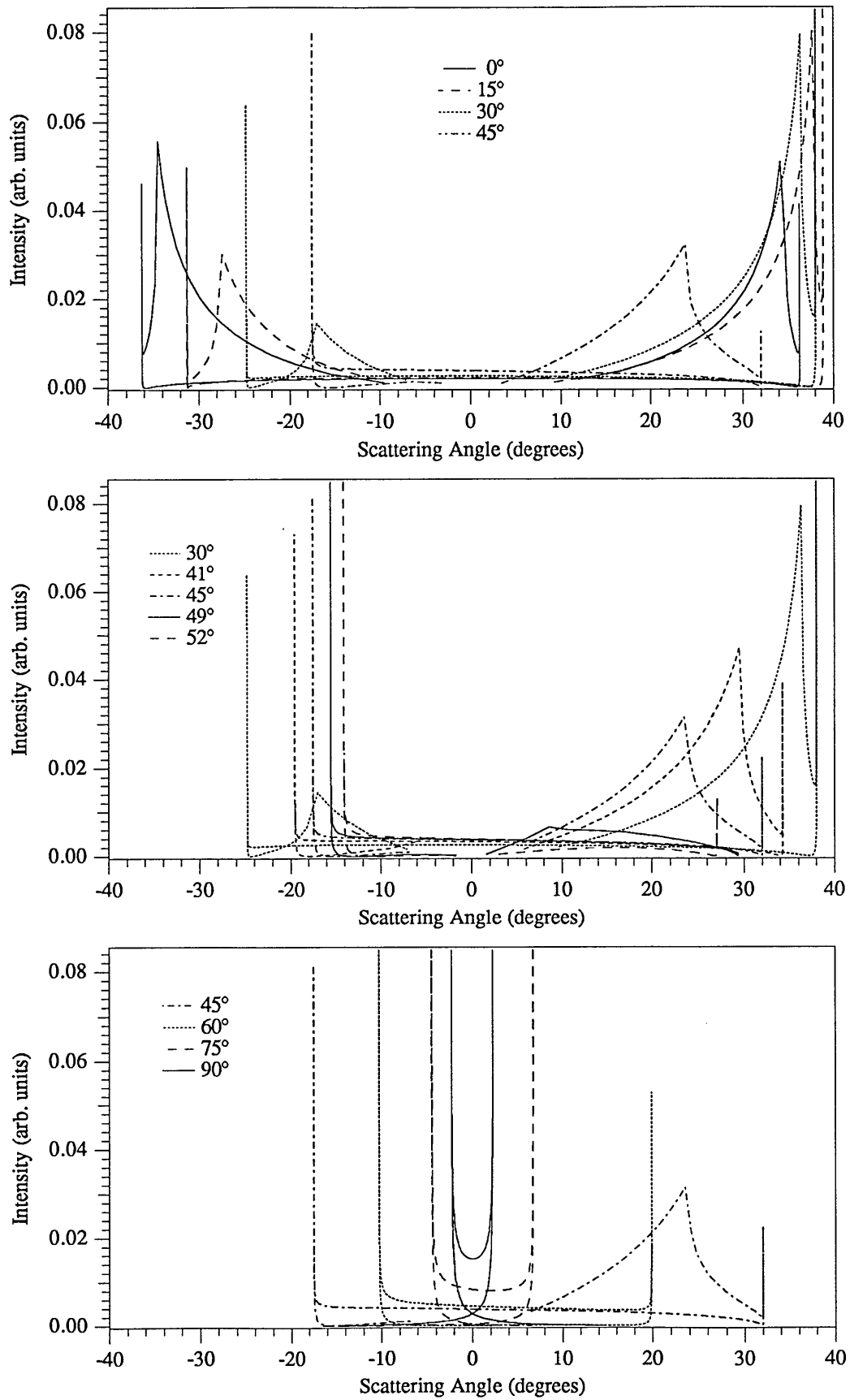


Figure 4.16: Graphs showing the results of raytraces through a cylinder with an elliptical cross-section of $e=1.15$ over a range of incident angles. Each graph contains the component of the light scattered after one internal reflection.

Table 4.5: Variations in the angular position of caustics formed by light incident on an elliptical cross-section $e = 1.15$ for a range of incident angles.

Angle of Inc. (degrees)	Angular Positions of Caustics (degrees)	
0	$+36.24 \pm 0.01$	-36.25 ± 0.01
15	$+38.93 \pm 0.01$	-31.24 ± 0.01
30	$+38.05 \pm 0.01$	-24.75 ± 0.01
41	$+34.28 \pm 0.01$	-19.51 ± 0.01
45	$+32.02 \pm 0.01$	-17.49 ± 0.01
49	$+29.36 \pm 0.01$	-15.52 ± 0.01
52	$+27.07 \pm 0.01$	-14.05 ± 0.01
60	$+19.90 \pm 0.01$	-10.26 ± 0.01
75	$+6.77 \pm 0.01$	-4.44 ± 0.01
90	$+2.29 \pm 0.01$	-2.29 ± 0.01

In nature, the ellipticity of the cross-section of a hair is determined by its racial origin. Table 4.6 summarizes the range of naturally occurring ellipticity indices for scalp hair produced by the three major races. These values have been obtained from a comparative study of beard and scalp hair published in reference [87].

Table 4.6: Naturally occurring range of ellipticities in human scalp hair.

Race	Ellipticity Index, e
Caucasoid	1.1 to 1.9
Negroid	1.5 to 2.3
Mongoloid	1.0 to 1.5

Bearing in mind the lack of transparency of highly pigmented negroid and mongoloid hair and therefore the unlikelihood of observing caustic production, a range of ellipticity indices was chosen for investigation using the raytrace program. The results for these are summarized in figures 4.17 and 4.18 for both incident polarizations and angles (0° and 90°). Note: as there was found to be very little variation in the front face reflected and directly transmitted components with ellipticity, the graphs illustrate only the results for the component of light transmitted after one internal reflection. Table 4.7 summarizes the angular position of any caustics that were generated for each ellipticity index and for both angles of incidence.

As can be seen from the graphs and tables, there is a wide spread in the range of angular position of caustics formed by ellipses at just two orientations. Thus, these broad variations in angular position explain the relatively wider caustic peaks

Table 4.7: Elliptical cross-sections and angular position of caustics.

Ellipticity Index e	Angle of Inc. (degrees)	Angular Position of Caustic p -polarization (degrees)
1.03	0	24.30 ± 0.01
1.03	90	13.65 ± 0.01
1.09	0	30.55 ± 0.01
1.09	90	7.31 ± 0.01
1.15	0	36.26 ± 0.01
1.15	90	2.15 ± 0.01
1.20	0	41.08 ± 0.01
1.20	90	0.01 ± 0.01
1.23	0	44.19 ± 0.01
1.23	90	—
1.30	0	49.42 ± 0.01
1.30	90	—
1.60	0	66.89 ± 0.01
1.60	90	—
1.90	0	83.84 ± 0.01
1.90	90	—

Note: caustics were not found for some elliptical indices and these cases are indicated by a dash.

observed from arrays of hairs compared to single fibres, refer to figures 3.4, 3.5, 3.24, and 3.25 in chapter three, and figures 5.11, 5.12, and 5.30 in chapter five.

4.3.6 Hair Horizontally

The output of the raytrace for a single cone in the xz and yz planes for front-face reflection produces an indefinitely thin vertical line at the specular angle. Experimentally, the specular peak formed by a hair has a definite width, due to the beam size, solid angle of detection, and random scattering elements on the hair. To model this effectively, the optical model of the hair was extended to include a range of scale angles, i.e. a series of conic sections each with a different cone angle.

An infinite series of cones, abutted as shown in figure 4.7, can be modelled by using only a single conic element. Rays that exit from the flat ends of the cone are ‘trapped for’ in the program, and reassigned new start co-ordinates so that they re-enter the same conic unit but at its other end. For angular intensity distributions, rays can be laterally shifted as long as their direction cosines remain unchanged.

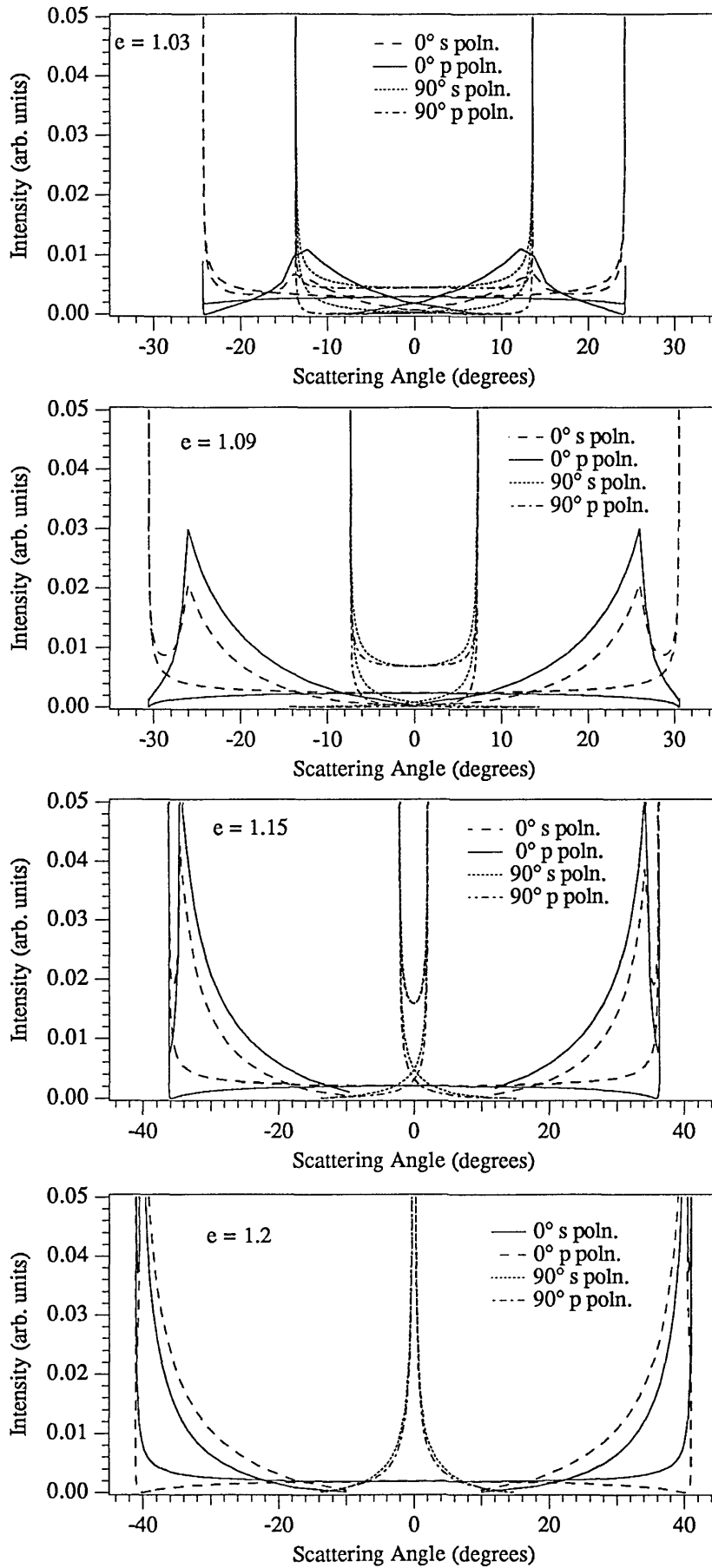


Figure 4.17: Graphs showing the results of raytraces through cylinders with varying elliptical cross-sections. Each graph contains the component of the light scattered after one internal reflection.

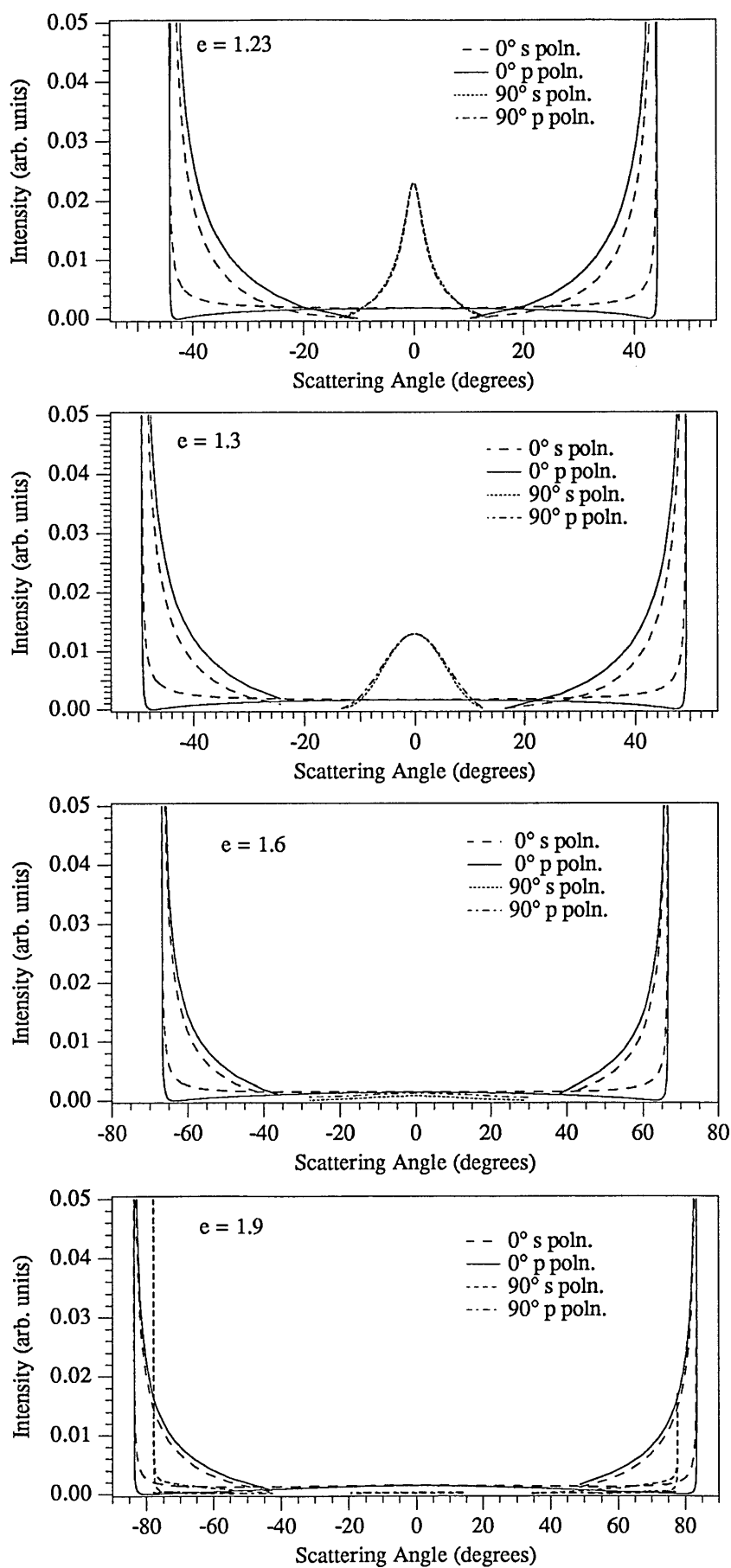


Figure 4.18: Graphs showing the results of raytraces through cylinders with varying elliptical cross-sections. Each graph contains the component of the light scattered after one internal reflection.

By repeating the raytracing process for many conic units each with a differing scale angle and then combining the results, giving each scale angle a weighting according to its probability of occurrence on the surface of a real human hair, it was possible to build an optical model of a hair orientated horizontally to an incident beam.

Probability of Occurrence for a Given Scale Angle

From the angular positions of the specular peaks produced by single hairs illuminated in this orientation (see chapter three, section 3.3), the average scale angle for human hair was found to be approximately 3° . However, this does not provide any information about the range of possible scale angles present on the hair surface, only the most common. To determine information about typical scale angle ranges, it was decided to make measurements of the surface profiles of a selection of hairs using a Talystep profiling instrument.

The Talystep operates by dragging a chisel-shaped stylus at a scan speed of $2.5\mu\text{ms}^{-1}$ along the surface of the hair. The dimensions of the stylus used are given in figure 4.19. To check to see if the tip was gouging into the hair surface, several samples were examined under both light and electron microscopes after being profiled but no evidence of scratching was observed. The results for six hair samples,

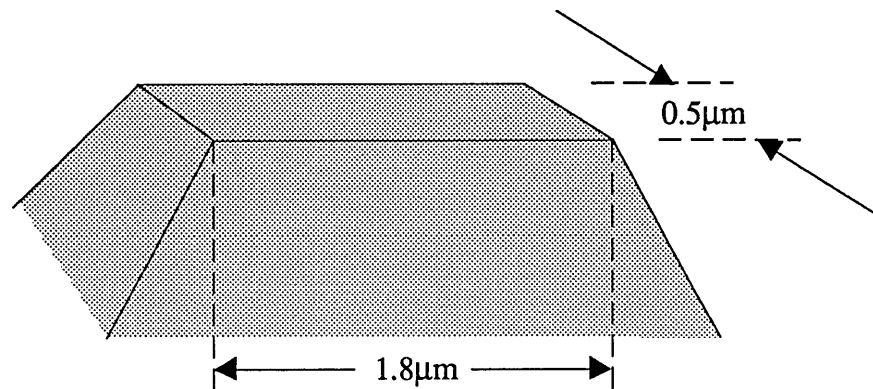


Figure 4.19: Diagram showing shape and size of the Talystep stylus used to take the profiling measurements along each hair. The maximum tip force used was 5.25mgf.

one from each of the groups of hair which form the basis of these investigations, are presented in figures 4.20, 4.21, and 4.22. Also presented in each of these figures is the corresponding frequency distribution of the slope angles (taken to be equivalent to scale angles), calculated by taking the first derivative[†] of the profile measurements for that section of hair. Superimposed on each histogram is the best fit Gaussian

[†] Derivative taken over each interval of $0.1\mu\text{m}$.

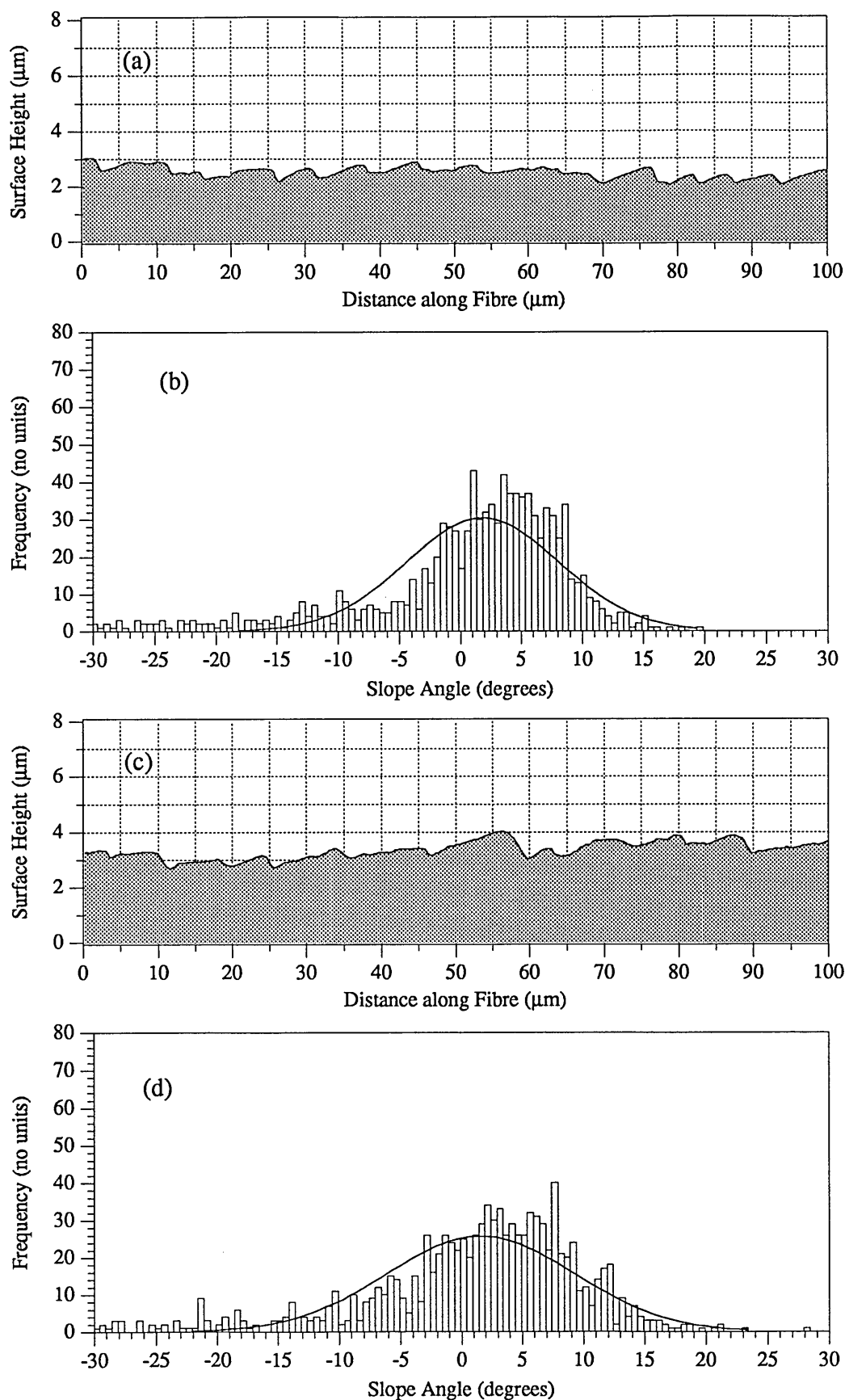


Figure 4.20: Graphs (a) and (c) show the results of Talystep profiling an Oriental black and Caucasian black hair respectively. Histograms (b) and (d) illustrate the corresponding frequency distribution of slope angles present along that section of surface.

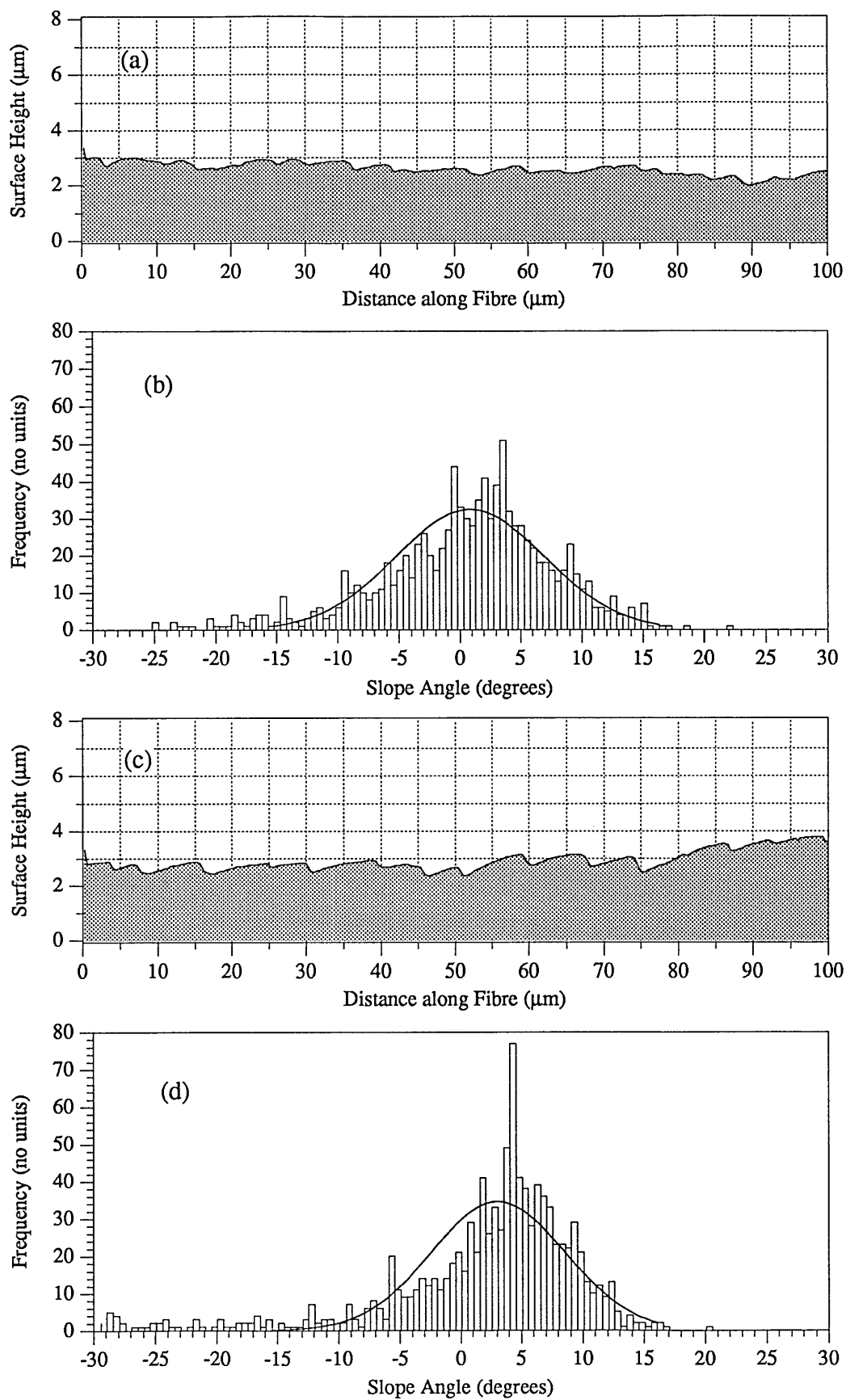


Figure 4.21: Graphs (a) and (c) show the results of Talystep profiling a brown and red hair respectively. Histograms (b) and (d) illustrate the corresponding frequency distribution of slope angles present along that section of surface.

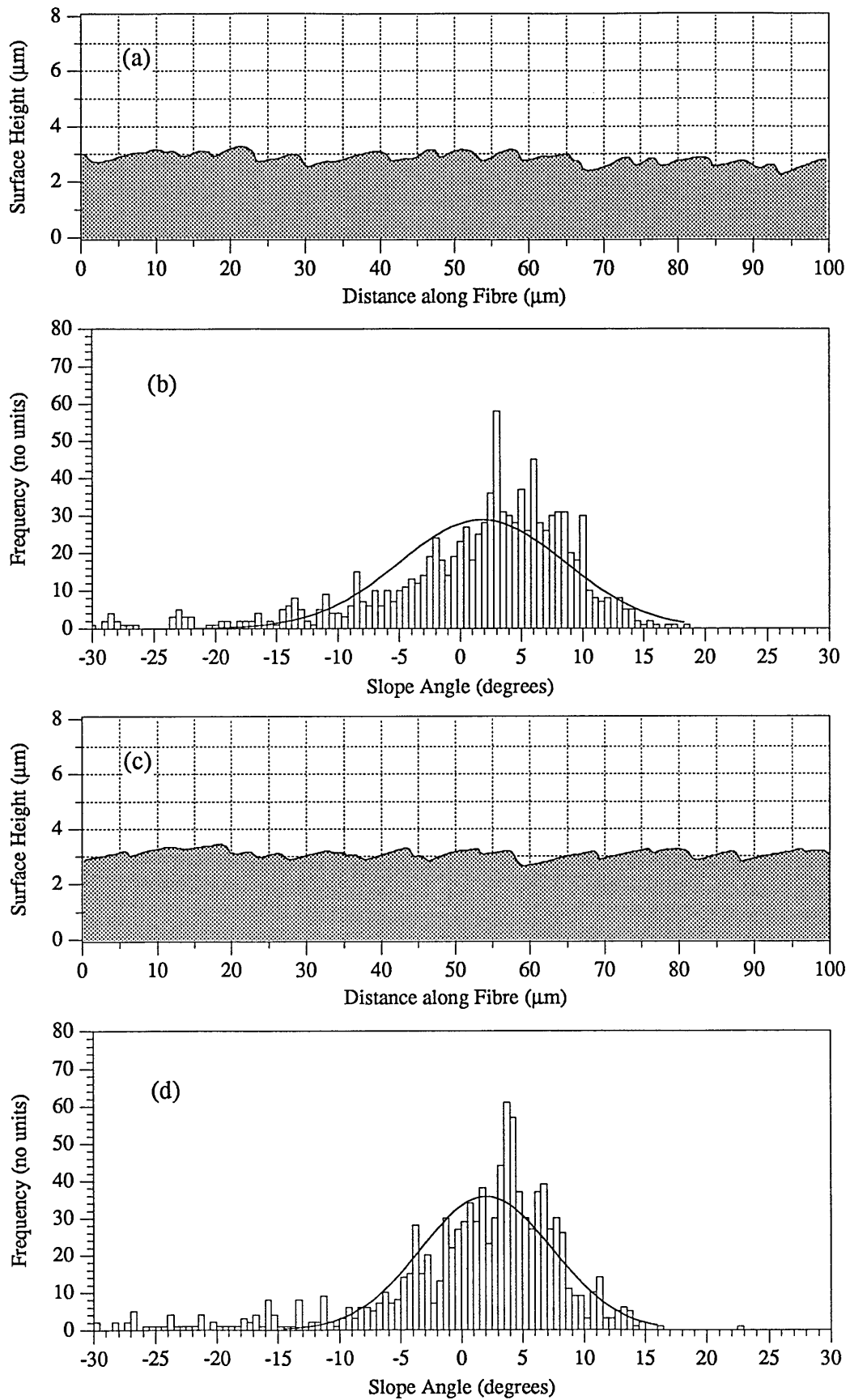


Figure 4.22: Graphs (a) and (c) show the results of Talystep profiling a blond and white hair respectively. Histograms (b) and (d) illustrate the corresponding frequency distribution of slope angles present along that section of surface.

curve, calculated using standard statistical methods from the frequency distribution data using the following equation:-

$$f(x) = \frac{N\Delta}{\sigma_D\sqrt{2\pi}} \exp \frac{-(x - \mu)^2}{2\sigma_D^2}, \quad (4.46)$$

where $f(x)$ is the probability density function, σ_D is the standard deviation, μ is the mean, Δ is the binwidth, N is the number of data points, and x is the varying quantity, in this case the slope angle. From table 4.8 it can be seen that, for all the hairs examined, the distributions of slope angles measured were centred about positive scale angles, as might be expected from the results in chapter three. Using this data it is possible to predict the probability of occurrence of a given scale angle on a typical hair surface and to use this information in the raytracing program.

Table 4.8: Parameters characterizing goniophotometric scans at three positions on each hair.

Hair Type	Mean Slope μ Av. Scale Angle	Standard Deviation σ_D
Oriental	1.84	5.81
Black	1.55	7.17
Brown	0.84	5.60
Red	3.05	4.99
Blond	1.79	6.27
White	2.03	4.85
Average	1.85	5.78

Absorption

To model the differences in the light-scattering envelopes which were produced by dark (opaque) and light (almost transparent) hairs, it was necessary to add a variable absorption factor into the raytracing program. Using the results of the work in section 4.2.4, at a wavelength $\lambda = 0.55\mu\text{m}$ the extinction coefficient of melanin in a KBr-like matrix $\alpha_m = 1.910 \times 10^4 \text{cm}^2 \text{g}^{-1}$; using this value the attenuation of intensity associated with a ray travelling a distance z inside the hair may be calculated from equation 4.7. Black, brown, and blond hairs may be modelled by varying the mass of melanin per unit total volume, σ_v .

Three raytraces with s -polarized light incident at 0° were produced for three values of σ_v . The results are given in figure 4.23. In each trace the most probable

Table 4.9: Summary of the mass of melanin per unit total volume as chosen for three hair colours.

Hair Type	Concentration σ_v
Black	10×10^{-8}
Brown	5×10^{-8}
Blond	3×10^{-8}

scale angle was chosen to be 2° and the range of scale angles present on the hair's surface to have a standard deviation of $\sigma_D = 6^\circ$.

These theory results may be compared to the experimental results given in figure 4.24 for black, brown, and blond hair fibres. It can be seen that there is a general agreement in the shape of the total light-scattering envelopes for each hair colour, and by varying the values of the standard deviation a closer match to a particular hair sample may be achieved. For instance, the FWHM (section 3.3.1) for the black hair was predicted by the raytrace to be $\approx 20^\circ$ and measured experimentally to be $\approx 10^\circ$, whilst for the blond it was found to be $\approx 40^\circ$ in both cases.

Away from normal incidence, the results of the raytrace are less successful at predicting the light-scattering distributions produced by partially transparent hairs orientated horizontally to lie in the plane of incidence. This is due to the increase in the number of rays being transmitted into cones with large apex angles and then travelling long distances inside them almost parallel to the surface. In a real hair, where internal inhomogeneities and variations in scale angle along the length of a hair exist, this occurrence is unlikely. So the contributions from rays which have been transmitted for a very long distance inside a single cone are unrealistic. Also, another problem occurs in the raytrace at one particular scale angle which varies depending on the angle of incidence. At this angle the group of three light rays reflected from the far side of the cone are retransmitted so that they are almost parallel and the area enclosed by them is very small, leading to a large intensity (caustic formation). This feature occurs in the raytrace but not experimentally, because in the cone shape chosen as the basis of the model the near and far side slope angles are identical. In a real hair this would be very unlikely, especially if the elliptical nature of a hair's cross-section is taken into account. Of course, this problem also arises for normal incidence in the model, but fortunately it is at a scale angle with a low probability of occurrence and is thus much reduced.

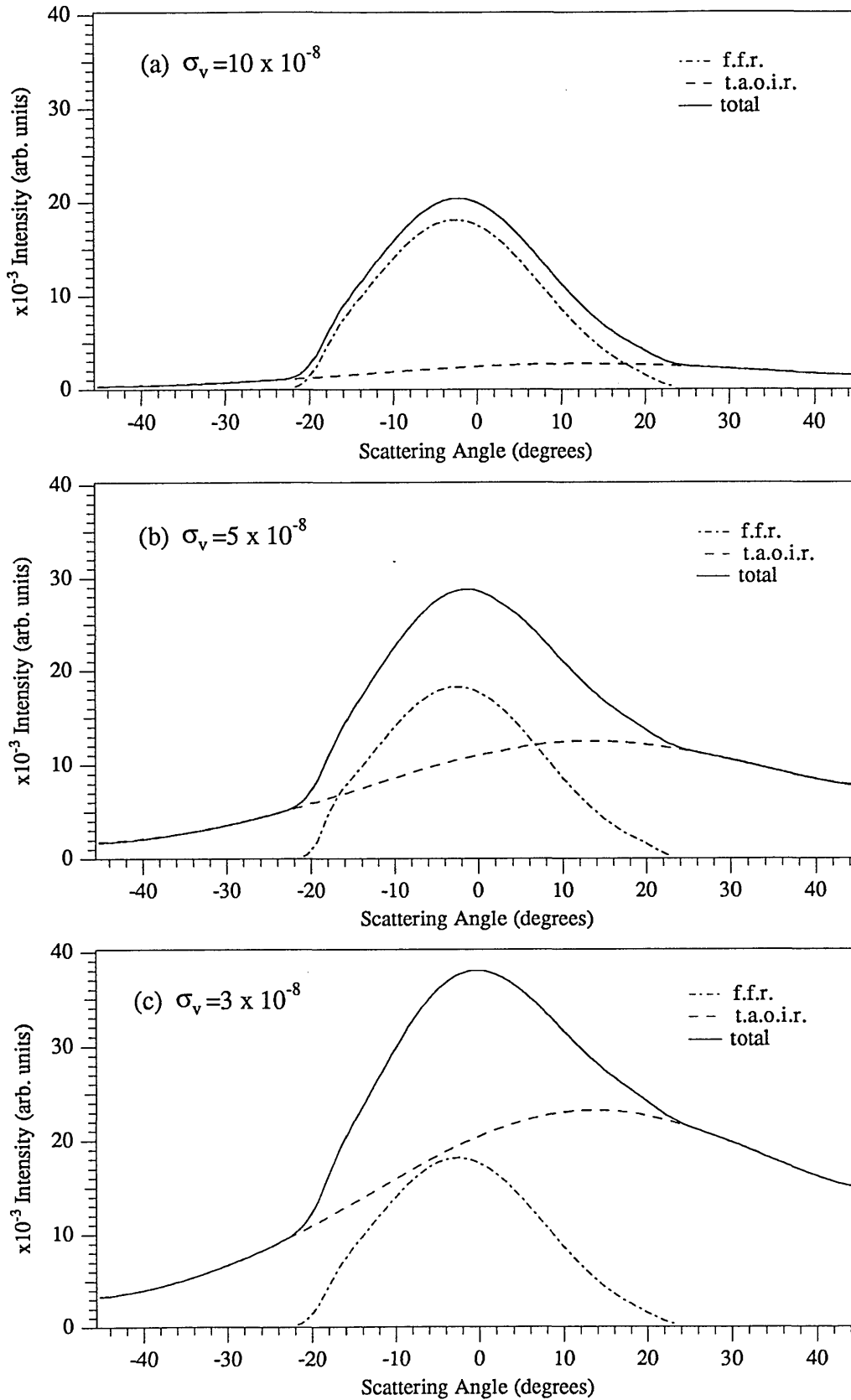


Figure 4.23: Results of raytraces through a model of a horizontal hair with three different effective concentrations of pigment. Each graph contains the components of the light reflected from the front face and scattered after one internal reflection, and their incoherent sum.

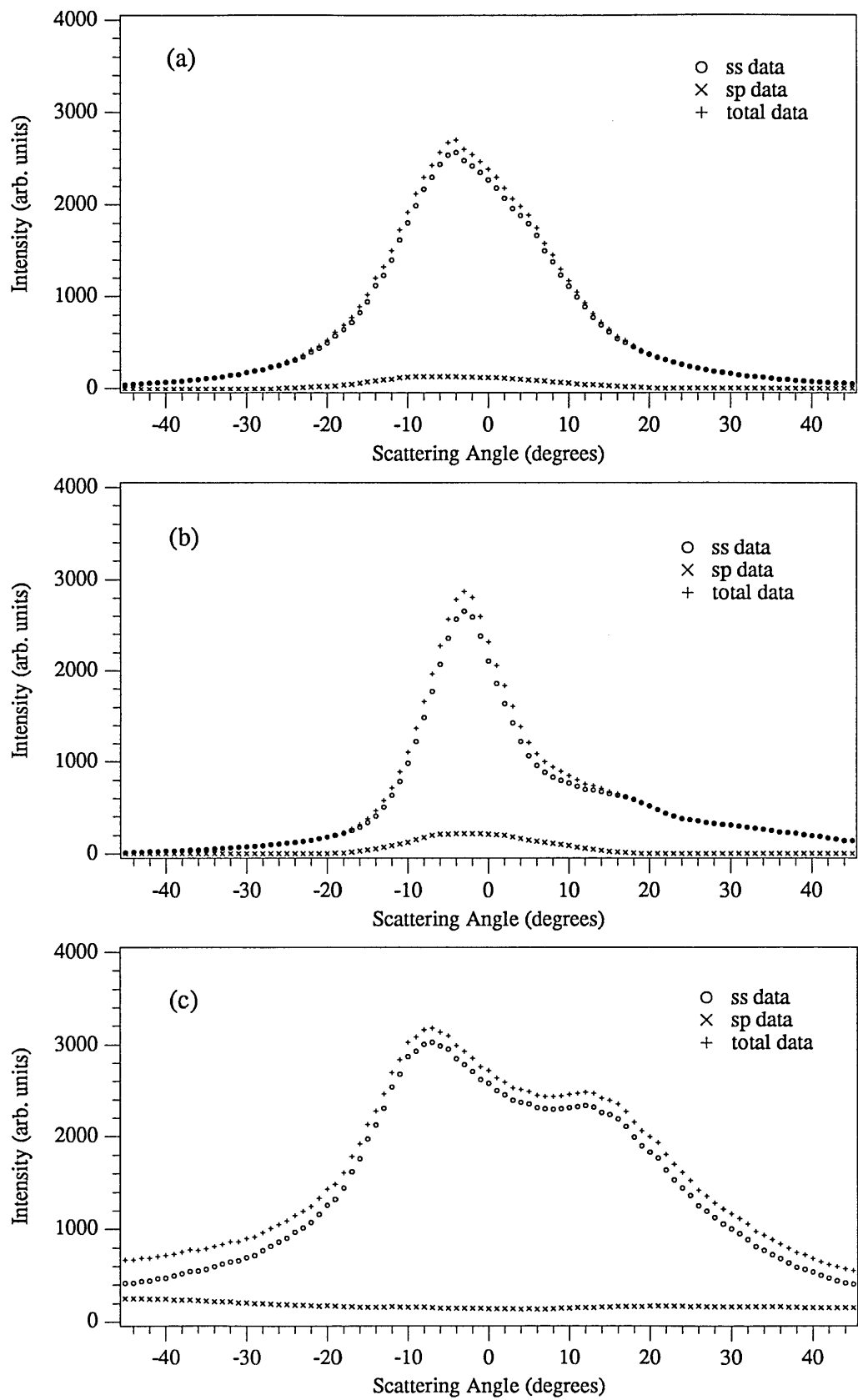


Figure 4.24: Graphs showing the results of *s*-polarized light-scattering experiments from horizontal hairs (a) black, (b) brown, and (c) blond. Each graph contains the components of co-polarized and cross-polarized light and their incoherent sum.

Further Work

In the current model, the slope angles at the near and far sides of each conic element are the same. By introducing variations in this factor it may be possible to achieve a more satisfactory optical model of a hair, which should give better results at non-normal angles of incidence. The inclusion of a medulla region would be a further refinement to the model.

Chapter 5

Goniophotometric Measurements on Arrays of Hair Fibres

5.1 Introduction

The results of light-scattering experiments on individual hairs critically depend on the condition of the particular hair fibre chosen from a sample, and may not therefore accurately represent the entire sample. It was found in single-fibre experiments that occasionally a selected hair exhibited signs of extreme weathering. Indeed, the cyclic nature of hair growth (see chapter one) gives rise to a small percentage ($\sim 10\%$) of fibres in a sample being substantially more weathered than the rest. One way of avoiding such errors would be to investigate many individual hairs from a sample before making any general comments about typical trends or properties. However, this process would be both time-consuming and laborious, and possibly still bear no relation to the real situation of a full head of hair. For some hair experiments where the position of each hair is not important, researchers have used tresses of hair [26], but for light-scattering experiments a tress of hair is not satisfactory as it is impossible to reproduce the exact positions and arrangement of the hairs for repeat measurements if they are only loosely bound at one end. Instead, it was decided to secure hairs parallel with respect to each other to form planar arrays, which will be henceforth referred to for brevity as hair *surfaces*. A surface of hairs is easy to make (see chapter two) and produces reliable, repeatable results. Double-layer or ‘thick’ surfaces have also been studied to enhance the possibility of detecting fibre-to-fibre scattering, especially with partially transparent hairs.

By using a planar array of 40 hairs the contribution to the total light-scattering envelope from each of these hairs is reduced, making this technique better suited to testing the effects of cosmetic treatments. Of course, all the hairs which are strung

to make a surface must be orientated in the same way (root-end-right or root-end-left). This precaution is highlighted by the results in figure 5.1 for a surface of hairs strung from a sample supplied to me after treatment by an external technician at SmithKline Beecham. The graph shows the light-scattering distributions produced by a horizontally arranged array of hairs illuminated with the quartz halogen source. Initially the sample of hairs produced two prominent peaks (corresponding to the

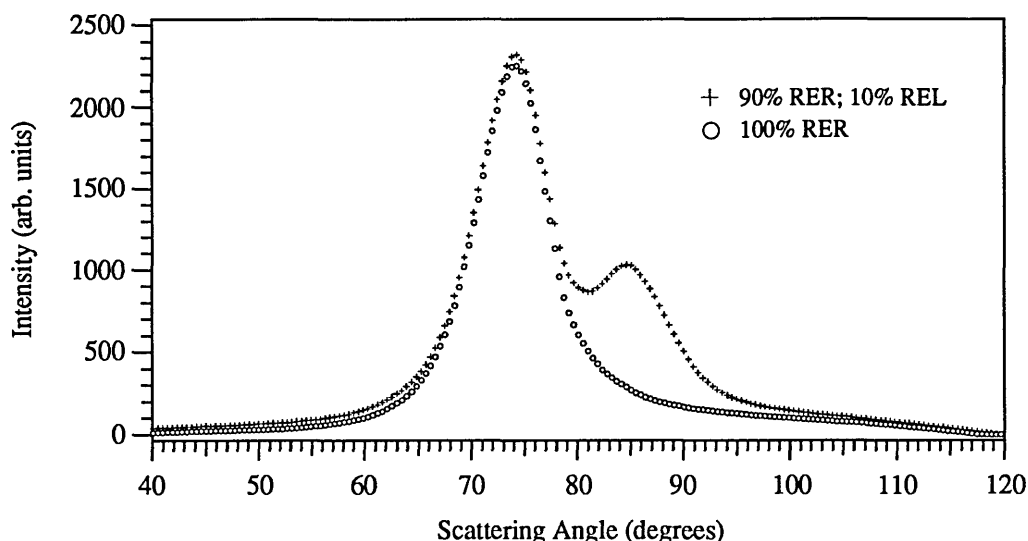


Figure 5.1: Goniophotometric curves from an array of dark-brown hairs orientated horizontally to the incident beam. Incident angle to the normal to hair fibre axis was 40° and light was unpolarized. The primary peak produced by the hairs orientated RER was found to occur at 74.6° , corresponding to a scale angle α of 2.7° . Thus, for hairs orientated REL their specular peak should occur at $85.4^\circ = 80^\circ + 2\alpha$, and from the graph this is confirmed.

‘+’ legend on the graph) which was surprising since the colour of this sample was mid- to dark brown. Upon visual examination it became obvious that four of the forty hairs had been strung in the reverse direction to the rest. This mix-up could have easily occurred during the treatment process when the main sample was split into smaller tresses, or at an even earlier stage when the hair was bound into tresses by the suppliers. When the four hairs were removed and the sample was re-scanned, the secondary peak was found to have disappeared (corresponding to the ‘o’ legend on the graph). The overall intensity in the light-scattering envelope was slightly reduced because there were now only 36 hairs contributing to the total result. This type of error may account for the unusually large secondary peak reported by Stamm et al. [57] for an array of 21 *dark-brown* fibres.

In many cases the light-scattering experiments from hair surfaces dealt with

in this chapter directly correspond to equivalent experiments in chapter three for individual hair fibres. To make comparisons between each set of results easy, this chapter has been structured in the same manner as chapter three, and where an equivalent result exists, the reader is referred to the appropriate section.

5.2 Laser Illumination

Following in the style of chapter three, this chapter begins with a section containing the goniophotometric experiments on parallel arrays of hair illuminated with coherent light sources (lasers); it is further subdivided into two sections according to the orientation of the hair surface to the plane of incidence. The two arrangements considered experimentally in this chapter are illustrated in figure 5.2.

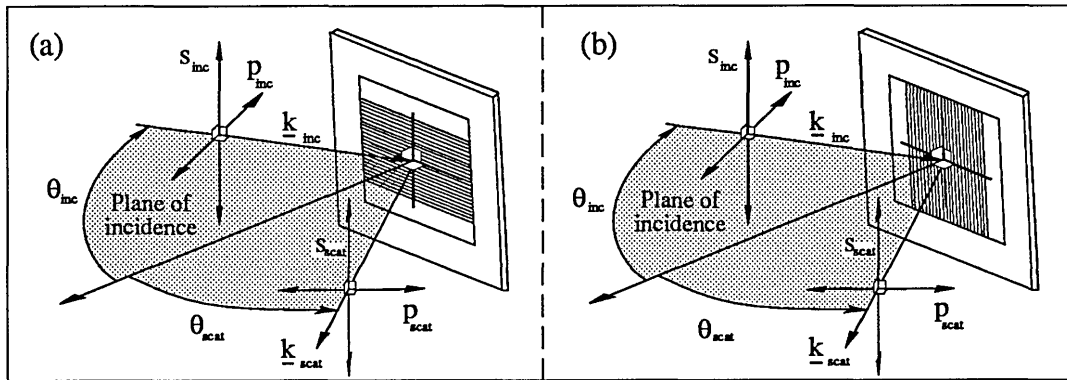


Figure 5.2: A schematic diagram of the scattering geometry showing incident and scattered polarizations with respect to the surface formed by a planar array of hairs (a) horizontally orientated and (b) vertically orientated to the plane of incidence.

5.2.1 Hair Surfaces Orientated Horizontally

As regards the individual horizontally orientated hair experiments discussed in section 3.2.1, the goniophotometric scanning range was chosen to encompass the distribution of the specularly reflected light. In general, this was taken to be $\pm 45^\circ$ about the direction of maximum front-face reflection. Although it would now be possible to determine the outward normal to a hair surface and measure all scattering angles with respect to this, it was decided, for ease of comparison with the single fibre work, to continue with the convention of measuring the scattering angle with respect to the incident beam.

Hairs from the six basis samples (see section 3.1) were strung into arrays and then mounted in turn on the goniophotometer. Each array was illuminated at an

angle of 30° to the outward normal of the hair surface. Polarized-light-scattering measurements were taken at three wavelengths (458nm, 514nm, and 633nm) to determine if there was any relationship between the wavelength of the illuminating radiation and the shape of the light-scattering envelope. A graphical summary of the results is presented in figures 5.3 to 5.7. The results have been normalized with respect to incident beam power and the total surface area of hair illuminated so that comparisons may be drawn between each set of data.

Since this investigation generated a large amount of data, it was decided to include the results for only one black hair type here (the Oriental sample was chosen). It was possible to do this without any loss of information as it was found that it was the hair's colour and not its racial origin which produced a variation in results as the illuminating wavelength was changed.

The first point to notice from the graphs in figures 5.3 to 5.7 is the smoothness of the traces obtained. If the graphs are compared with figure 3.1 for a laser-illuminated individual hair, it can be seen that the larger area of illumination possible with a surface of hairs has reduced the magnitude of the speckle noise so that it is no longer a problem. With the exception of the results for the black hair samples which were found to produce negligible cross-polarized return, each graph consists of three data sets. The co-polarized return (legends labelled *ss data* or *pp data*), the cross-polarized return (legends labelled *sp data* or *ps data*), and the incoherent sum of the co- and cross-polarized returns (legend labelled *total*).

Experimental observations showed that the black and white hair surfaces exhibited very little wavelength dependence in terms of the magnitude and shape of their light-scattering distributions. The white hair did show a slight increase in the magnitude of the co- and cross-polarized returns at the He-Ne laser wavelength of 633nm. The light-scattering envelopes formed by the brown, red, and blond samples all followed the same trend of increasing magnitude in the light-scattering contributions to the internal peak as the wavelength varied from the blue (458nm) end of the visible spectrum to the red (633nm).

As mentioned in chapter one, the appearance of hair is dominated to a large extent by its colour. The colour of a hair sample has also been shown in chapter three to affect the instrumental measurement of gloss; it is therefore an important quantity to take into account during gloss measurements. To take it into account properly, the colour of each hair sample must be objectively and unambiguously

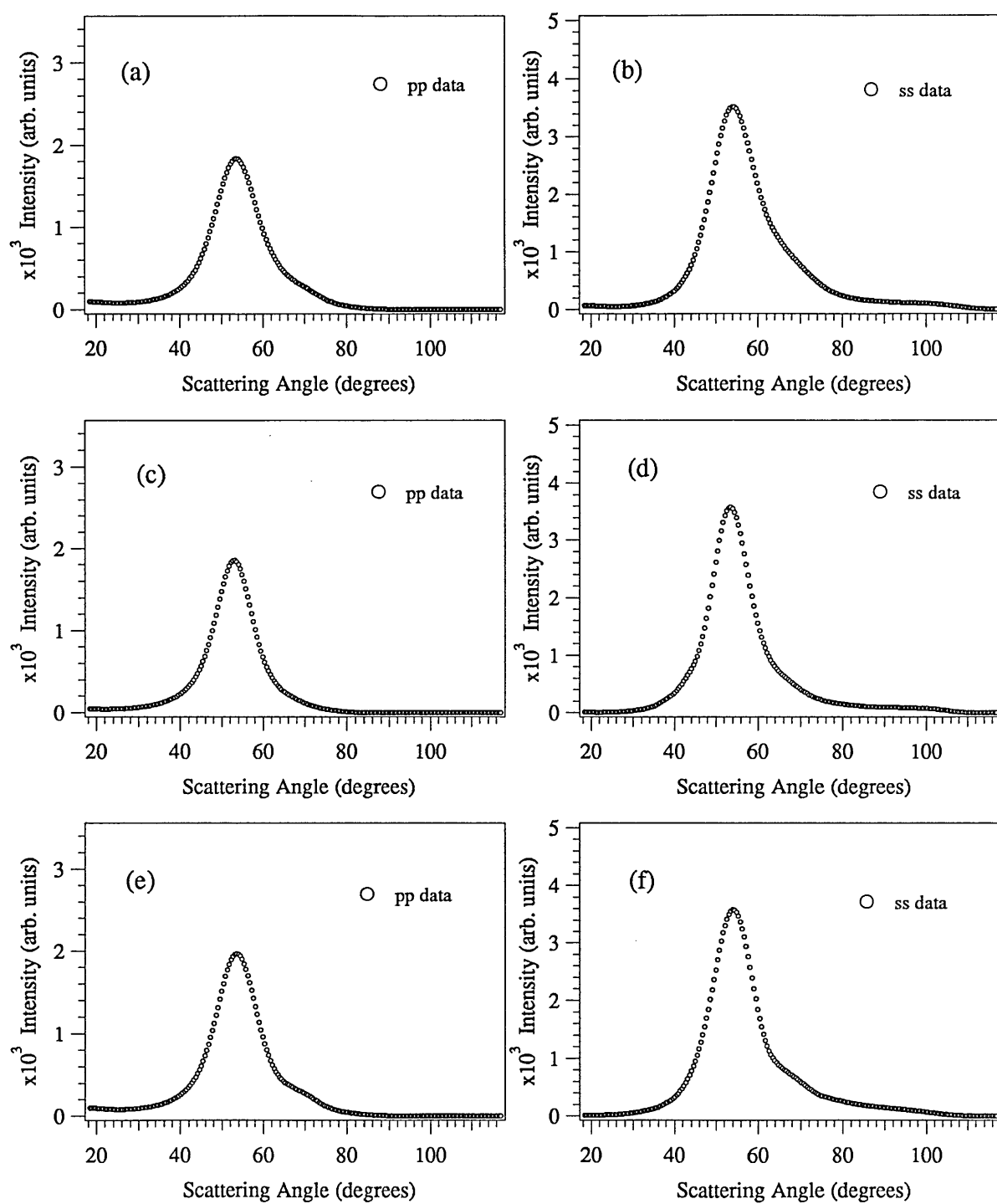


Figure 5.3: Normalized goniophotometric curves from a surface of black hairs with: (a) *p*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (b) *s*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (c) *p*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (d) *s*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (e) *p*-polarized light incident at wavelength $\lambda = 633\text{nm}$, and (f) *s*-polarized light incident at wavelength $\lambda = 633\text{nm}$.

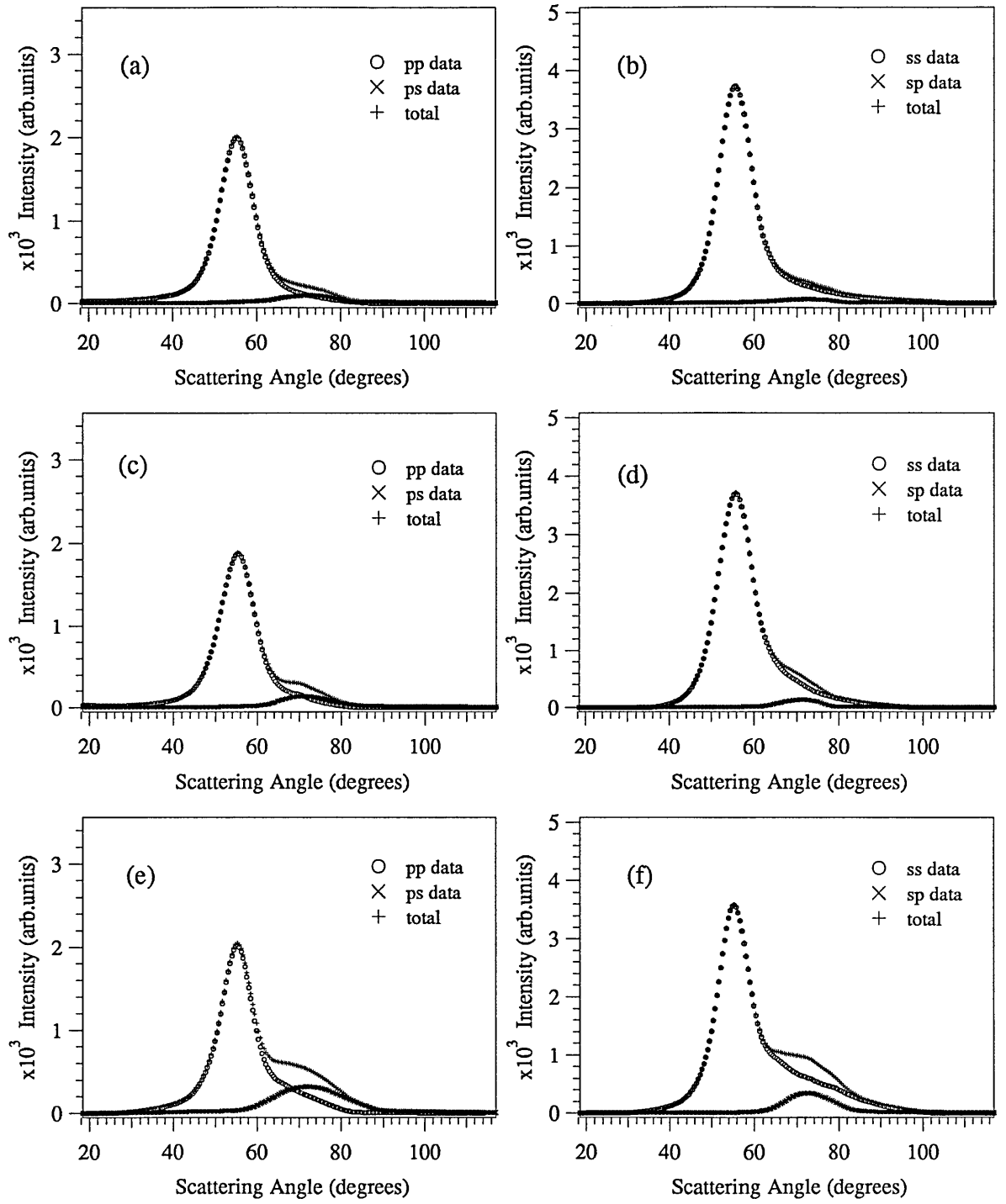


Figure 5.4: Normalized goniophotometric curves from a surface of brown hairs with: (a) *p*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (b) *s*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (c) *p*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (d) *s*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (e) *p*-polarized light incident at wavelength $\lambda = 633\text{nm}$, and (f) *s*-polarized light incident at wavelength $\lambda = 633\text{nm}$.

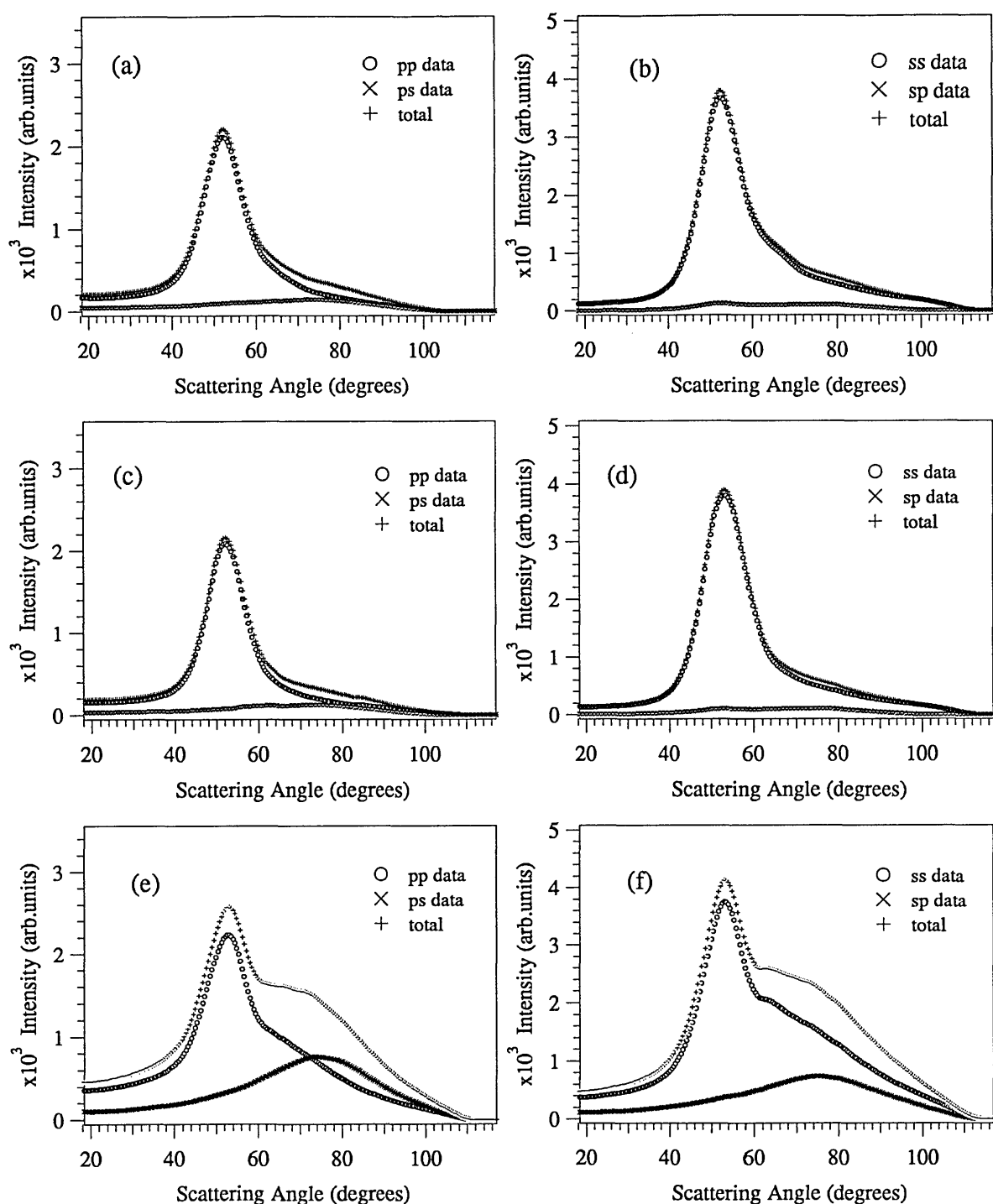


Figure 5.5: Normalized goniophotometric curves from a surface of red hairs with: (a) p -polarized light incident at wavelength $\lambda = 458\text{nm}$, (b) s -polarized light incident at wavelength $\lambda = 458\text{nm}$, (c) p -polarized light incident at wavelength $\lambda = 514\text{nm}$, (d) s -polarized light incident at wavelength $\lambda = 514\text{nm}$, (e) p -polarized light incident at wavelength $\lambda = 633\text{nm}$, and (f) s -polarized light incident at wavelength $\lambda = 633\text{nm}$.

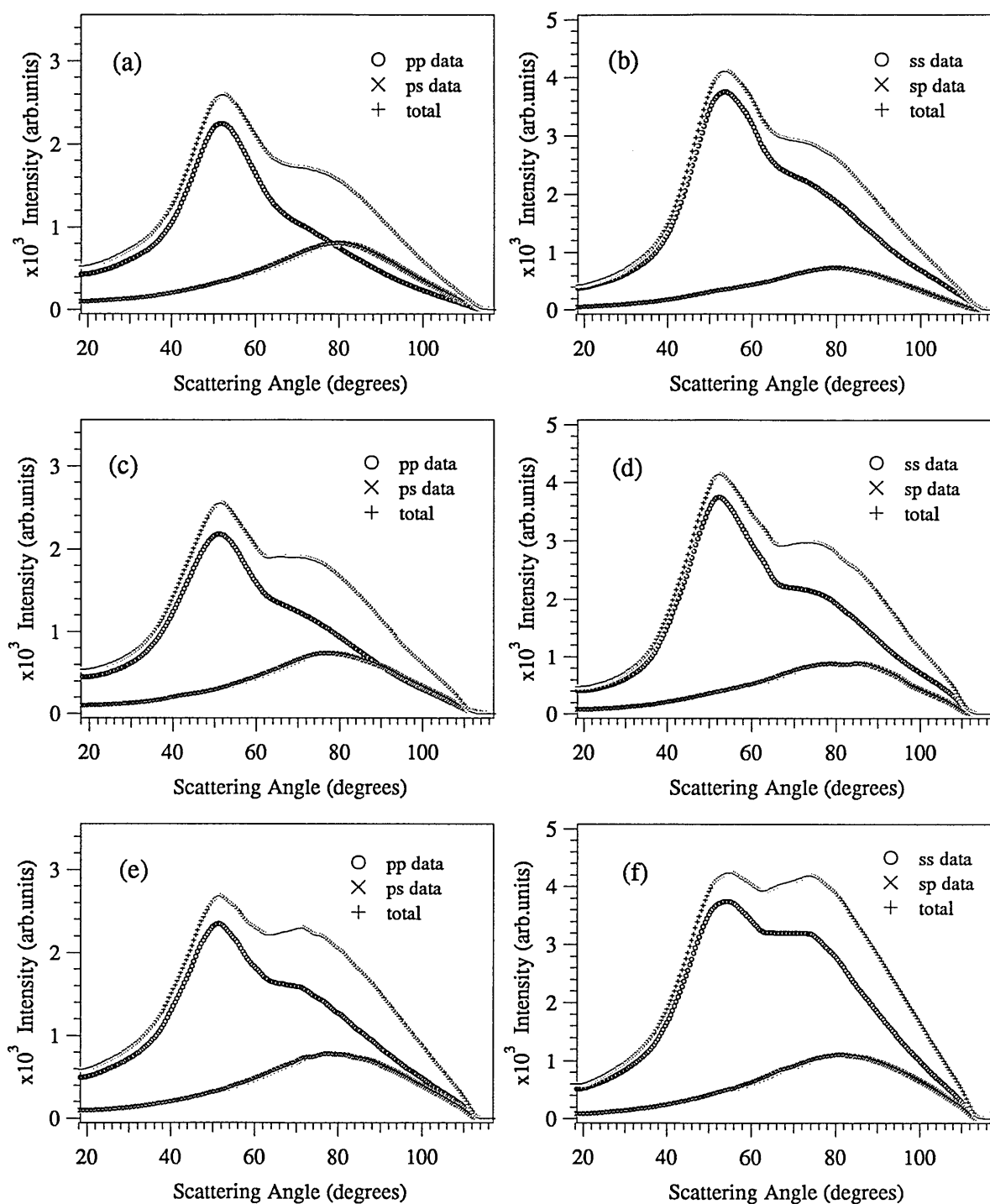


Figure 5.6: Normalized goniophotometric curves from a surface of blond hairs with: (a) *p*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (b) *s*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (c) *p*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (d) *s*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (e) *p*-polarized light incident at wavelength $\lambda = 633\text{nm}$, and (f) *s*-polarized light incident at wavelength $\lambda = 633\text{nm}$.

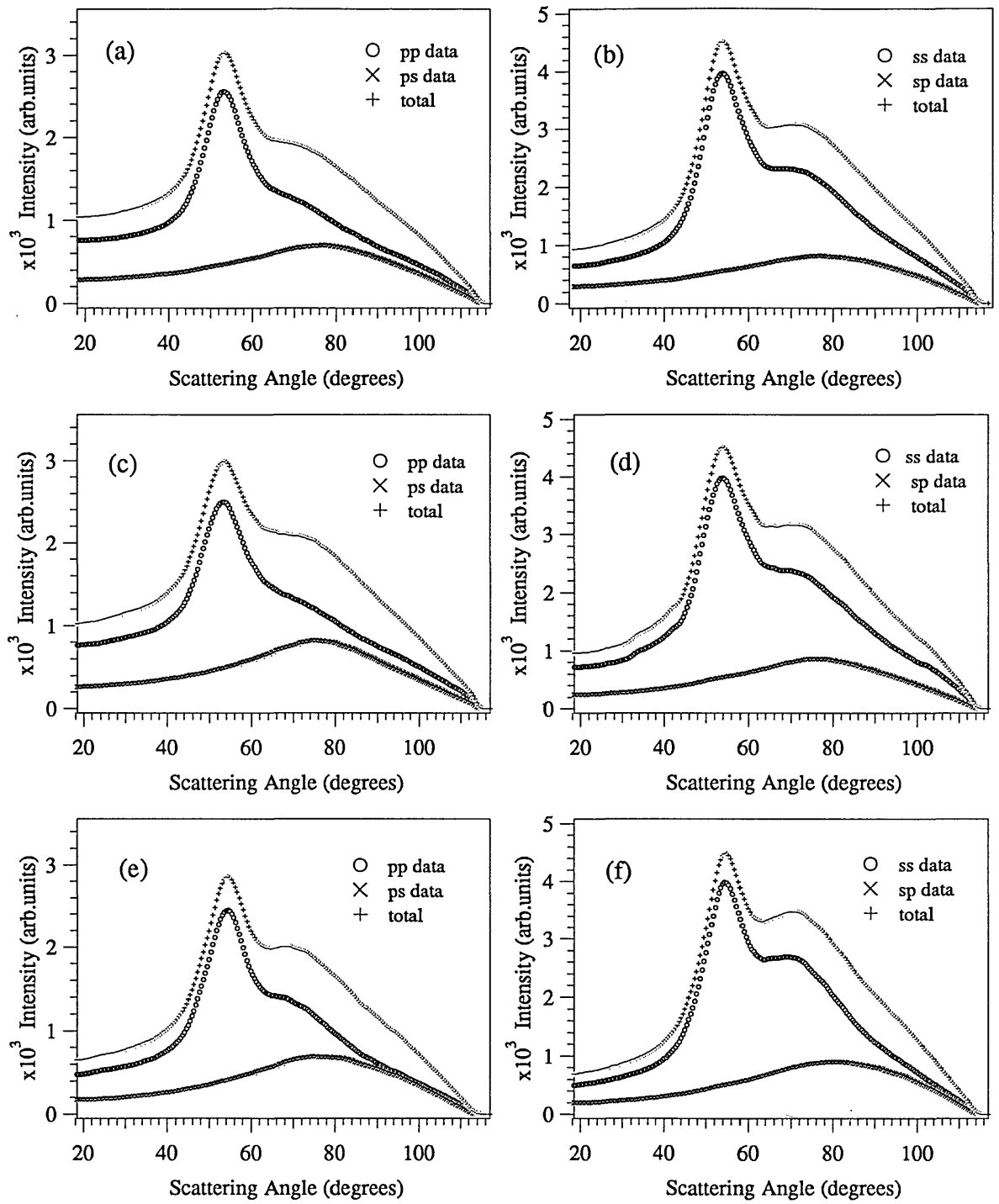


Figure 5.7: Normalized goniophotometric curves from a surface of white hairs with: (a) *p*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (b) *s*-polarized light incident at wavelength $\lambda = 458\text{nm}$, (c) *p*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (d) *s*-polarized light incident at wavelength $\lambda = 514\text{nm}$, (e) *p*-polarized light incident at wavelength $\lambda = 633\text{nm}$, and (f) *s*-polarized light incident at wavelength $\lambda = 633\text{nm}$.

classified. However, research concerned with quantifying hair colour and colouring has been hampered by descriptions of hair colours not having names with consistent or universal meanings. For instance, what might be described as a warm mid-brown by one observer could be called red-brown or auburn-brown by another. Instrumental measurements of hair colour have been undertaken by several researchers [26, 27] in which they have described hair colours in terms of a standard tristimulus system. As explained in chapter one, section 1.3.1, the tristimulus system is a scheme which allows a colour to be described in terms of the amount of red, green, and blue light it reflects. Experimentally, to describe a colour in terms of such a system, three separate measurements to determine the amounts of red, green, and blue light reflected from the sample are required. The measurements taken in this section to investigate the wavelength dependence of light scattering by human hair already provide three sets of scattering data at each wavelength, which it may be possible to use to calculate the tristimulus chromaticity co-ordinates for each sample.

The first stage was to identify and select the portion of the goniophotometric curve which contained the colour information about the hair. Den Beste and Moyer [26] also faced this problem; in their investigation they took a single unpolarized goniophotometric scan for each hair sample at red, green, and blue wavelengths. Realising that it was the internally scattered light which carries colour information about a hair sample (see chapter three, section 3.3) they decided to analyse the light-scattering envelope by dividing the area under the curve into two smaller areas at the mirror angle of reflection — that is, the angle at which a mirror would reflect light if it were mounted in the place of a hair tress. For hair orientated RER, the area under the curve to the right of this imaginary dividing line (i.e. corresponding to the ‘secondary peak’, which is due to light internally reflected by the hair) was taken to be a measure of the hair’s colour. However, the broad spread of the specular peak produced by a tress of hair meant that this method unavoidably included a contribution of light specularly reflected from the front face. The studies in chapter three have shown that specularly reflected light carries no colour information about the hair sample; rather it appears to be the colour of the illuminating source. The size of this specular contribution may also vary from sample to sample, depending on the surface roughness of the hairs and the condition of the sample. In consequence, such variations will alter the values determined for the chromaticity co-ordinates and hence the classification of the hair’s colour.

Considering these drawbacks in the Den Beste and Moyer method, it was decided to try and develop a more satisfactory technique of separating the colour information from the goniophotometric curves. Bearing in mind the fact that the colour information is contained almost exclusively in the secondary peak, the problem reduces to separating this component from the light reflected at the front face of the hair. One advantage of taking polarization-sensitive measurements is that this is already partially achieved. It was discussed in chapter three how a change in the polarization state between incidence and detection was indicative of the light being internally scattered, so calculating the area under the cross-polarized return could be used as a method of separating part of the internally scattered light from the total light-scattering envelope. Of course, the remainder of the colour information is contained in the co-polarized return which also includes the specularly reflected light, and again it is not simple to separate these two components.

However, if the assumption could be made that the ratio of colour information split between the co- and cross-polarized returns was independent of wavelength, then taking only the cross polarized return as a indication of hair colour would be valid (the normalized chromaticity co-ordinates would be unvaried as each contribution at red, green, and blue wavelengths would be altered in the same ratio*. Unfortunately, even to determine if this assumption is reasonable is not straightforward. Consider a typical goniophotometric result for a blond hair as shown in figure 5.6b: the area under the *ss data* curve (the co-polarized) may be split into two such that:-

$$A_{co} = A_{spec} + A_{int1} , \quad (5.1)$$

where A_{co} is the total area under the co-polarized return, A_{spec} is the area under the specularly reflected light (unknown), and A_{int1} represents the area which corresponds to light internally scattered and then detected with the same polarization state as the incident light (also unknown). The area under the cross-polarized return A_x corresponds to the remainder of the light internally scattered such that $A_x = A_{int2}$. The total area enclosed by the two internally scattered components equals the total area carrying colour information; that is,

$$A_{colour} = A_{int1} + A_{int2} , \quad (5.2)$$

where A_{colour} corresponds to that area. If it is to be valid to use A_{int2} alone to

*Note: it is the relative amounts of red, green, and blue radiation which determine the chromaticity co-ordinates, not absolute values.

represent A_{colour} in the chromaticity calculations, then at all wavelengths $A_{int1} = \kappa A_{int2}$, where κ is a fixed constant (independent of wavelength). To test this, the ratios of the areas under the co- and cross-polarized returns were determined. If $A_{int1} = \kappa A_{int2}$, then equation 5.1 may be rewritten to give $A_{co} = A_{spec} + \kappa A_{int2}$. Taking the ratio of A_{co} and A_x gives

$$\left(\frac{A_{co}}{A_x}\right) = \left(\frac{A_{spec}}{A_{int2}}\right) + \kappa . \quad (5.3)$$

Assuming that, for a given sample, A_{spec} is independent of wavelength (from Fresnel equations this is a reasonable assumption) then the only wavelength-varying factor in equation 5.3 should be A_{int2} .

Table 5.1 summarizes values of $\left(\frac{A_{co}}{A_x}\right)$ averaged over the two incident polarization states for the four samples considered in this section. It can be seen that for the sample of white hair, where A_{int2} and the ratio of $\left(\frac{A_{co}}{A_x}\right)$ were approximately constant with wavelength, κ must also have been invariant. For the other hair samples, where A_{int2} was found to vary considerably with wavelength, it was not possible to make conclusive comments about any wavelength dependence of κ , but for the blond and brown samples, A_{int2} steadily increased with increasing wavelength and the ratio $\left(\frac{A_{co}}{A_x}\right)$ was correspondingly found to decrease; this is as would be expected if κ were a constant or only decreased slightly with increasing wavelength. Although this quick test is not conclusive it does not invalidate the suggested method either. So, keeping this in mind, it was decided to analyse the data using both techniques (the area enclosed by the cross-polarization curve and Den Beste's method using the appropriate areas under the *total* data curves) and then compare the results produced.

In the tristimulus system, any colour (C) may be described in terms of the amounts of red (R), green (G), and blue (B) radiation it reflects:-

$$C.(C) \equiv R.(R) + G.(G) + B.(B) . \quad (5.4)$$

In the light scattering from human hair, each sample was measured with incident stimuli at red ($\lambda_R = 633\text{nm}$), green ($\lambda_G = 514\text{nm}$), and blue ($\lambda_B = 458\text{nm}$) wavelengths (which were chosen by the experimenter as convenient wavelengths). Now, as mentioned earlier, it is the relative amounts of R , G , and B that are important in calculating chromaticity co-ordinates of a colour, thus equation 5.4 may be normalized, so that $C = 1$, giving the unit equation:-

$$(C) \equiv r.(R) + g.(G) + b.(B) \quad (5.5)$$

Table 5.1: Areas enclosed by the cross-polarized curves and the ratio of areas enclosed by the co- and cross-polarized curves at each wavelength and for each hair sample.

Hair Sample & Wavelength	Area under Cross-poln A_{int2} (arb. units)	Ratio of Areas $\left(\frac{A_{co}}{A_x}\right)$ (no units)
Brown(633nm)	$27,786.4 \pm 139$	6.2 ± 0.04
Brown(514nm)	$11,173.7 \pm 56$	14.1 ± 0.1
Brown(458nm)	$9,198.4 \pm 46$	23.5 ± 0.2
Red(633nm)	$142,745.7 \pm 714$	2.7 ± 0.02
Red (514nm)	$22,772.5 \pm 114$	10.5 ± 0.07
Red(458nm)	$25,857.5 \pm 129$	9.5 ± 0.07
Blond(633nm)	$201,882.5 \pm 1009$	4.2 ± 0.03
Blond(514nm)	$170,925.5 \pm 855$	3.5 ± 0.02
Blond(458nm)	$158,410.8 \pm 792$	3.3 ± 0.02
White(633nm)	$191,075.5 \pm 955$	2.7 ± 0.02
White(514nm)	$203,777.0 \pm 1019$	2.8 ± 0.02
White(458nm)	$201,886.0 \pm 1009$	2.7 ± 0.02

where $r = \frac{R}{R+G+B}$, $g = \frac{G}{R+G+B}$, $b = \frac{B}{R+G+B}$ and $r + g + b = 1$.

In any area of science, where results need to be compared between different organizations or groups of workers, the measurements must either be made on or converted to a standard basis. In colorimetry, the C.I.E. system (see chapter one, section 1.3.1) was developed and adopted for this purpose, and by using it, a unit equation describing a colour in terms of three measurement stimuli may be transformed into a new unit equation defined in terms of a set of standard reference stimuli ((X), (Y), and (Z)). Thus, a colour, C , may be re-expressed as

$$(C) = x.(X) + y.(Y) + z.(Z) , \quad (5.6)$$

where x , y , and z correspond to the C.I.E. chromaticity co-ordinates, i.e. the tristimulus values of the C.I.E. system of colorimetry, normalized to unity, give the co-ordinates of a colour in the C.I.E. colour triangle. The mechanics of the conversion process, not being central to the discussion, are given in appendix 3.

In fact, the location of a colour, C , on the chromaticity chart requires that only two of the co-ordinates (conventionally (x, y)) be defined. The co-ordinates for each hair were calculated using both Den Beste's and the cross-polarization methods of data analysis and are presented graphically on C.I.E. chromaticity charts in figures 5.8 and 5.9. Comparing both sets of points it could be seen that a good agreement

was to be found between the results generated by the two methods of colour extraction, with differences in the co-ordinates for each hair colour being small. General agreement was also obtained between the distribution of these natural hair colours as shown on the chart and the results of previous work in this field [25, 26]. Note: the colour of a dyed hair usually falls outside the area in which the co-ordinates of natural hair colours are clustered.

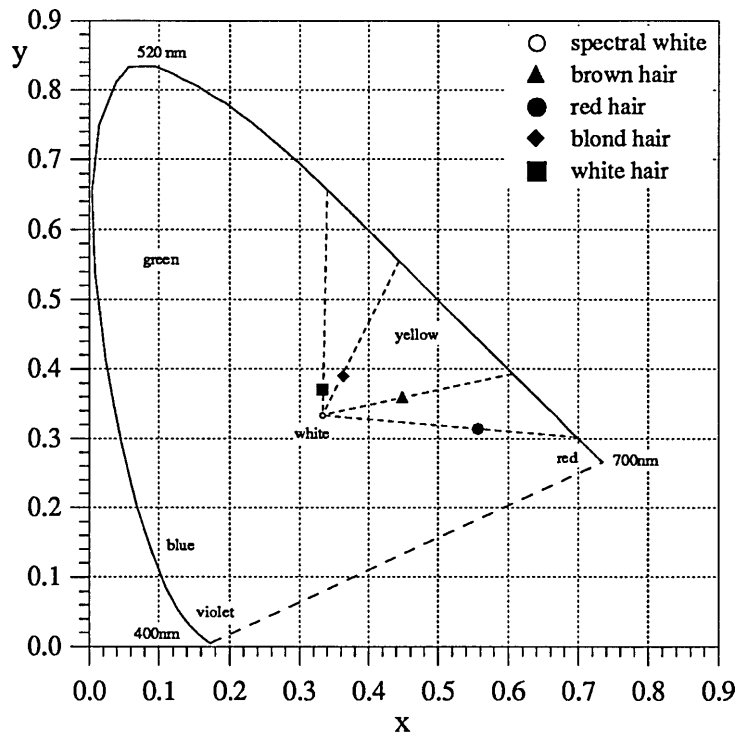


Figure 5.8: C.I.E. chromaticity diagram showing the x and y co-ordinates of the pure spectrum locus and the chromaticity co-ordinates of four natural hair colours as calculated from the areas under the cross-polarized goniophotometric curves.

Although this classification of colour is useful, unless the chromaticity co-ordinates are plotted out it is not easy to see at a glance which colour is the more saturated or the more red. Thus, further colour specifications were developed, these include the dominant wavelength, λ_d , and the purity (degree of saturation) of a colour. They have been calculated for each hair sample from its chromaticity co-ordinates by drawing a line from the co-ordinates of spectral white (0.333, 0.333) through the hair colour co-ordinate to the spectrum locus. The wavelength at which this line intersects the spectrum locus is deemed to be the dominant wavelength for the sample, and the ratio of the length of line between the colour co-ordinates and the

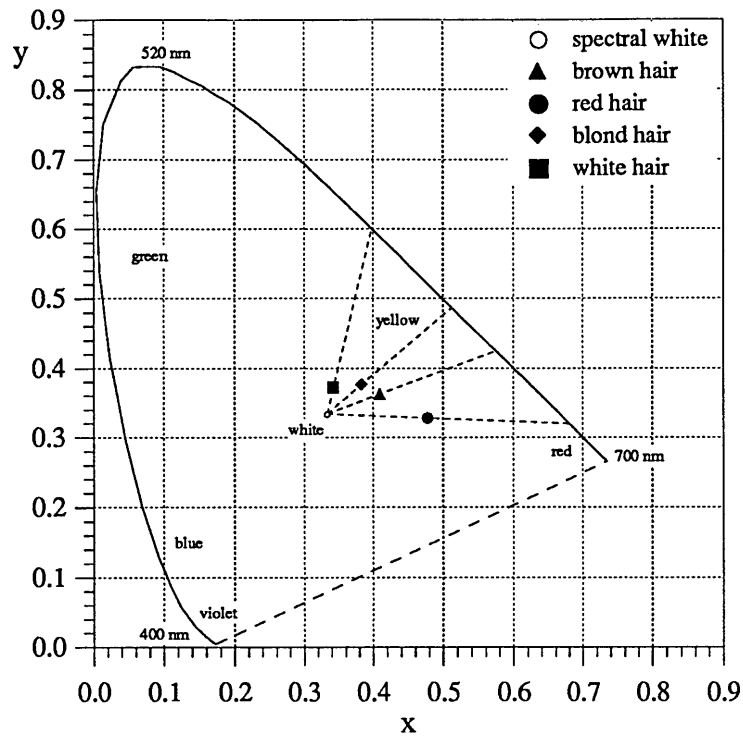


Figure 5.9: C.I.E. chromaticity diagram showing the x and y co-ordinates of the pure spectrum locus and the chromaticity co-ordinates of four natural hair colours as calculated following Den Beste and Moyer's method using a proportion of the area under the goniophotometric curves.

co-ordinates of spectral white to that of the total length of the line is a measure of the hair colour's purity. Tables 5.2 and 5.3 summarize these values for the hair samples as calculated from the co-ordinates produced by the two methods.

It can be seen that, for every hair sample, the tabulated values of purity were higher when calculated via the cross-polarization method than when using Den Beste's technique, and the red and brown hairs were found to have longer dominant wavelengths, and the white and blond samples shorter dominant wavelengths. These differences may be interpreted either as the effects of the addition of part of the specular component to each of the measurement values in Den Beste's method or in terms of a wavelength dependence in κ .

The third attribute which describes any colour is its luminosity or luminance ratio, β , if the object is not self-luminous. The C.I.E. reference stimuli are chosen such that two of them ((X) and (Z)) have zero luminous efficiencies, thus the amount of light represented by the colour equation is given directly by the third tristimulus

Table 5.2: Colour specification in terms of dominant wavelength, purity, and luminance factor as calculated from the cross-polarized goniophotometric data.

Hair Sample	Dominant Wavelength λ_d in μm	Purity (no units)	Luminance Factor $\beta' \times 100$ (no units)
Brown	0.598 ± 0.005	0.423 ± 0.008	7.6 ± 0.5
Red	0.622 ± 0.005	0.618 ± 0.008	26.6 ± 0.5
Blond	0.570 ± 0.005	0.261 ± 0.008	89.4 ± 0.5
White	0.546 ± 0.005	0.117 ± 0.008	—

Table 5.3: Colour specification in terms of dominant wavelength, purity, and luminance factor as calculated following the Den Beste and Moyer method of analyzing goniophotometric data.

Hair Sample	Dominant Wavelength λ_d in μm	Purity (no units)	Luminance Factor $\beta' \times 100$ (no units)
Brown	0.591 ± 0.005	0.265 ± 0.008	13.6 ± 0.5
Red	0.615 ± 0.005	0.423 ± 0.008	30.6 ± 0.5
Blond	0.580 ± 0.005	0.120 ± 0.008	92.6 ± 0.5
White	0.564 ± 0.005	0.115 ± 0.008	—

value (Y). From equation 5.4, a colour, C , may be described in terms of any three stimuli such that

$$C.(C) \equiv X.(X) + Y.(Y) + Z.(Z) ,$$

and so in this case its luminous flux, F , will be

$$F = j(X.V_{.(x)} + Y.V_{.(y)} + Z.V_{.(z)}) ,$$

where j is a constant and $V_{.(x)}$, $V_{.(y)}$, and $V_{.(z)}$ are the spectral luminous efficiencies at these wavelengths. Since $V_{.(x)}$ and $V_{.(z)}$ are arranged to be zero in the C.I.E. system, the equation may be simplified to give

$$F = jY.V_{.(y)} = j'Y ,$$

where j' is a new constant. Therefore, the radiant flux, Y , is a direct measure of the amount of light represented by the tristimulus equation for C . For hair, not being self-luminous, it is appropriate to measure its luminance ratio, β , which is defined as the ratio of the light quantity from the test sample to that from a perfect white reflector, usually a magnesium oxide surface. In the case of the hair surfaces, which in reality have many gaps and are not true surfaces in the normal sense, it would

not be as meaningful to compare amounts of reflected light with such a reflector. So instead it was decided to take comparisons between the amount of light reflected by each hair sample and that reflected by the white hair sample and call them modified luminance factors (β') — values for which are also included in tables 5.2 and 5.3. Both methods of analysing the data produced identical trends of increasing β' from brown through red to blond.

5.2.2 Hair Surfaces Orientated Vertically

The six basis samples strung for the previous experiment were mounted on the scatterometer described in section 2.2.2 so that the fibres were orientated vertically as shown in figure 5.2 (b). For these experiments the scatterometer was used in preference to the dedicated goniophotometer, as it was able to provide more information in the direction of backward scatter. The surfaces were illuminated at 0° and 30° with linearly polarized laser light at a wavelength of 633nm and with equal incident power for both *s*- and *p*-polarization states. The range of scattering angles was confined to $\pm 90^\circ$ measured with respect to the normal to the surface in the half-plane of backward scatter (see figure 5.2). In the cases of the black, blond, and white hair samples, both single- and double-layer surfaces were investigated. Co- and cross-polarized scans were taken for each surface but the cross-polarized returns are not included in the graphical summaries of the results. This is because the level of the cross-polarized return for the dark hairs was negligible compared to the co-polarized, and for the light (almost transparent) hairs, although measurable (approximately 10% of the value of the co-polarized return at 0°), it was almost invariant with scattering angle, merely tapering off at $\pm 90^\circ$.

The results for this experiment are summarized into figures 5.10, 5.11, and 5.12. It can be seen that, unlike the individual hair fibre results, the intensity distribution of both polarization states drops to zero at the limits of the scan range: this is as a consequence of the surface arrangements of the hairs in their supporting frame. The apparent change in size of the illumination area on the hair surface, as seen by the detector as it rotates, depends on the cosine of the angle the detector subtends to the normal to the surface. Thus at $\pm 90^\circ$, the cosine of the angle subtended by the detector is zero and the illumination area can no longer be seen, so the scattered intensity detected at this angle drops to zero.

The main feature in these results, as it was for the individual fibre experiments,

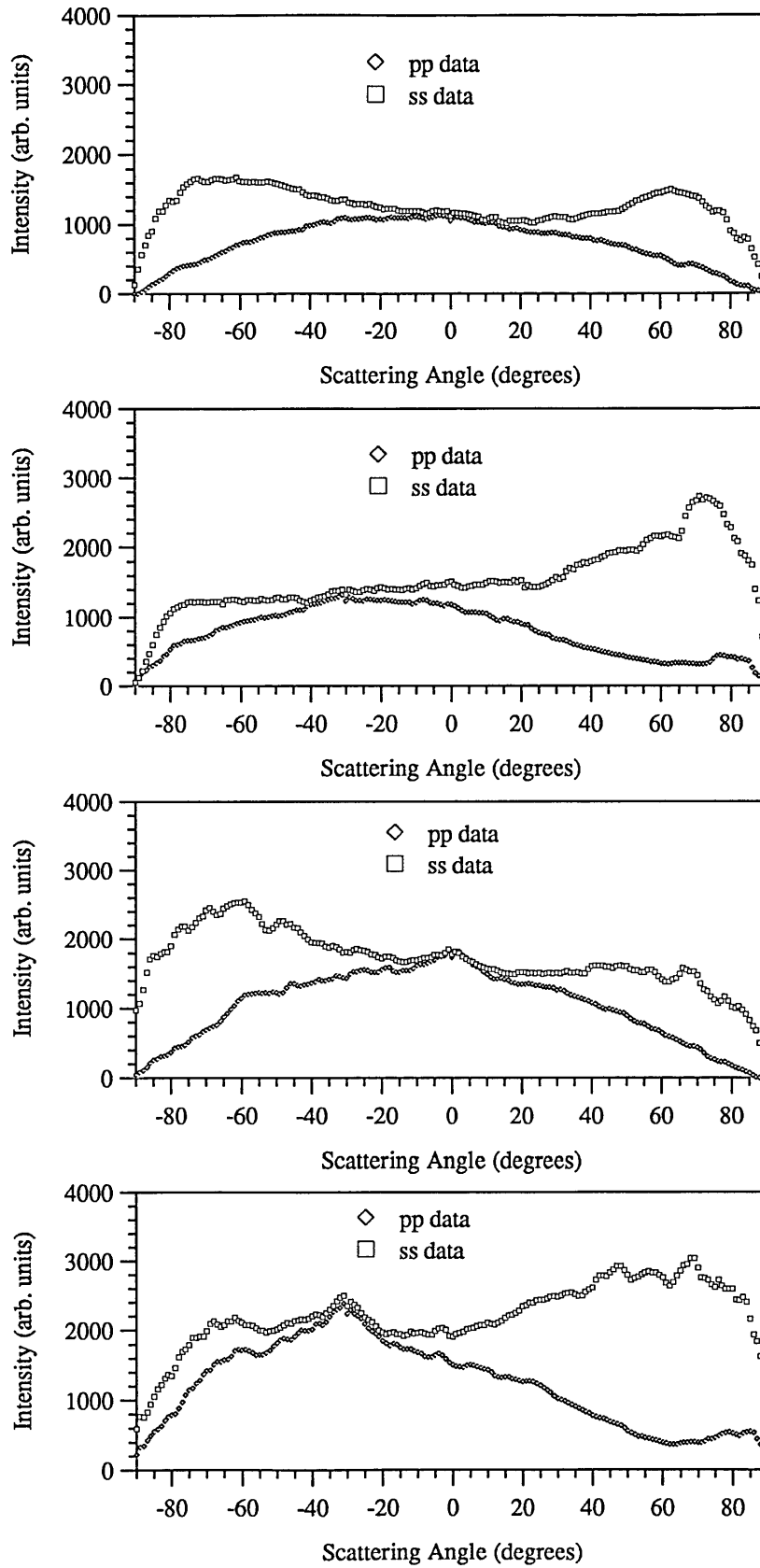


Figure 5.10: Goniophotometric curves from a single-layer surface of black hairs at (a) normal incidence and (b) 30° incidence, and from a double-layer surface of black hairs at (c) normal incidence and (d) 30° incidence.

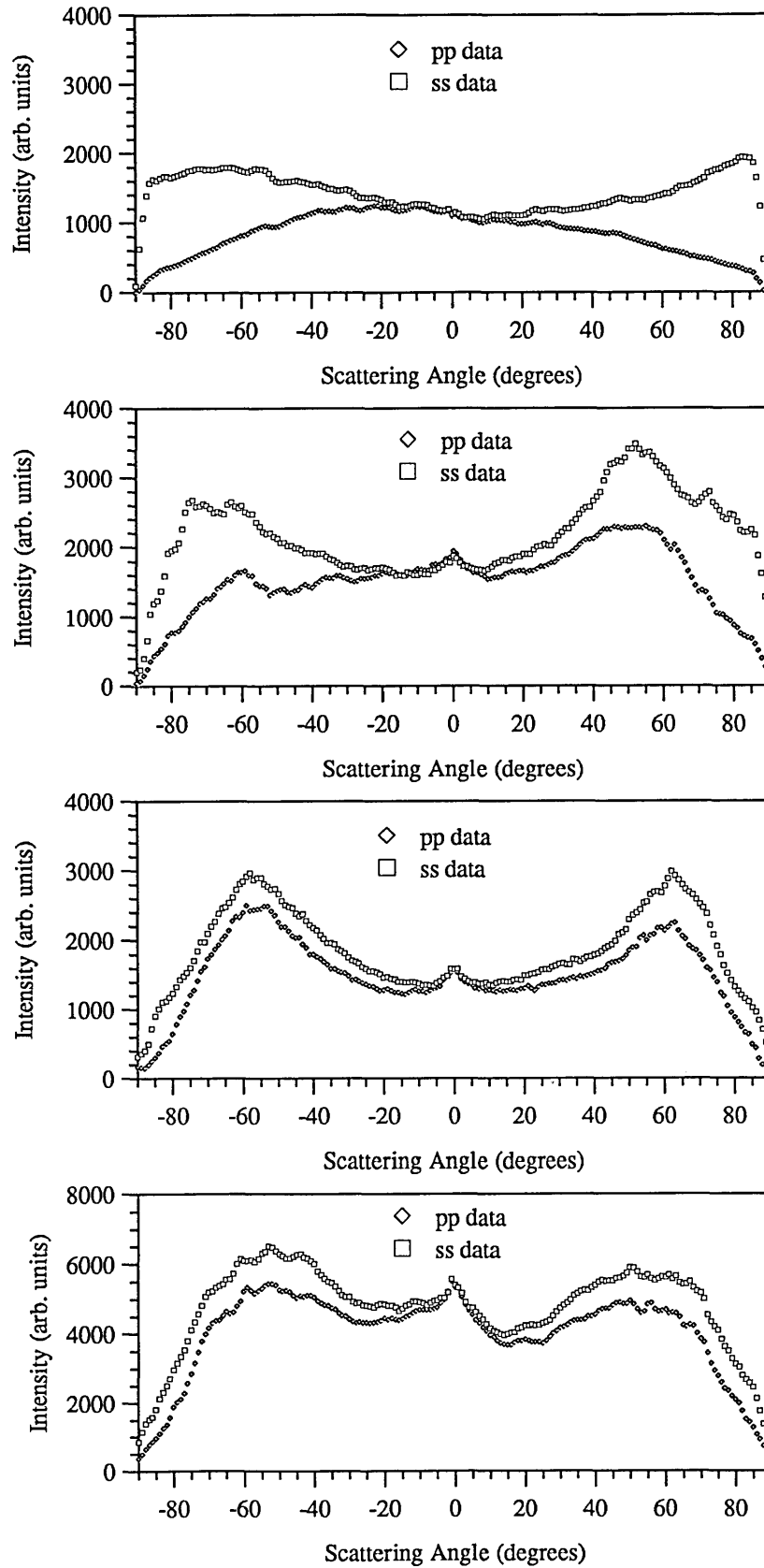


Figure 5.11: Goniophotometric curves from: (a) a single-layer surface of brown hairs at normal incidence, (b) a single-layer surface of red hairs at normal incidence, (c) a single-layer surface of blond hairs at normal incidence, and (d) a double-layer surface of blond hairs at normal incidence.

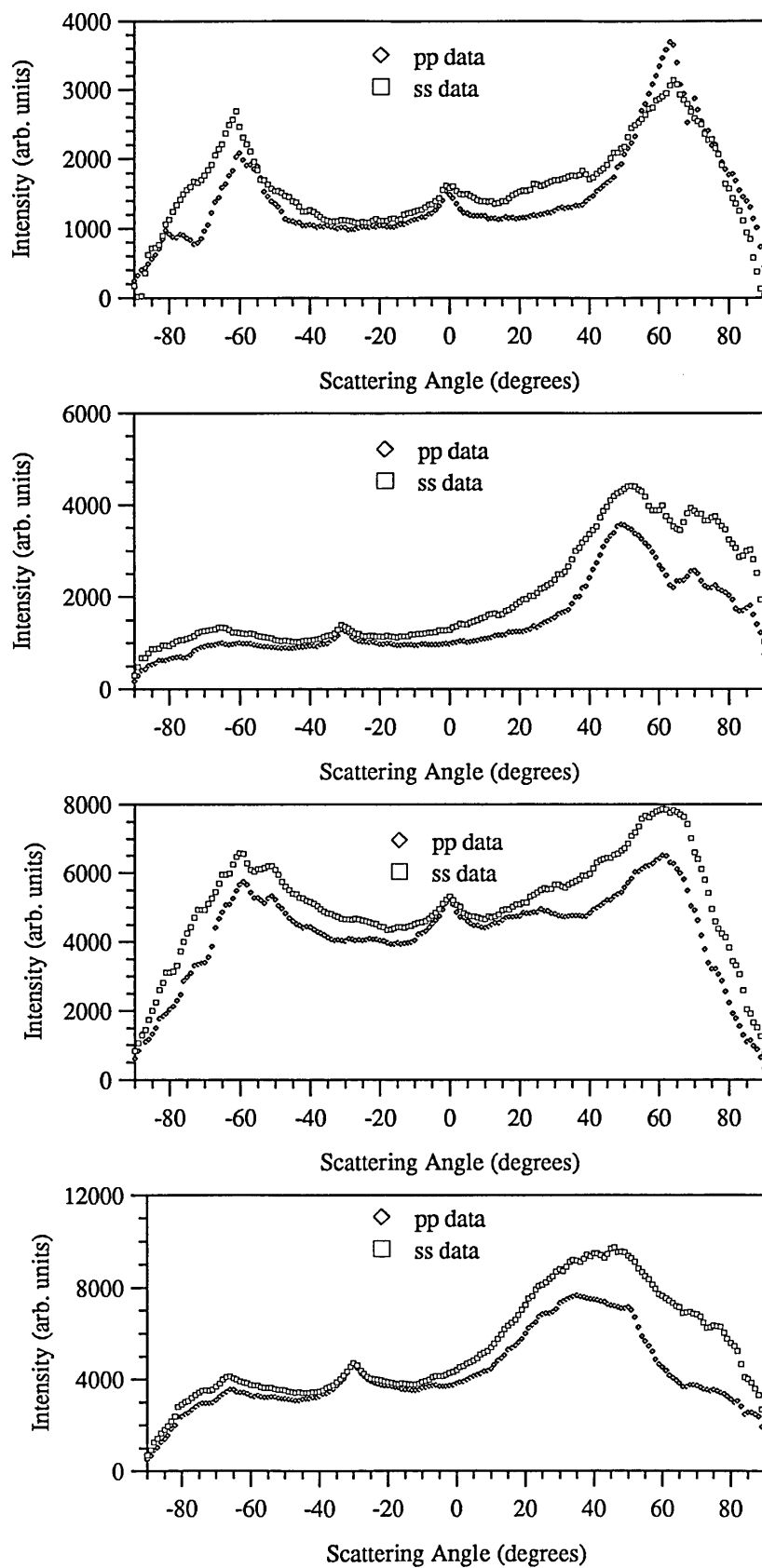


Figure 5.12: Goniophotometric curves from a single-layer surface of white hairs at (a) normal incidence and (b) 30° incidence, and from a double-layer surface of white hairs at (c) normal incidence and (d) 30° incidence.

is the difference in shape of the scattering envelope depending on the degree of pigmentation of the hair sample, i.e. its colour. Again the light-scattering distributions produced by the dark hairs conform to one shape and those produced by the light (almost transparent) hairs conform to another.

The shapes of the curves produced by the surfaces of black hairs at normal incidence (in figure 5.10(a) and (c)) were basically very similar to the light-scattering distributions produced by an individual black hair fibre in the same orientation and thus share a common explanation (see section 3.2.2). It was noted that the double-layer surface included a slight enhancement of intensity in the direction of backscatter which was not observed in the single-layer data for either the black or brown hair samples. Away from 0° incidence, noting that the scattering angle is still measured with respect to the outward surface normal, the distribution of light is modified according to Fresnel's equations of reflection, e.g. the dip in the *p*-polarized data at $\approx 65^\circ$ is influenced by the Brewster effect. The intensity does not fall completely to zero as the surface of hairs cannot be considered to be smooth or flat.

The results for the partially transparent hairs, summarized in figure 5.11 (b), (c), and (d) and in figure 5.12 (a), (b), (c), and (d), show that the *ss data* and *pp data* are very similar in shape and distribution, except that the magnitude of the *pp data* is generally less than that of the *ss data* for all angles. The broad peaks on both sides of normal incidence correspond to the addition of all of the sharper 'caustic' peaks produced at slightly varying angles by each hair in the surface. The variation in angle will depend on the exact orientation to the incident beam of each hair's elliptical cross-section.

The feature of an enhancement of intensity in the backscatter direction, which was noted to be present in the light-scattering envelopes for double-layer surfaces of dark hairs, was also observed experimentally for single- and double-layer surfaces of red, blond, and white hairs. Re-examining the results for individual hair fibres, it was found that the red, blond, and white hairs also exhibited a slight enhancement of intensity in the backscatter direction (see figures 3.4 and 3.5).

For hair fibres with low concentrations of pigment granules, it is possible for light incident on the hair to be internally scattered before re-emerging and being detected. The caustic peaks, observed experimentally, are formed by light which has undergone one internal reflection before transmission (see chapter four). If the

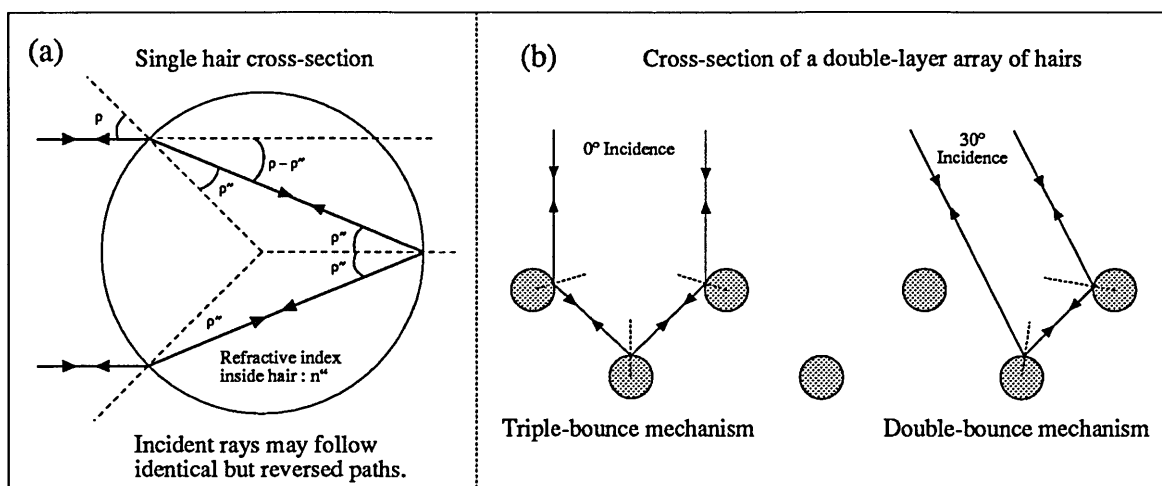


Figure 5.13: These diagrams illustrate two possible mechanisms for explaining intensity enhancement in the backscatter direction in terms of physical geometry.

ray path inside a hair is such that the emergent light is in direct opposition to the incident light then it has been scattered into the backscatter direction. When this occurs it is also possible for a portion of the incident light to follow the reverse path, i.e. if there were no obstructions to the forward path then there would be no obstructions to the reverse; such paths form forward and time-reversed pairs.

The diagram in figure 5.13 (a) illustrates forward and time-reversed ray paths from the inside of a partially transparent hair. In this simple example, the path of the ray traced is symmetrical about the horizontal diameter of the circular cross-section. Although a circular cross-section is shown here, in reality the partially transparent hairs exhibiting retro-reflection, generally being Caucasian, are more likely to have elliptical cross-section, but this does not alter the basic principle. So, in the backscatter direction the possibility of two paths (forward and time-reversed) exists, whereas generally at any other angle there would be only one; this will double the density of light paths in the backscatter direction and produce an enhancement. The path difference between light waves following each one of a pair of paths will be zero (they will have the same amplitude and phase) and so they will interfere constructively, which will also produce an enhancement.

Thus, the possibility of light scattered as in figure 5.13 (a) may explain the observed enhancement in the backscatter direction for partially transparent hairs (both individual and surface arrangements) but it does not explain the enhancement observed for double-layer surfaces of dark hairs where the levels of pigmentation in the cortex of the hair would be such that virtually all the light entering the hairs

would be absorbed. The clue to deducing a mechanism capable of explaining this enhancement lies in the fact that single layers of dark hairs (and individual fibres) do not exhibit this phenomenon. Obviously, the second layer of hairs must make it possible for forward and time-reversed pairs of ray paths to exist. Figure 5.13 (b) illustrates two such ray paths for light incident at angles investigated experimentally in this section. The first, at 0° incidence, involves three hairs and is called a triple-bounce mechanism (or 3-fold event), and the second, at 30° incidence, involves two hairs and is called a double-bounce mechanism (or a 2-fold event).

For double-layer surfaces of partially transparent hairs, both types of mechanism (retro-reflection inside an individual hair and multiple scattering between hairs) will be possible. This is confirmed by the increased size of the backscatter peak for these hair surfaces when compared with those from the double-layer, dark-hair surfaces or single-layer, light-hair surfaces.

5.3 Quartz Halogen Illumination

Following in the general structure of chapter three, the experiments described in this section were all carried out with the quartz halogen lamp as the light source; it is subdivided into two main sections which depend on the orientation to the incident beam geometry of the parallel hairs in the array (see figure 5.2). All measurements using the 'white' light source were conducted using the dedicated goniophotometer.

5.3.1 Hair Surfaces Orientated Horizontally

For ease of comparison of these results (from hair surfaces) with those from single fibres, described in chapter three, the policy of measuring the scattering angle with respect to the incident beam has been continued here. As mentioned in the introduction to the individual hair fibre experiments, it is in this chapter that a more comprehensive analysis of gloss measurements has been undertaken together with other techniques for evaluating the goniophotometric curves.

This section begins with a general discussion about the types of gloss measurement that may be used to evaluate the appearance of human hair; this is followed by the description of a series of experiments on untreated hair samples (examining variations in colour, racial origin, and incident angle) and on a smaller group of treated samples (both ultra-violet irradiated and chemically altered). In each ex-

periment, an evaluation of the goniophotometric curve has been made in terms of both gloss and statistical indices.

Finally, a short conclusion is presented on these findings, in particular commenting on the rapidity of each calculation together with its degree of correlation with visual observations.

Methods of Objectively Evaluating the Appearance of Hair

As was discussed in chapter one, section 1.3.5, the appearance of human hair has traditionally been subjectively assessed via half-head tests in the salon. These qualitative tests are not reliable, as they depend on the illumination conditions and on the subjective opinion of the judges, and both factors may vary enormously. Several researchers have sought objective methods of assessing the appearance of an object and some of these may be applied to human hair. Although gloss measurements may be taken for light reflected in all directions, this would involve an infinite number of measurements per sample. It has therefore become customary to confine gloss measurements to angles in the plane of incidence — a custom which has also been adopted for the assessment of hair gloss. This restriction on the type of gloss measurement that it is practicable to adopt is particularly important in a commercial environment where it would not be possible to spend long periods of time on each sample.

Of the six types of gloss described in chapter one, the most appropriate one for assessing the appearance of hair is *contrast gloss*. The other gloss types tend to be more applicable either to very shiny surfaces (e.g. specular gloss and distinctness-of-image gloss) or to those with unusual scattering properties (e.g. bloom and sheen).

Stamm et. al. calculated the contrast gloss of hairs using spot values (g_c) where only two intensity measurements were required (one at the specular angle, s , and the other at the normal to the surface, d), and using integrated values (G_c) where the full set of data points was used. In the latter case the area under the goniophotometric curve (bounded by the limits of the scan range) was evaluated and deemed to equal $S + D$ (the area enclosed by the specular and diffusely scattered light). Then the area enclosed by a rectangle of width equal to the full angular extent of the data set and of height d was calculated and set to be equal to D , from these evaluations S and $S - D$ may be determined by subtraction. In both cases they employed Nickerson's

modified form of contrast gloss:-

$$g_c = \frac{s - d}{s} \quad \text{and} \quad G_c = \frac{S - D}{S} .$$

Contrast gloss (G_c and g_c) together with the FWHM parameter (which in chapter three was shown to be linked to the transparency of hair) has been calculated for the surfaces of hairs examined in the following experiments.

An alternative method of characterizing monoplane goniophotometric results via statistics has also been considered. In the analysis of a frequency distribution, mathematical statistics have shown that three indices are important. These are: the dispersion index, σ , the skewness index, Sk , and the kurtosis index, K . The dispersion index, σ , also known as the variance or standard deviation, is a measure of the *dispersion* or *scatter* of the values of the random variable, a , about the mean. It is defined as

$$\sigma = \left(\frac{\sum_{i=1}^n f_i a_i^2}{\sum_{i=1}^n f_i} \right)^{\frac{1}{2}} \quad [\text{same as for } a]. \quad (5.7)$$

where f_i is in our case the fractional reflection at a_i , the i th departure from the mean. Following Nimeroff [51], who applied classical statistics to scattering experiments in 1952, the mean is set equal to the specular angle and a_i is measured in degrees. Thus, the skewness or asymmetry of the peak about the specular direction may be estimated. A distribution is skewed if one of the *tails* of the distribution is longer than the other; for instance, if the *right tail* is longer then the distribution is said to be *skewed to the right*. The index (or coefficient) of skewness is defined as

$$Sk = \left(\frac{\sum_{i=1}^n f_i a_i^3}{\sum_{i=1}^n f_i} \right) \frac{1}{\sigma^3} \quad [\text{no units}]. \quad (5.8)$$

The measure of Sk will be positive or negative according to whether the distribution is skewed to the left or right respectively. For a symmetrical distribution $Sk = 0$.

The index (or coefficient) of kurtosis is a measure of the degree of peakedness of a distribution, i.e. it is an indication of how closely concentrated the values of the

distribution are to the mean and hence the size of the peak. It is given by

$$K = \left(\frac{\sum_{i=1}^n f_i a_i^4}{\sum_{i=1}^n f_i} \right) \frac{1}{\sigma^4} \quad [\text{no units}]. \quad (5.9)$$

The lower the value the ‘flatter’ the curve; for instance a normalized Gaussian distribution has a kurtosis index $K = 3$, and a skewness index $Sk = 0$. Previous experiments [51] have shown that the kurtosis index summarizes information in a goniophotometric curve in a meaningful way. Good correlation has been obtained [51, 88] between this index and distinctness-of-reflected-image gloss and also specular gloss. It is also hoped that it will be as useful in analysing goniophotometric data from human hair samples.

As with the subject of colorimetry, the standardization of gloss measurements is necessary if a common basis for rapid comparison is to be established. Since no such basis has yet been suggested for human hair, the following sections aim to review the range of methods and recommend the most appropriate for adoption. It is therefore important that other variables which would affect the light scattering are clearly stated. These include the angular resolution of the detector and the degree of collimation of the incident light (dealt with in chapter two), and the variation in the orientation of the sample (one of the topics investigated here).

Colour and Racial Origin

Polarization-scattering measurements were taken from parallel arrays of hair constructed from the six samples (oriental, black, brown, red, blond, and white) of hair which form the basis group of these studies. The results for each surface of hair are given in figures 5.14 to 5.16. The work in this section is comparable to the experiments described in section 3.3.1 (polarization measurements) on individual hair fibres; whilst the same angle of incidence (45°), source, and polarizing filters were used, the area of illumination and therefore the intensity of detected light were different. So although qualitative comparisons between the shapes of the graphs in figures 3.14 to 3.16 and those in figures 5.14 to 5.16 are meaningful, quantitative comparisons are not.

Within each experiment the intensities have been normalized with respect to each other for the purposes of direct quantitative comparison.

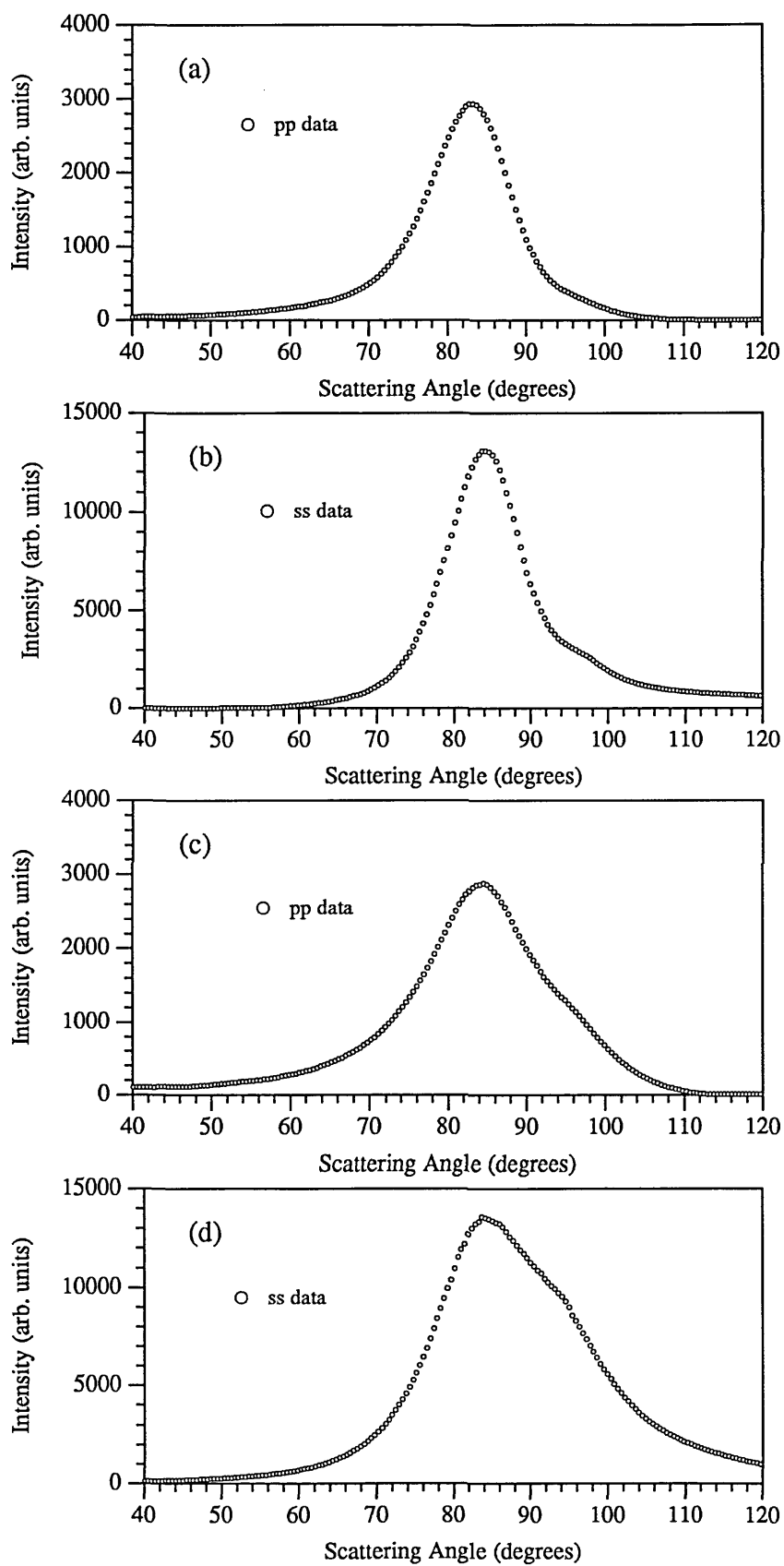


Figure 5.14: Scattering data: (a) Oriental hair — p -polarized light incident, (b) Oriental hair — s -polarized light incident, (c) black hair — p -polarized light incident, and (d) black hair — s -polarized light incident.

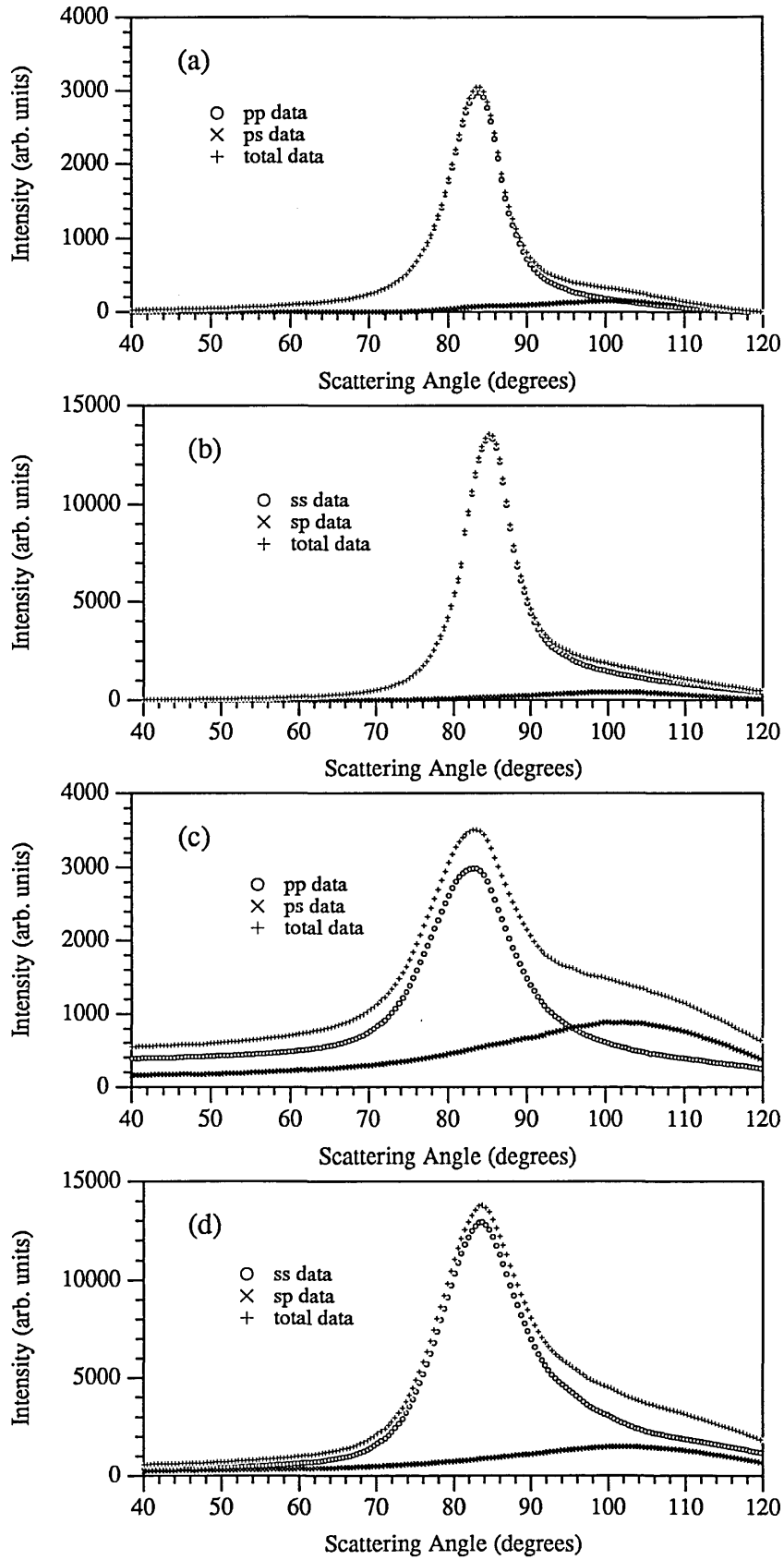


Figure 5.15: Scattering data: (a) brown hair — p -polarized light incident, (b) brown hair — s -polarized light incident, (c) red hair — p -polarized light incident, and (d) red hair — s -polarized light incident.

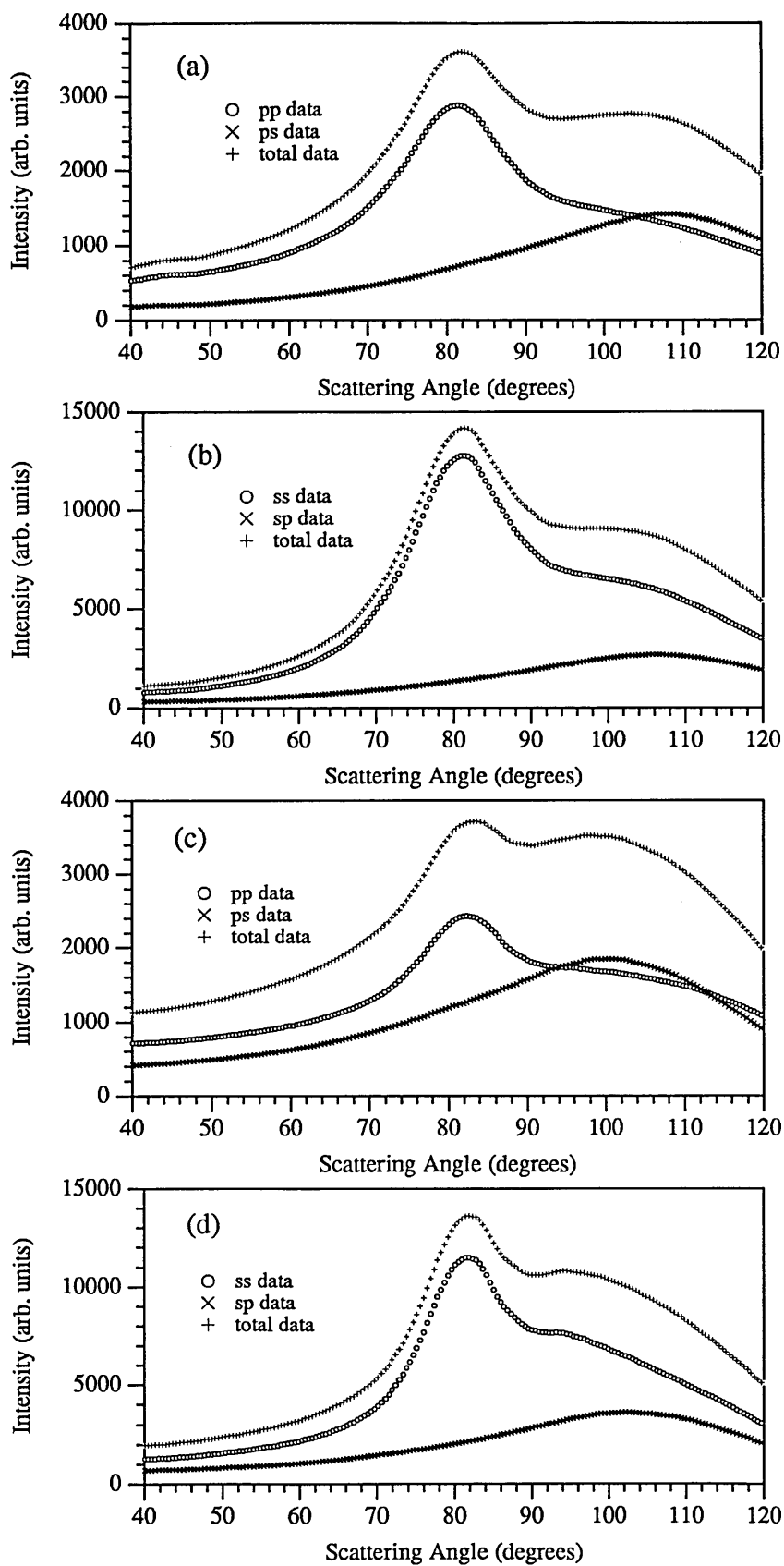


Figure 5.16: Scattering data: (a) blond hair — p -polarized light incident, (b) blond hair — s -polarized light incident, (c) white hair — p -polarized light incident, and (d) white hair — s -polarized light incident.

From the two sets of figures it can be seen that, for any given hair colour, the shapes of the light-scattering envelopes from individual and surface arrangements of hair are very similar. The relative magnitudes of the co- and cross-polarized signals from the black hair surfaces meant that on the same measurement scale the cross-polarized return was negligible. For the single fibres the cross-polarized return was sometimes very small but in most cases it was still large enough to measure on the same scale as the co-polarized return. For hair surfaces a reduction in the relative magnitude of the cross-polarized return with respect to the co-polarized return was observed for all the hair samples irrespective of colour. In general, it was found that the goniophotometric curves were smoother from the surfaces of hair and were not as sensitive to variations in the position of the illumination on the hairs. As there were only minor differences between the two sets of results, the reader is referred to section 3.3.1 for a general discussion on the shape of the light-scattering envelope.

A more detailed analysis, involving the calculation of a group of parameters which might describe the angular distribution of the scattered light is undertaken here. These parameters have been separated into two groups merely for the purposes of presentation. Table 5.4 contains a summary of the contrast gloss parameters calculated for each curve, using spot and integrated values of the diffuse and specular components.

Table 5.4: Contrast gloss measurements characterizing the six hair samples studied.

Hair Type & Polarization	Spec. Int. s (arb. units)	Dif. Int. d (arb. units)	Con. Gloss g_c (no units)	Int. Con. Gloss G_c (no units)
Oriental (s)	13082 ± 65	0	1.000 ± 0.007	1.000 ± 0.006
Oriental (p)	2939 ± 15	53 ± 2	0.982 ± 0.007	0.872 ± 0.006
Black (s)	13581 ± 67	157 ± 2	0.988 ± 0.007	0.953 ± 0.006
Black (p)	2880 ± 14	111 ± 2	0.961 ± 0.007	0.791 ± 0.006
Brown (s)	13559 ± 68	30 ± 2	0.998 ± 0.007	0.982 ± 0.006
Brown (p)	3051 ± 15	32 ± 2	0.989 ± 0.007	0.910 ± 0.006
Red (s)	13806 ± 70	619 ± 4	0.955 ± 0.007	0.774 ± 0.006
Red (p)	3511 ± 18	565 ± 6	0.839 ± 0.007	0.038 ± 0.006
Blond (s)	14160 ± 72	1248 ± 8	0.912 ± 0.007	0.730 ± 0.006
Blond (p)	3607 ± 18	808 ± 7	0.776 ± 0.007	0.279 ± 0.006
White (s)	13610 ± 67	2093 ± 11	0.846 ± 0.007	0.479 ± 0.006
White (p)	3716 ± 19	1183 ± 11	0.682 ± 0.007	-0.161 ± 0.006

All the calculations in this table and the next were based on the curve representing the incoherent sum of the co- and cross-polarized returns, except in the

cases of the black surfaces where the data sets of the co-polarized return were used. The values of contrast gloss, g_c , based on spot measurements, were found to decrease steadily with increasing level of hair transparency, this trend being directly attributable to the changes in the value of d . For black hair in good condition, d was usually measured to be very small or even zero, producing gloss values near unity (the upper limit of its range). The variation in d also affected the calculations of the integrated contrast gloss values, G_c , so that they too showed large changes in value with variations in the level of hair pigmentation. Although the concentration and type of pigment in hair do affect its visual appearance, the strong influence they have on these types of gloss measurement could well mean that a dull, damaged black hair sample (as observed visually) would be predicted by this method to be glossier than a shiny, pristine sample of blond hair. A human observer is capable of differentiating the hair's colour from its glossiness and therefore would rate the blond sample above the black in a subjective visual assessment, and this is where instrumental and human results diverge. The human eye is not sensitive to the polarization state of light, but instrumental contrast gloss measurements have been found to show a strong dependence on the polarization state of the light incident on the hair sample. The integrated contrast gloss measurement was producing reasonable values until the area enclosed by the diffusely scattered light, as calculated following Stamm et al., became greater than the area representing specularly reflected light. This case generates a negative gloss value, which is outside the recognized range of physical values for contrast gloss (see chapter one).

The statistical indices and FWHM information which may also be used to analyse the goniophotometric curves is summarized for these hair surfaces in table 5.5. The FWHM provides a good indication of the observed transparency of the hair and also takes into account to some extent the range of scale angles present along the hair's surface (a narrower range of scale angles correlates to a higher angular concentration of light in the specular peak). For instance, the brown sample (known naturally to possess a smaller range of scale angles than the Caucasian black sample — see chapter four) was found to have a smaller FWHM than either of the black hair samples, despite having a lower level of pigmentation.

The index of skewness (a measure of asymmetry) also exhibited a degree of correlation with hair colour. This was anticipated from the work in chapter three, where a reference was made to the link between the asymmetry of the light-scattering distri-

Table 5.5: Statistical parameters characterizing the six hair samples studied.

Hair Type & Pol ⁿ	FWHM (degrees)	Spec. Angle θ_s (degrees)	Skewness Sk (no units)	Kurtosis K (no units)
Oriental (s)	$12.0 \pm .5$	$84.2 \pm .5$	+0.095	6.077
Oriental (p)	$12.2 \pm .5$	$83.3 \pm .5$	-0.098	6.864
Black (s)	$21.6 \pm .5$	$83.7 \pm .5$	+0.188	3.950
Black (p)	$17.8 \pm .5$	$84.6 \pm .5$	-0.055	5.112
Brown (s)	$7.4 \pm .5$	$84.6 \pm .5$	+0.322	5.428
Brown (p)	$8.2 \pm .5$	$84.2 \pm .5$	+0.165	5.758
Red (s)	$14.5 \pm .5$	$83.7 \pm .5$	+0.667	3.446
Red (p)	$18.0 \pm .5$	$83.7 \pm .5$	+0.145	2.758
Blond (s)	$41.9 \pm .5$	$82.0 \pm .5$	+0.650	2.490
Blond (p)	$52.6 \pm .5$	$82.2 \pm .5$	+0.399	2.246
White (s)	$41.9 \pm .5$	$82.2 \pm .5$	+0.515	2.360
White (p)	$54.7 \pm .5$	$83.7 \pm .5$	+0.273	2.171

bution produced by a hair and its level of pigmentation, i.e. degree of transparency. All the light-scattering distributions of the hairs were found to be skewed by varying amounts to the left, with the exception of two. These distributions, produced by p -polarized incident light on black hair surfaces, were found to be very slightly skewed to the right. In these cases the intensity in the left-hand tail fell more rapidly below the measurement resolution than in the tail to the right of the specular peak, but, since the value was very close to $Sk = 0$, the scattered distribution of light could be said to be almost symmetric about the direction of maximum specular reflection. The most asymmetric light-scattering distributions were generally those (usually with s -polarized light incident) produced by hairs with low levels of eumelanin and/or a significant proportion of ph  melanin pigment, e.g. red, blond, and white hairs.

The range of values calculated for the kurtosis index (or coefficient) varied from 6.864 (for Oriental black) to 2.171 (for Caucasian white), showing that this index also exhibited a dependence on hair colour and the polarization state of the incident light, although these variations were found to be less than for the integrated gloss measurements and the results were always sensible. For the dark hair samples, the p -polarized incident light curves consistently produced larger values of K than the s -polarized, but this situation is reversed when the hair colours become more transparent, i.e. at the red sample.

In conclusion, it was felt that this investigation indicated that as the integrated

contrast gloss measurement was the least physically reliable — being based on an odd method of calculating D — could be abandoned at this stage without loss of extra meaningful information.

Angle of Illumination

This experiment was designed to investigate the effects of ~~varying the angle of incidence on the contrast gloss~~, and kurtosis index of the hair. It has a corresponding section (of the same name) in the individual hair fibre experiments in chapter three. For the purposes of comparison, the same procedure was adopted as before with regard to illumination geometry — each hair surface was illuminated at four angles of incidence (30° , 40° , 50° , and 60°) with s -polarized white light. The results are presented graphically for the Oriental black and Caucasian black and brown hair surfaces in figures 5.17(a), (b), and (c); and for the Caucasian red, blond, and white hair surfaces in figures 5.18(a), (b), and (c).

Each data set was collected using the same incident beam power and then the four sets of data per hair surface were normalized (as in chapter three, section 3.3.1) so that a best fit to the curve of the Fresnel reflection coefficient, $R_s \times I_0$, was obtained, where I_0 was the incident intensity — in this case normalized to unity. Thus each curve may be quantitatively compared with the rest. Note: in the graphs the plot symbols conventionally used have been abandoned so as to maintain clarity of presentation with the large number of curves per graph.

As in the single fibre experiments, the maximum values of the specular peak were found to follow closely the values of the Fresnel intensity reflection coefficient, R_s , which was calculated for a refractive index of 1.545, and an incident beam s -polarized. In terms of the shapes of the graphs, the two sets of data (individual and surface) were found to agree closely. It was also in this experiment (where goniophotometric data were collected for high angles of incidence from parallel arrays of hair) that it was thought that perhaps ‘the equal angle peak’ reported by Stamm et al. in reference [57] might become observable. However, no such peak was ever discovered, although the Oriental surface did produce a small shoulder to the right of the specular peak, i.e. at high scattering angles. This could not be connected to the peak that Stamm et al. were referring to as they interpreted it as being the result of an internal wedge of air between the cuticle and cortex layers. The black Oriental hair is highly pigmented, so any light transmitted inside the hair is

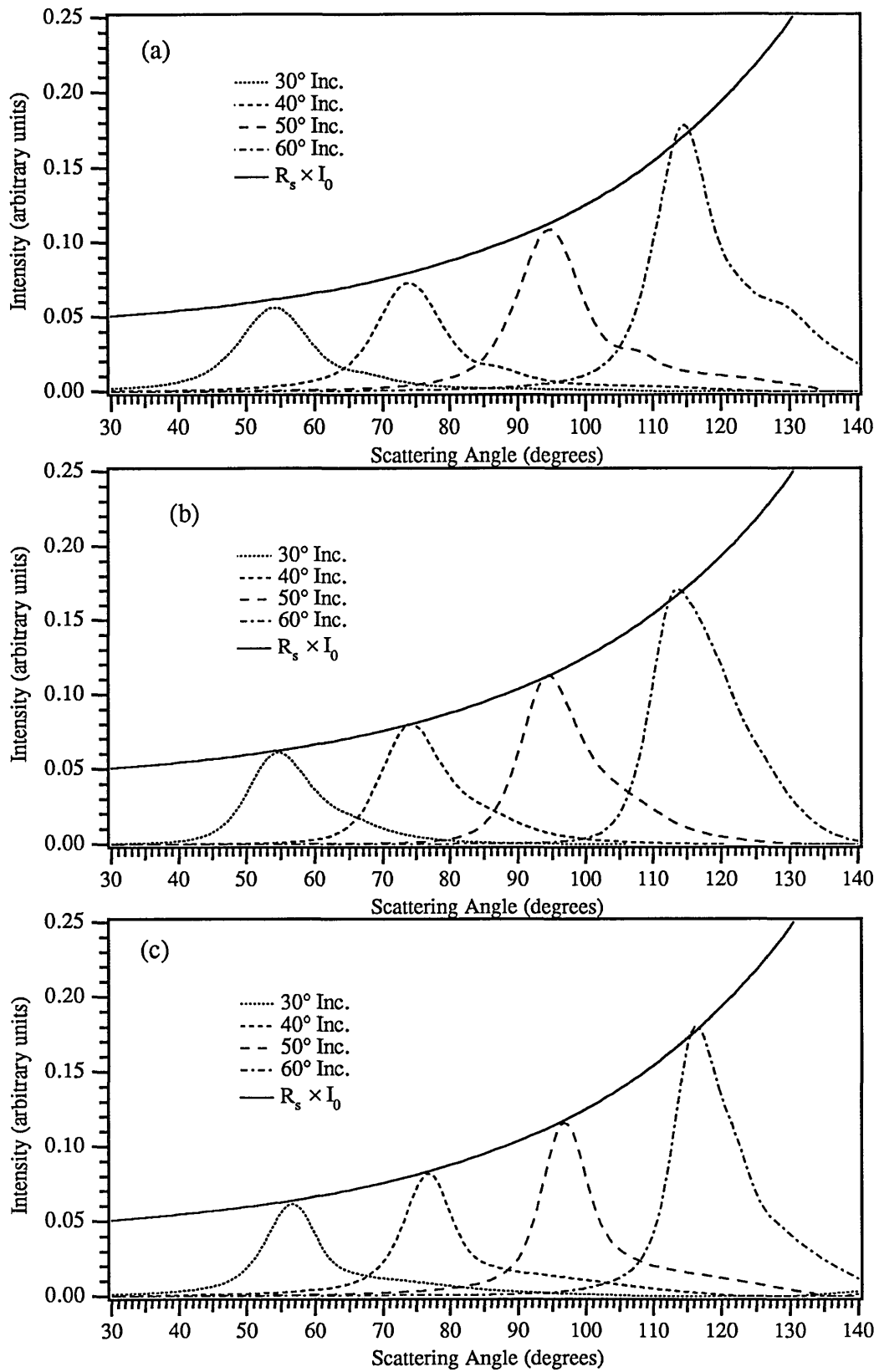


Figure 5.17: Normalized light-scattering envelopes produced by (a) an Oriental hair, (b) a black hair, and (c) a brown hair at four angles of incidence using *s*-polarized light.

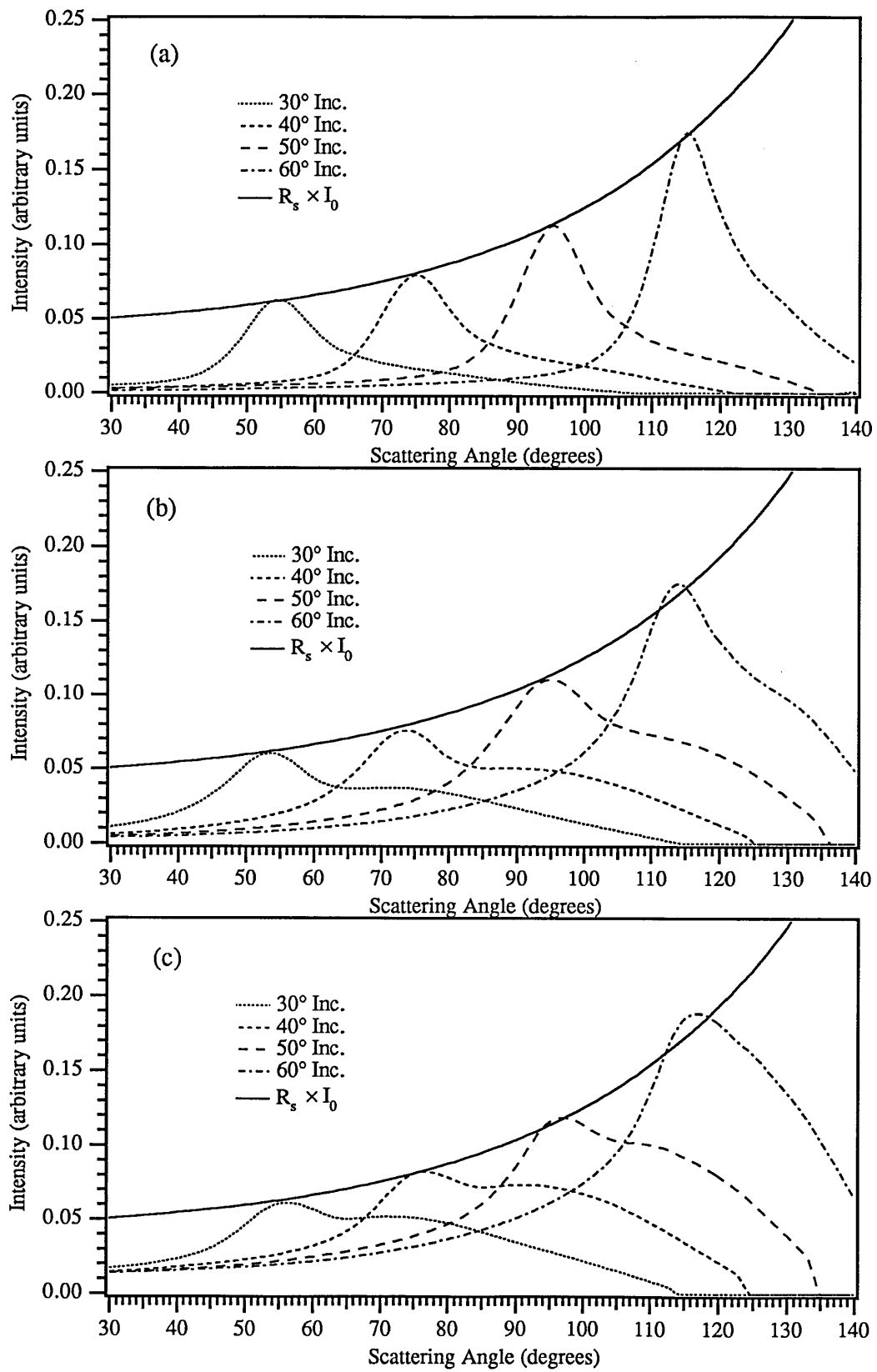


Figure 5.18: Normalized light-scattering envelopes produced by (a) a red hair, (b) a blond hair, and (c) a white hair at four angles of incidence using s-polarized light.

almost completely absorbed. The absence of this so-called ‘equal angle peak’ in all the experiments contained in this body of work, whether co- or cross-polarized, with scatterometer or dedicated goniophotometer, can only lead to the conclusion that the peak observed by Stamm et al. must have been due to a reflecting surface other than the hair. Indeed, a painted wall behind the sample, even several metres away has been found to provide sufficient reflection to register in the scan and add a spurious contribution. This type of additional artifact in the light-scattering envelope may be detected and eliminated by initially taking a set of readings without a hair sample in place, if this set is then subtracted from all subsequent measurements, it can be certain that the light-scattering distribution is due to the hair sample alone.

The parameters characterizing the changes in the goniophotometric data are summarized in table 5.6 for the black and brown surfaces and in table 5.7 for the red, blond, and white surfaces.

Table 5.6: Summary of parameters calculated from the curves produced by surfaces of Oriental black and Caucasian black and brown hairs measured over a range of incident angles.

Inc. Angle (degrees)	Scale Angle α (degrees)	Con. Gloss g_c (no units)	Kurtosis K (no units)
Oriental 30°	$2.9 \pm .5$	$0.965 \pm .006$	9.261
Oriental 40°	$3.1 \pm .5$	$0.989 \pm .006$	7.468
Oriental 50°	$2.7 \pm .5$	$0.996 \pm .006$	6.097
Oriental 60°	$2.7 \pm .5$	$0.998 \pm .006$	2.930
Black 30°	$2.6 \pm .5$	$0.994 \pm .006$	7.952
Black 40°	$2.9 \pm .5$	$0.997 \pm .006$	6.773
Black 50°	$2.8 \pm .5$	$0.998 \pm .006$	4.229
Black 60°	$3.1 \pm .5$	$0.999 \pm .006$	2.690
Brown 30°	$2.3 \pm .5$	$0.991 \pm .006$	11.350
Brown 40°	$2.4 \pm .5$	$0.993 \pm .006$	8.681
Brown 50°	$2.4 \pm .5$	$0.997 \pm .006$	5.817
Brown 60°	$2.6 \pm .5$	$0.998 \pm .006$	3.813

Both the contrast gloss and the kurtosis index exhibited a change in value with variation in the angle of incidence. However, in the case of the kurtosis index this is because the shape of the light-scattering envelope also changed, unlike the contrast gloss measurement, which would still have produced a different value even if the light-scattering envelope had been identical in shape but merely shifted in angle (s would be the same but d would have changed).

This difference in behaviour is reflected in the results: whilst the contrast gloss

Table 5.7: Summary of parameters calculated from the curves produced by surfaces of Caucasian red, blond and white hairs measured over a range of incident angles.

Incidence Angle (degrees)	Scale Angle α (degrees)	Contrast Gloss g_c (no units)	Kurtosis K (no units)
Red 30°	$2.6 \pm .5$	$0.918 \pm .006$	8.776
Red 40°	$2.8 \pm .5$	$0.949 \pm .006$	5.001
Red 50°	$2.7 \pm .5$	$0.958 \pm .006$	6.872
Red 60°	$2.8 \pm .5$	$0.979 \pm .006$	6.569
Blond 30°	$3.3 \pm .5$	$0.819 \pm .5$	3.508
Blond 40°	$3.1 \pm .5$	$0.879 \pm .5$	3.173
Blond 50°	$2.7 \pm .5$	$0.914 \pm .5$	4.001
Blond 60°	$2.9 \pm .5$	$0.943 \pm .5$	4.693
White 30°	$3.0 \pm .5$	$0.716 \pm .006$	3.111
White 40°	$2.7 \pm .5$	$0.785 \pm .006$	3.020
White 50°	$2.6 \pm .5$	$0.836 \pm .006$	4.047
White 60°	$2.3 \pm .5$	$0.885 \pm .006$	3.839

always increases with higher angles of incidence independent of hair colour, the behaviour of the kurtosis index was found to vary depending on the level and type of pigmentation in the hair sample. For the dark hairs it steadily decreased with increasing angle of incidence, whilst for the very light hairs (blond and white) it did not follow any discernible trend.

In this experiment, a much wider range of values was obtained for the kurtosis index than for the contrast gloss parameter, particularly with regard to the dark-coloured hairs (all the contrast gloss values are crowded into a region between 0.95 and 1). This indicates that the kurtosis index is more sensitive than the contrast gloss measurement to small changes in the intensity distribution of the goniophotometric data.

Ultraviolet Irradiated Hairs

The effects of sunlight, and in particular, ultraviolet radiation on the physical properties of human hair have been of interest to many researchers although little quantitative data is available. Beyak et al. [89] investigated the effects of prolonged exposure to ultraviolet radiation on the tensile properties of hair and found that there was a correlation between the length of exposure time and the loss of tensile properties. Many scientists [90, 12, 91, 6, 92, 93] have undertaken research into the chemical and photobleaching of human hair. Early results suggested that eumelanin

(the black pigment) was more photostable than phæmelanin (red pigment), but this did not fit in with the visual assessments of the bleaching effects of sunlight on full heads of hair, which indicated that brunettes were more affected than redheads. Wolfram and Albrecht specifically investigated the chemical and photobleaching of brown and red hair [12], and found that changes in both hair colours occurred after prolonged exposure to sunlight. They reported that the red pigment, phæmelanin, was more resistant to photodegradation than the black pigment, eumelanin, in direct opposition to earlier findings which had seemed to predict the reverse, but in agreement with qualitative visual observations of hair colour over a period of summer months.

Thus, for the purpose of selecting a hair colour for investigating the effects of visible and ultraviolet irradiation of hair, a sample of warm, mid-brown hair was chosen. Hair of this colour contains a mixture of both pigment types and is known from qualitative visual assessments to be subject to lightening after exposure to sunlight.

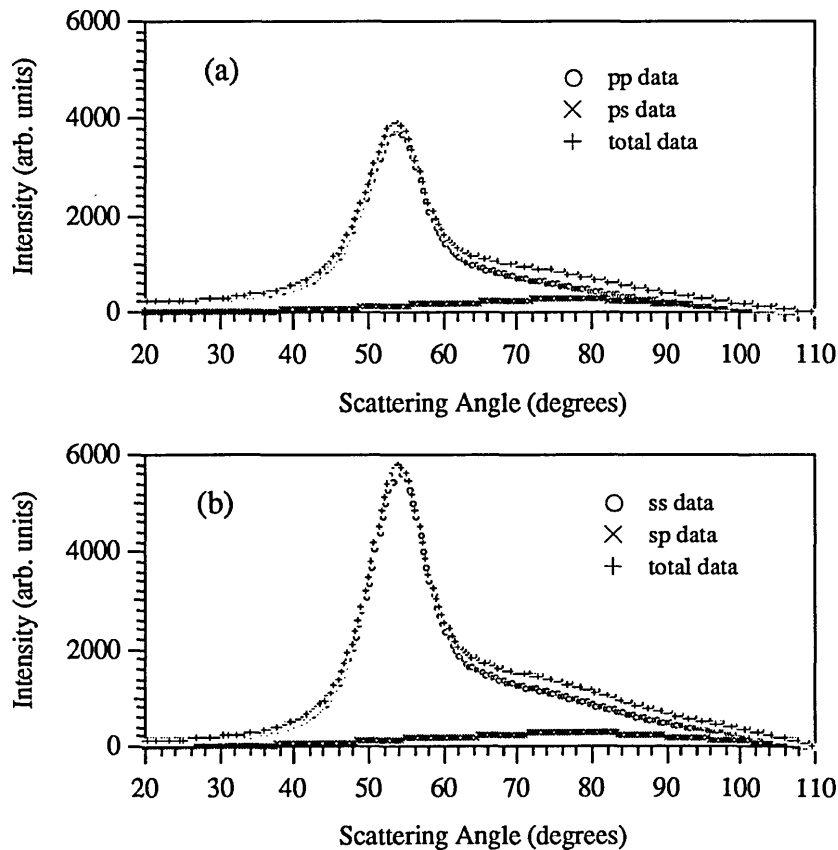


Figure 5.19: Scattering data from an untreated sample (the control) of mid-brown hair, (a) *p*-polarized light incident and (b) *s*-polarized light incident.

Five tresses, approximately 10cm long, of this mid-brown hair were prepared at SmithKline Beecham, and one tress, the control, was put to one side. From each of the other four tresses approximately 100 hairs were mounted on card covered in silver foil to reflect as much light as possible. These four samples were then placed under an ultraviolet source (Heraeus Suntest Unit) for differing lengths of time. Periodically the samples were removed and washed in water before being returned for further irradiation. The first sample was removed after a total exposure of 140 hours, the second after 195 hours, the third after 240 hours, and the fourth after 280 hours. The output of this solar simulator is not dissimilar to the spectrum of natural sunlight, and includes both visible and ultraviolet wavelengths. Beyak et al. [63] presented data which showed that the degree of damage suffered by a hair correlates more closely with the total amount of radiation received than with its spectral character, and that hair irradiated by an artificial source exhibited the same magnitude of damage as that exposed to natural sunlight.

Five hair surfaces were strung from these treated samples and the control tress. Polarized-scattering measurements were taken with the hairs oriented horizontal to the plane of incidence. The results of these scans are presented in figures 5.19, 5.20, and 5.21. Each pair of graphs per sample corresponds to *s*- and *p*-polarized light incident at 30° to the outward normal. The graphs highlight several trends which occur with increasing length of time of exposure to the radiation: firstly, a reduction in the magnitude of the intensity in the specular direction and, secondly, an increase in the size of the cross-polarized component. This result corresponds to the photobleaching effect on the melanin pigment in the hairs — visually the irradiated samples appeared lighter in shade than the control sample, and not as shiny.

Further analysis of the curves is summarized by the parameters given in table 5.8. The calculations of contrast gloss, g_c , and kurtosis coefficient, K , were based on the curve representing the incoherent sum of the co- and cross-polarized returns (labelled *total data* on the graphs). Both parameters (g_c and K) followed a general trend, with respect to the control sample, that increasing the length of the exposure time decreased the magnitudes of g_c and K and increased the FWHM of the specular peaks. These variations in the light-scattering envelope correspond to changes in the condition of the hair samples. The photodegradation of keratin which occurs when hairs are exposed to ultraviolet irradiation (natural sunlight or artificial source) for

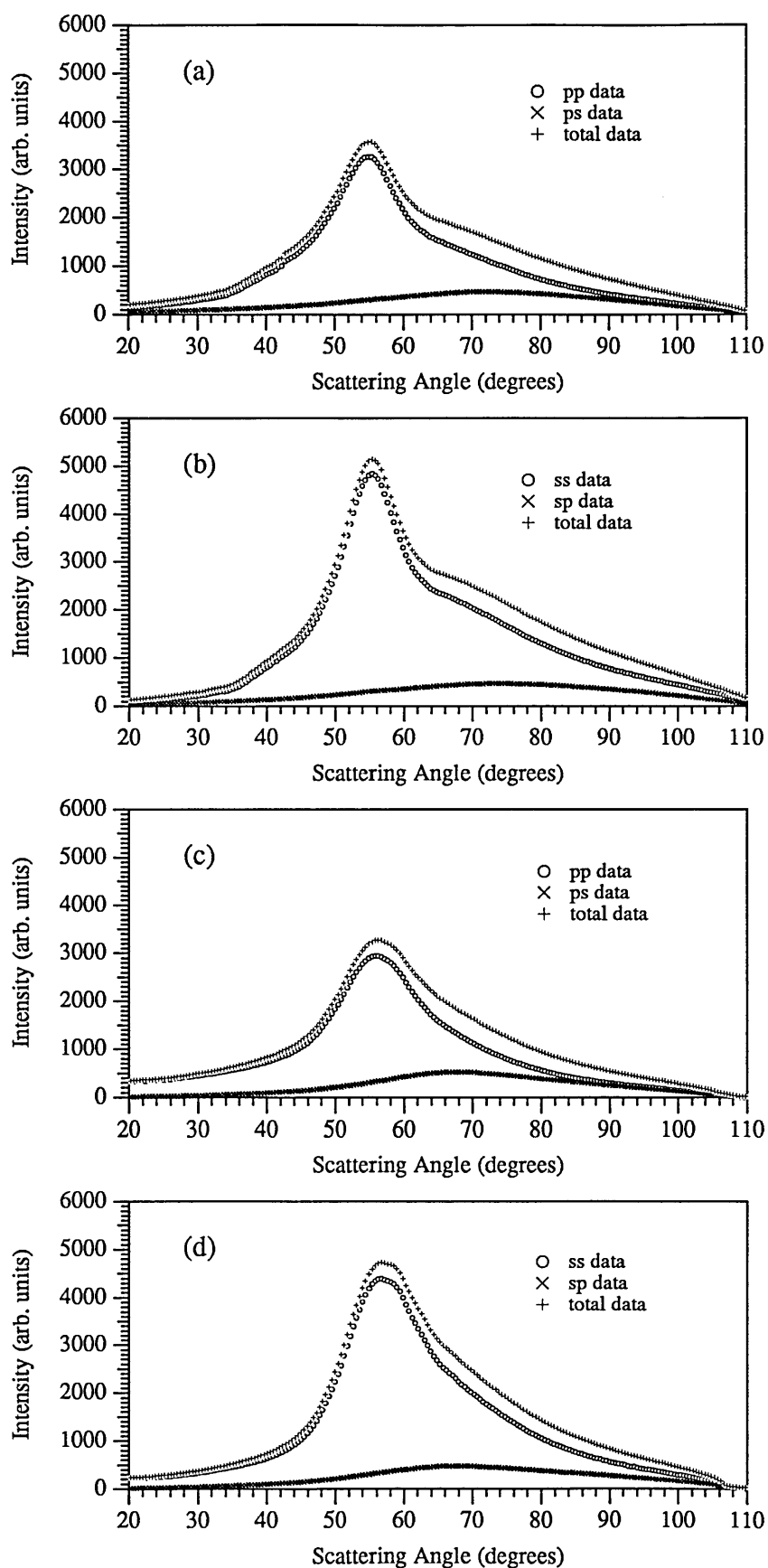


Figure 5.20: Scattering data from irradiated samples of mid-brown hair: (a) irradiated for 140 hours, p -polarized light incident; (b) irradiated for 140 hours, s -polarized light incident; (c) irradiated for 195 hours, p -polarized light incident; and (d) irradiated for 195 hours, s -polarized light incident.

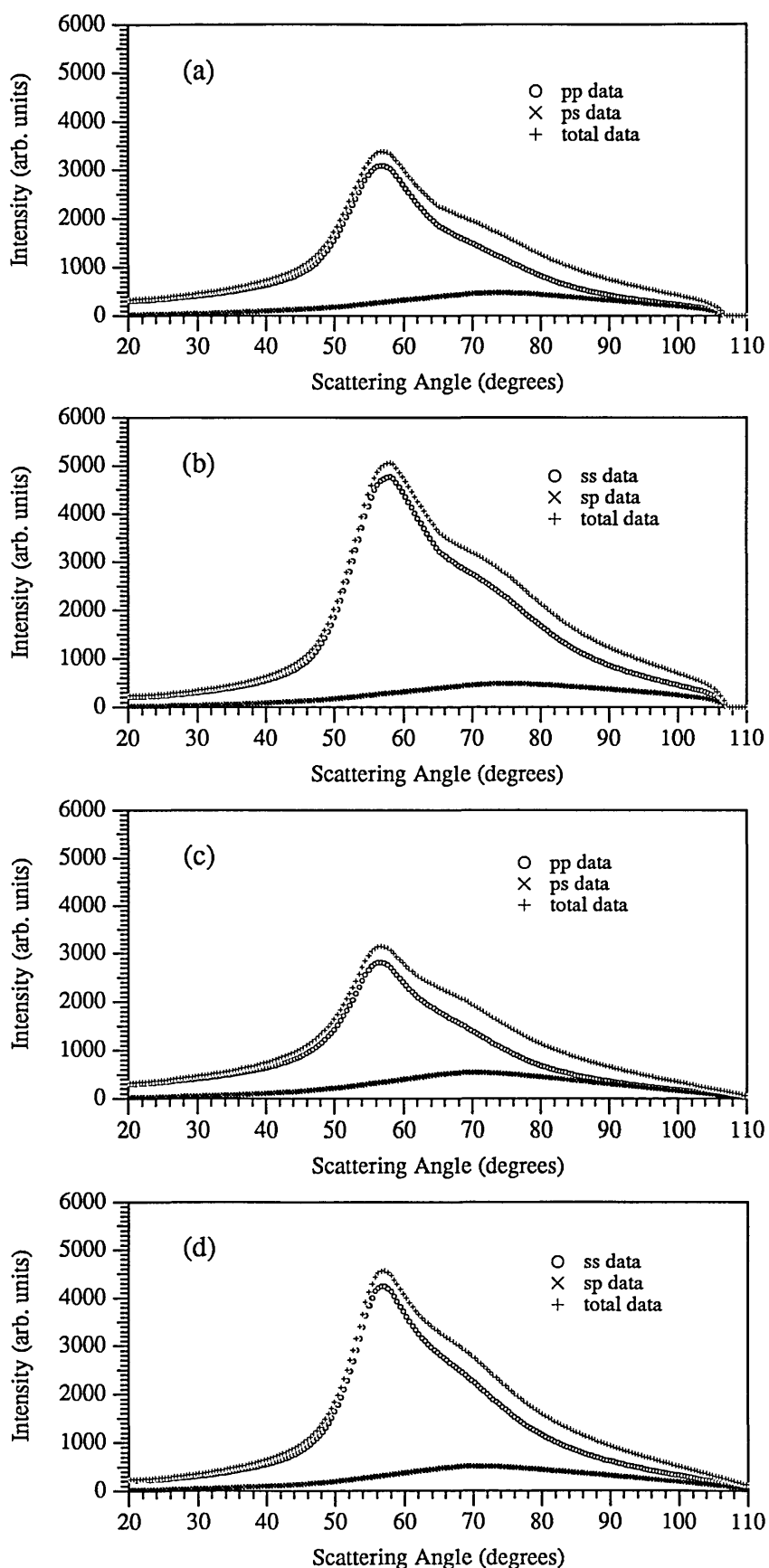


Figure 5.21: Scattering data from irradiated samples of mid-brown hair: (a) irradiated for 240 hours, p -polarized light incident; (b) irradiated for 240 hours, s -polarized light incident; (c) irradiated for 280 hours, p -polarized light incident; and (d) irradiated for 280 hours, s -polarized light incident.

Table 5.8: Summary of parameters calculated from the curves produced by the surfaces of ultraviolet-irradiated hairs.

Sample & Pol ⁿ State	Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss g_c (no units)	Kurtosis Index K (no units)
Control (s)	$3.0 \pm .5$	$10.4 \pm .5$	$0.969 \pm .006$	4.392
Control (p)	$3.2 \pm .5$	$10.5 \pm .5$	$0.930 \pm .006$	4.309
140 hours (s)	$2.3 \pm .5$	$19.9 \pm .5$	$0.943 \pm .006$	3.302
140 hours (p)	$2.3 \pm .5$	$21.4 \pm .5$	$0.891 \pm .006$	3.253
195 hours (s)	$1.7 \pm .5$	$15.6 \pm .5$	$0.921 \pm .006$	3.441
195 hours (p)	$1.9 \pm .5$	$22.0 \pm .5$	$0.850 \pm .006$	3.219
240 hours (s)	$1.0 \pm .5$	$25.6 \pm .5$	$0.932 \pm .006$	3.087
240 hours (p)	$1.4 \pm .5$	$24.3 \pm .5$	$0.862 \pm .006$	2.952
280 hours (s)	$1.4 \pm .5$	$22.8 \pm .5$	$0.922 \pm .006$	3.293
280 hours (p)	$1.7 \pm .5$	$24.3 \pm .5$	$0.851 \pm .006$	3.054

prolonged periods is well documented [12, 94, 90, 70], and it is also thought to be the underlying mechanism of the weathering process. As a result of the absorbence of the UV component of sunlight by the protein components of hair, such as cystine, tyrosine, phenylalanine and tryptophane residues, free radicals are formed. In the presence of water, hydroxyl radicals can act as mobile radical centres, which causes the photochemical decomposition to be widely spread — this was the reason for intermittent washing of samples during the exposure periods. Free radical attack is not specific, but histological factors (such as the structure of the hair proteins) will preferentially promote certain reactions; studies have suggested that interactions occur with long-chain molecules, in particular at the disulphide bonds. For the non-pigmented fibres, the lightening process is called photo-yellowing [94]. The degradation of the keratin may also account for the reduction in the average scale angle, α , for increasing lengths of irradiation.

In pigmented keratin, the melanin granules, by virtue of their polymer nature (i.e. extensive systems of conjugated carbonyl groups), act initially as energy sinks. This has the effect not only of trapping a large portion of the incident radiation, but also of immobilizing many of the newly formed radicals before they are transported into the keratin matrix. Although both keratin degradation and melanin photobleaching proceed via the formation of free radicals, the processes involve different reactions — for instance, the oxidation of melanin generally accounts for the bleaching.

Ultraviolet irradiation has also been found to alter the tensile properties of hair fibres [93, 89], so it is therefore possible that other properties of exposed fibres, such

as the refractive index may have been altered too.

Chemically Treated Hairs

In general, chemical hair treatments are cosmetic procedures that involve chemical reactions taking place in the hair. The integrity of a hair fibre lies in the interchain and intrachain cross-linking of the polypeptide chains by disulphide bonds of cystine, and by ionic bonds between ammonium and carboxyl groups. Chemical treatments result in the breaking of these disulphide bonds, and even under optimal conditions only 90% of them are re-formed later. This leaves the hair physically weakened and susceptible to further damage. Changes to the physical properties of hair fibres incurred as a result of cosmetic treatments, such as bleaching, permanent waving, oxidative dyeing and straightening, combined with the effects of natural weathering, can be significant [95]. Researchers [20, 69, 96, 63, 64, 22, 97, 98] have found that the treatments may lead to premature fracture of the hair, separation of the cortex from the cuticle, loss of shine, and increased absorption of moisture.

Given the human preoccupation with styling hair [99], despite its damaging effects, it is not surprising that a huge amount of effort has been made to develop hair-care products which reduce and protect the hair from damage. However, in order to develop effective products, it is helpful first to understand and second to quantify the damage. This section concentrates on determining the effects of cosmetic treatments on the appearance of hair via light-scattering measurements. Because of the hysteresis effect encountered in the wetting and drying process of hair [63], it is not possible to have the hair taut during treatment, since tension values before and after will be different and this would alter the measurement with respect to a control surface of hairs. Consequently, the surfaces are strung after treatment. These experiments were based on three samples of commercially supplied hair. One sample was described as dark brown, another as strawberry blond (reddish blond), and the third as *ninety per cent* grey. This phrase refers to a sample which the suppliers guaranteed would consist of 90% grey hairs and 10% of other coloured hairs, usually black. The cosmetic treatments basically fell into three groups: the first was the darkening by a surface dye contained in a proprietary darkening shampoo and conditioner set, the second by permanent (oxidative) and semipermanent dyeing and tinting agents, and the third by peroxide bleaching and permanent waving of hair. All the treatments were carried out by the author at the research laboratories

of SmithKline Beecham. Hair samples were separated into one-gramme tresses of approximately 10cm length and tightly bound at the tip end, leaving the root end free for treatment and later investigation. Except where the preparation instructed otherwise, all the samples, including those destined to be put aside as controls, were washed in a mild anionic detergent (a herbal shampoo — Silvikrin Aloe Vera) before treatment.

The first experiment was to record the effects of an *adsorbing*[†] dye included in a shampoo and conditioner application, and continues from earlier work published by the author in reference [70]. Briefly, this darkening shampoo contains a chemical which prepares specific sites on the surface of a hair where another chemical in the conditioner can react. At these sites a compound is formed which is chemically bonded to the hair, the appropriate choice of reactants producing a compound which is black in colour. Thus, this is a two-stage process, and without both stages the appearance of a hair sample should remain unchanged. Visually repeated applications of the darkening shampoo and conditioner have been assessed to result in a darkening of the appearance of a sample of grey hairs. To investigate the effects of this treatment on the light-scattering distribution of hair and its gloss, four tresses of the 90% grey hair samples were selected, two of which were washed in herbal shampoo and the other two in the darkening shampoo. One of the herbal shampooed tresses (designated to be the control) and one darkening shampooed tress were put aside, and the remaining tresses were treated with darkening conditioner. The treatment of these samples, labelled A to D, is summarized in table 5.9.

Table 5.9: Summary of treatments applied to samples A to D.

Sample	Herbal Shampoo	Darkening Shampoo	Darkening Conditioner
A	Yes	No	No
B	No	Yes	No
C	No	Yes	Yes
D	Yes	No	Yes

Approximately 40 hairs from each sample group were strung to form single-layer surfaces. Polarized-light-scattering measurements from these surfaces mounted horizontally on the scattering rig are presented graphically in figures 5.22 and 5.23. Using the curve which represents the total light-scattering envelope for each incident

[†]Note: an adsorbing versus an absorbing dye is one which colours the hair by forming a thin film on its surface rather than staining the cortex inside the hair.

polarization, the scale angle, FWHM, contrast gloss, g_c , and kurtosis index, K , were calculated for each result and are summarized in table 5.10.

Table 5.10: Summary of parameters calculated from the curves produced by the surfaces of cosmetically treated hairs.

Sample & Pol ⁿ	Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss g_c (no units)	Kurtosis Index K (no units)
A (s)	$2.6 \pm .5$	$32.7 \pm .5$	$0.902 \pm .006$	2.776
A (p)	$2.7 \pm .5$	$33.9 \pm .5$	$0.828 \pm .006$	2.696
B (s)	$2.4 \pm .5$	$33.4 \pm .5$	$0.897 \pm .006$	2.752
B (p)	$2.3 \pm .5$	$34.7 \pm .5$	$0.821 \pm .006$	2.630
C (s)	$2.1 \pm .5$	$14.3 \pm .5$	$0.921 \pm .006$	2.904
C (p)	$2.1 \pm .5$	$17.9 \pm .5$	$0.862 \pm .006$	2.798
D (s)	$2.1 \pm .5$	$39.7 \pm .5$	$0.840 \pm .006$	2.609
D (p)	$2.2 \pm .5$	$41.8 \pm .5$	$0.750 \pm .006$	2.537

Experimental observations showed that the light-scattering envelope from sample C exhibited a reduction in the magnitude of the co- and cross-polarized returns over the range of scattering angles which generally correspond to the angular position of secondary peak. This indicates a reduction in the portion of light being internally scattered and fits with the visual observations of darkening in this sample. This is confirmed by a significant reduction in the FWHM of sample C compared to samples A, B, and D. Treatment with this proprietary darkening agent was also found to increase the contrast gloss and kurtosis index of the hair sample, but in many ways a more interesting trend was the reduction of the average scale angle of all the treated samples compared to the control (sample A). This may be attributed to the *adsorbing* action of these compounds: as they chemically alter the surface of the hair they may also leave a residue which fills in the step-like surface structure, effectively flattening the scales. Although the literature provides no evidence to prove that surface dyes have a permanent deleterious effect on the structure of hair fibres, it is thought [95] that the most damaging aspect of surface dyes is the increase in the frictional coefficient between hairs due to the dye deposits on the surface. This, in conjunction with everyday grooming techniques, would certainly lead to accelerated attrition of the cuticle layers, but may be reduced by the use of lubricating conditioners and other hair preparations.

The second group of treatments were undertaken to investigate the effects on the light-scattering properties of hair of absorbing colouring agents — these chemicals

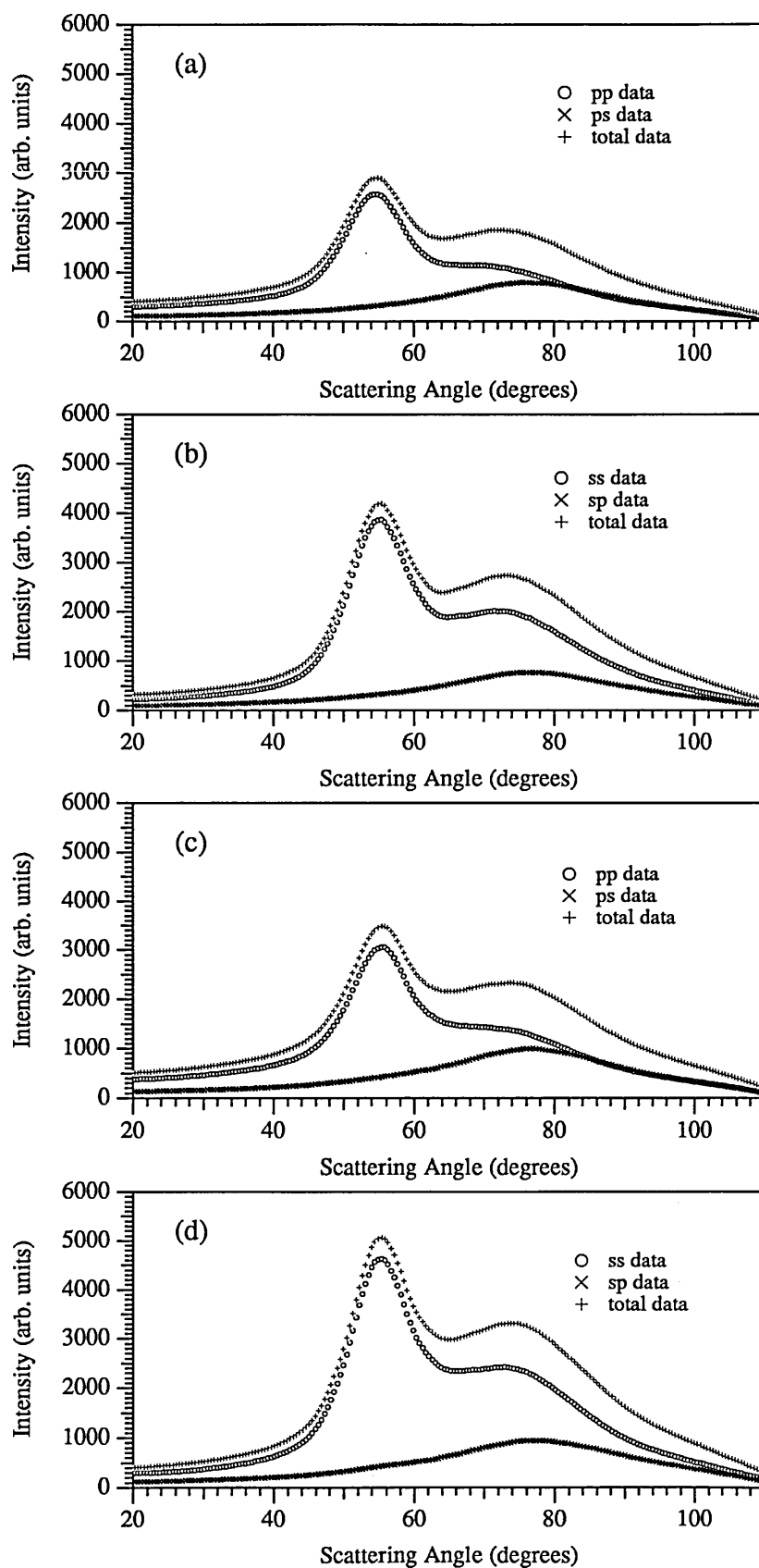


Figure 5.22: Goniophotometric curves from a single-layer surface of 90% grey hairs after treatment: (a) sample A, *p*-polarized light incident; (b) sample A, *s*-polarized light incident; (c) sample B, *p*-polarized light incident; and (d) sample B, *s*-polarized light incident.

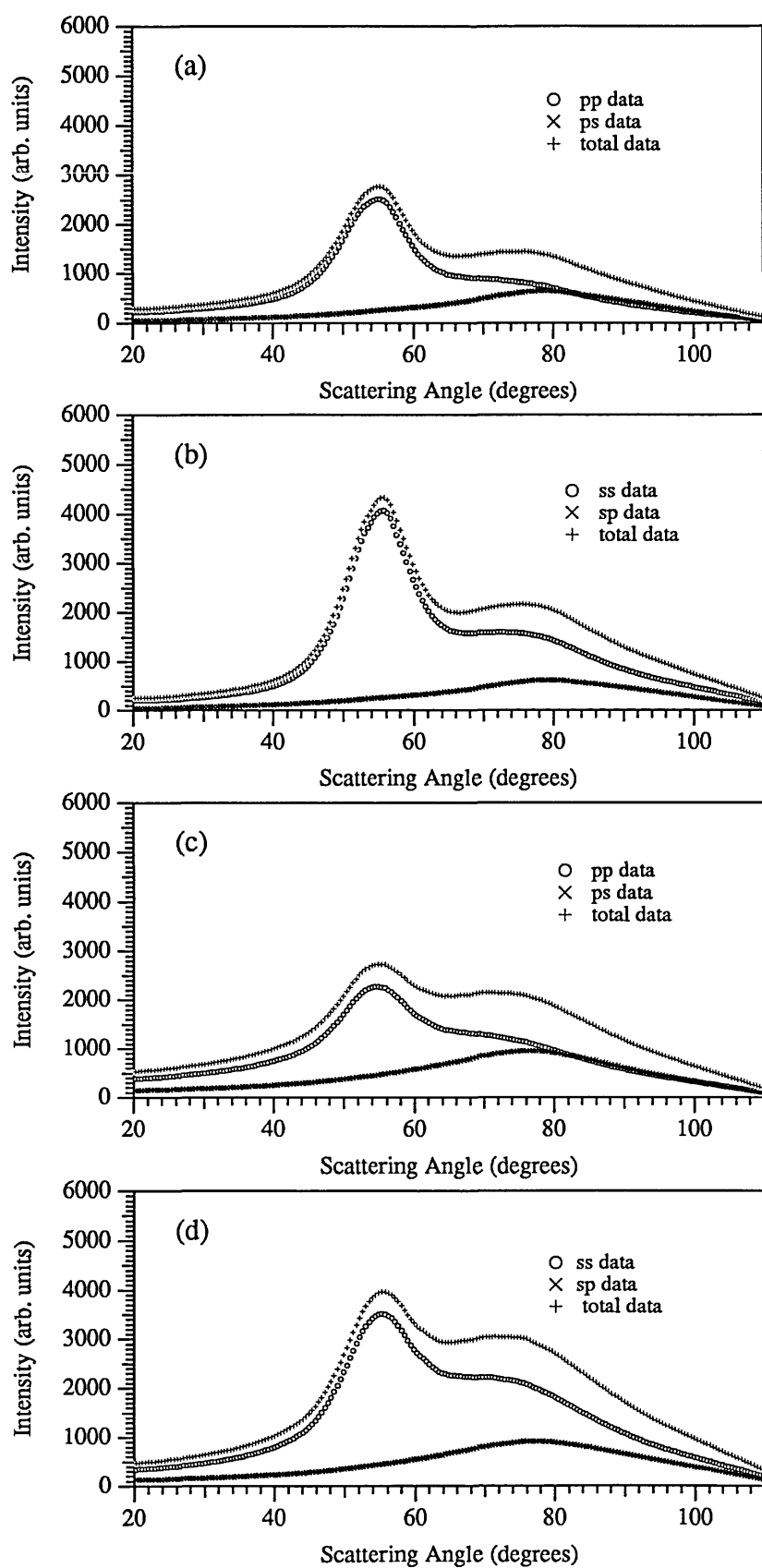


Figure 5.23: Goniophotometric curves from a single-layer surface of 90% grey hairs after treatment: (a) sample C, *p*-polarized light incident; (b) sample C, *s*-polarized light incident; (c) sample D, *p*-polarized light incident; and (d) sample D, *s*-polarized light incident.

include permanent and temporary dyeing agents which enter the hair shaft.

Samples of strawberry blond hair were separated into one-gramme tresses, washed in herbal shampoo (if appropriate), and then treated with either a dyeing or tinting preparation. The treatments are summarized in table 5.11.

Hairs from each sample were strung into surfaces and their light-scattering distributions recorded. The results for samples E and F are given graphically in figure 5.24 and their characterizing parameters are printed in table 5.12.

The effects of the temporary tints (toner and shader) on the visual appearance of the hairs and on their light-scattering envelopes were found to be very slight and so have been omitted. Indeed, semipermanent dyes have not been reported in any investigations to have caused irreversible damage to hairs.

Table 5.11: Summary of treatments applied to samples E to H.

Hair Sample	Herbal Shampoo (Aloe Vera)	Boots Brunette brown	Silvikrin Shader Ash Whisper	Silvikrin Toner Rich Mahogany
E	Yes	No	No	No
F	Yes	Yes	No	No
G	No	No	Yes	No
H	No	No	No	Yes

Table 5.12: Summary of parameters calculated from the curves produced by the surfaces of cosmetically treated hairs.

Sample & Pol ⁿ	Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss g_c (no units)	Kurtosis Index K (no units)
E (s)	$1.9 \pm .5$	$24.7 \pm .5$	$0.929 \pm .006$	3.250
E (p)	$2.0 \pm .5$	$25.0 \pm .5$	$0.875 \pm .006$	3.065
F (s)	$2.0 \pm .5$	$9.3 \pm .5$	$0.968 \pm .006$	4.249
F (p)	$2.0 \pm .5$	$9.7 \pm .5$	$0.945 \pm .006$	3.829

However, the effects of the permanent dye were found to be visually very obvious, and they also had a large effect on the light-scattering distribution as recorded by the goniophotometer. This sample of blond hair had a naturally small average scale angle of $\approx 2^\circ$ and was not found to be altered by the treatment, which fits in with the absorbing nature of this darkening agent. However, contrast gloss values and kurtosis indices were shown to be increased by this treatment, as it increased the ‘peakedness’ of the specular peak. There is little information in the literature on the effects of dyes, but the general consensus seems to be that oxidative dyeing produces

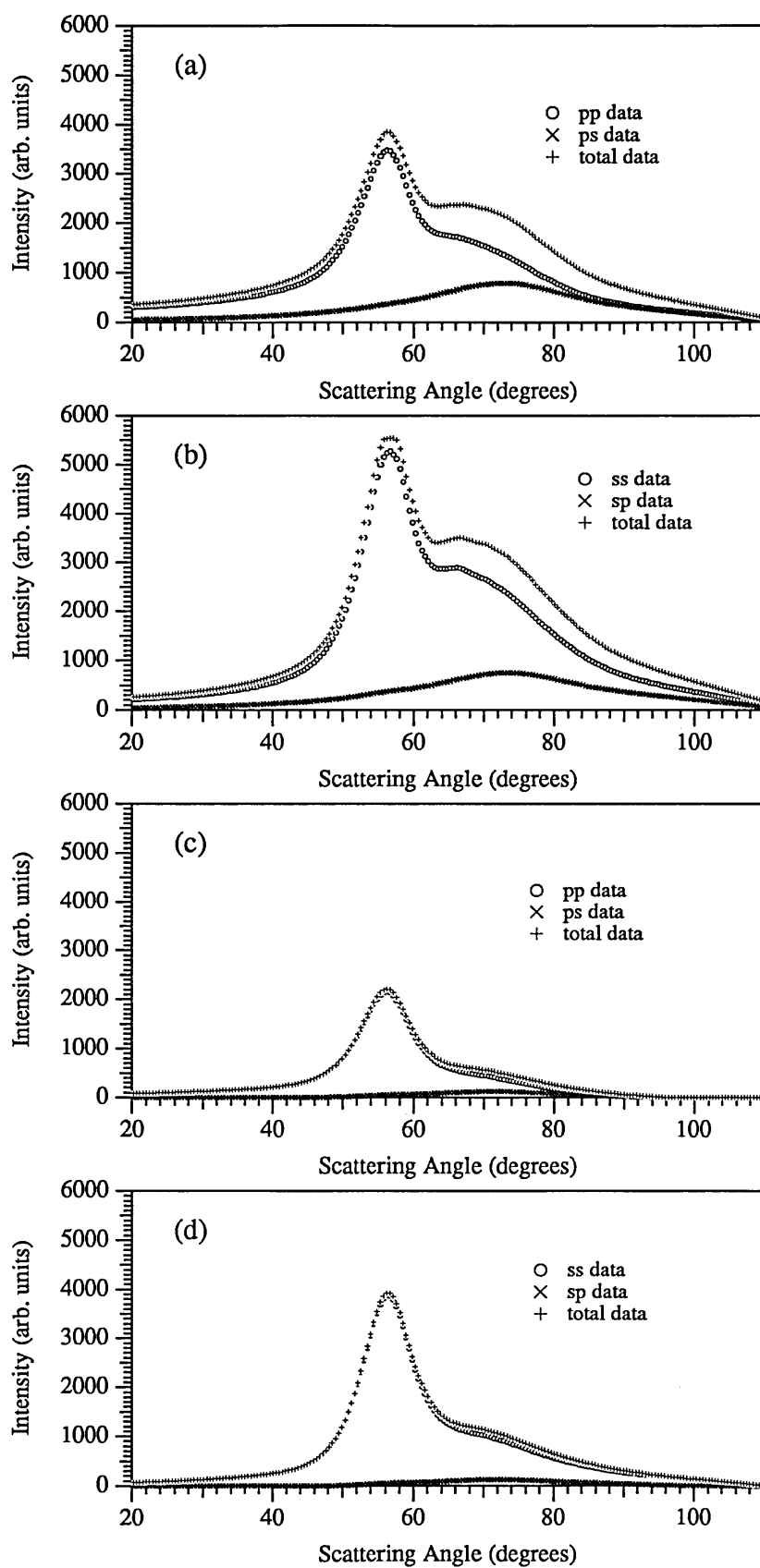


Figure 5.24: Goniophotometric curves from a single layer surface of blond hairs after treatment: (a) sample E, p -polarized light incident; (b) sample E, s -polarized light incident; (c) sample F, p -polarized light incident; and (d) sample F, s -polarized light incident.

structural changes in the hair similar to bleaching, but to a lesser extent. Thus, a detailed discussion of the changes will be dealt with in the next subsection on hair bleaching.

The third area of investigation, is generally concerned with chemical bleaching and permanent waving of hair. Many researchers have published data providing evidence that these two popular hair treatments are the most damaging processes to which hair fibres are commonly subjected. (Note: in very low pH conditions (around 2), the effects of chlorination are catastrophic to the hair's surface but this treatment is not usually applied for cosmetic purposes [17, 18].)

Samples of dark-brown hair were bound into one-gramme tresses, washed in herbal shampoo (if appropriate), and then individually treated with a selection or combination of proprietary products, as summarized in table 5.13.

Table 5.13: Summary of treatments applied to samples I to M.

Hair Sample	Herbal Shampoo (Aloe Vera)	Poly Highlights (bleach)	Silvikrin Softly Blond	Perm. waving soln.
I	Yes	No	No	No
J	Yes	Yes	No	No
K	No	No	Yes	No
L	Yes	No	No	Yes
M	Yes	Yes	No	Yes

With the exception of the sample treated with Silvikrin Softly Blond (which showed results similar to, but less significant than, those of the hair treated with Poly Highlights), the light-scattering distributions are presented in figures 5.25 and 5.26, and the corresponding analysis parameters of contrast gloss, etc., are given in table 5.14.

The contrast gloss and kurtosis index of all the treated samples were reduced in value in comparison with the control sample I. Bleaching sample J for 20 minutes resulted in an increase in the cross-polarized return (negligible for sample I) and in the FWHM, both of which are characteristic of a reduction in the degree of pigmentation. During the bleaching process, sample J was observed to change in colour from dark brown to light reddish-brown. No significant change was noted for the average scale angle as a result of this treatment, and this tends to indicate that the cuticle cells were not structurally altered. In the bleaching process [12, 91, 95] the natural pigments are selectively decolourized by the controlled reaction of an

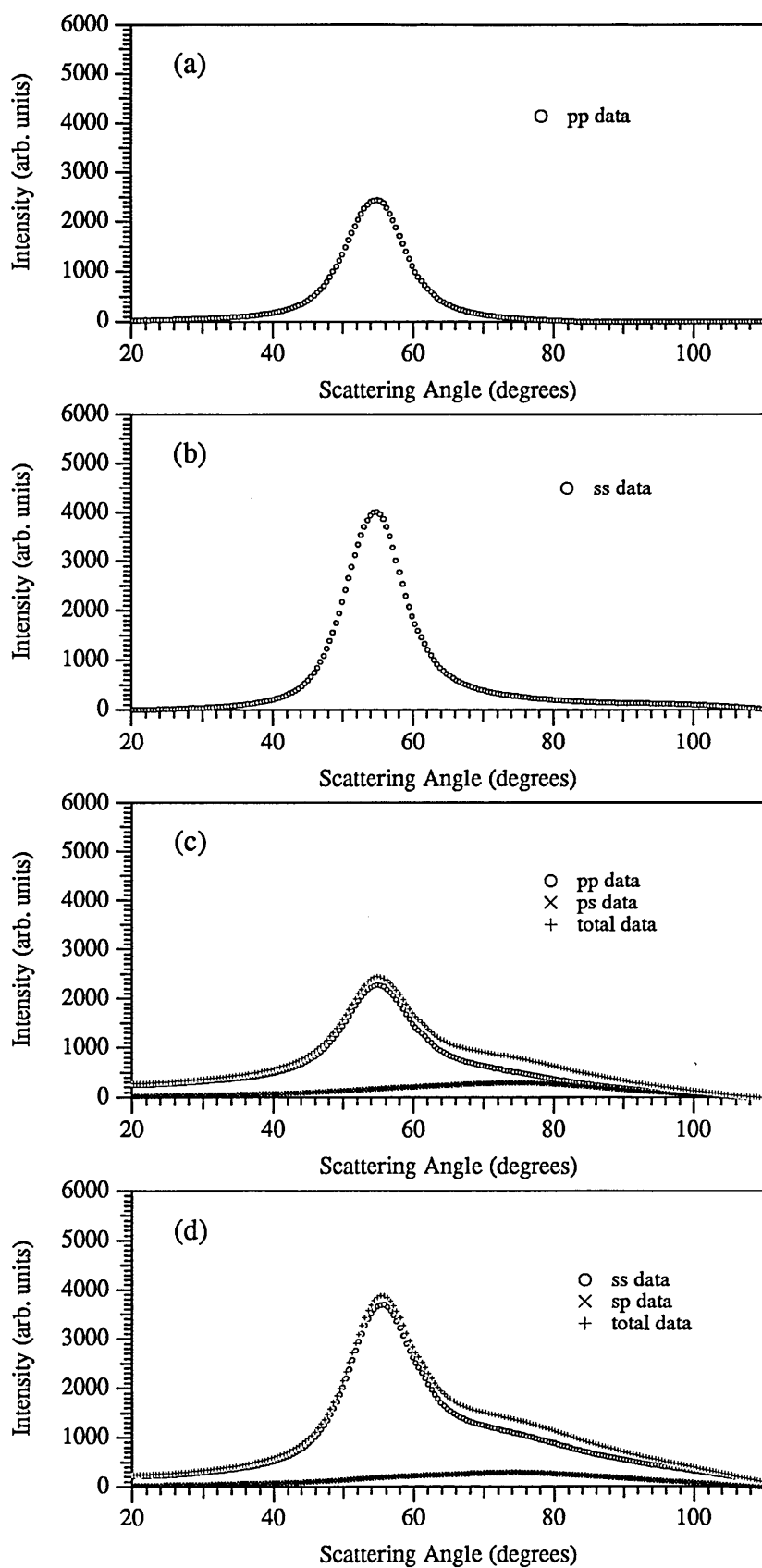


Figure 5.25: Goniophotometric curves from a single layer surface of dark brown hairs after treatment: (a) sample I, *p*-polarized light incident; (b) sample I, *s*-polarized light incident; (c) sample J, *p*-polarized light incident; and (d) sample J, *s*-polarized light incident.

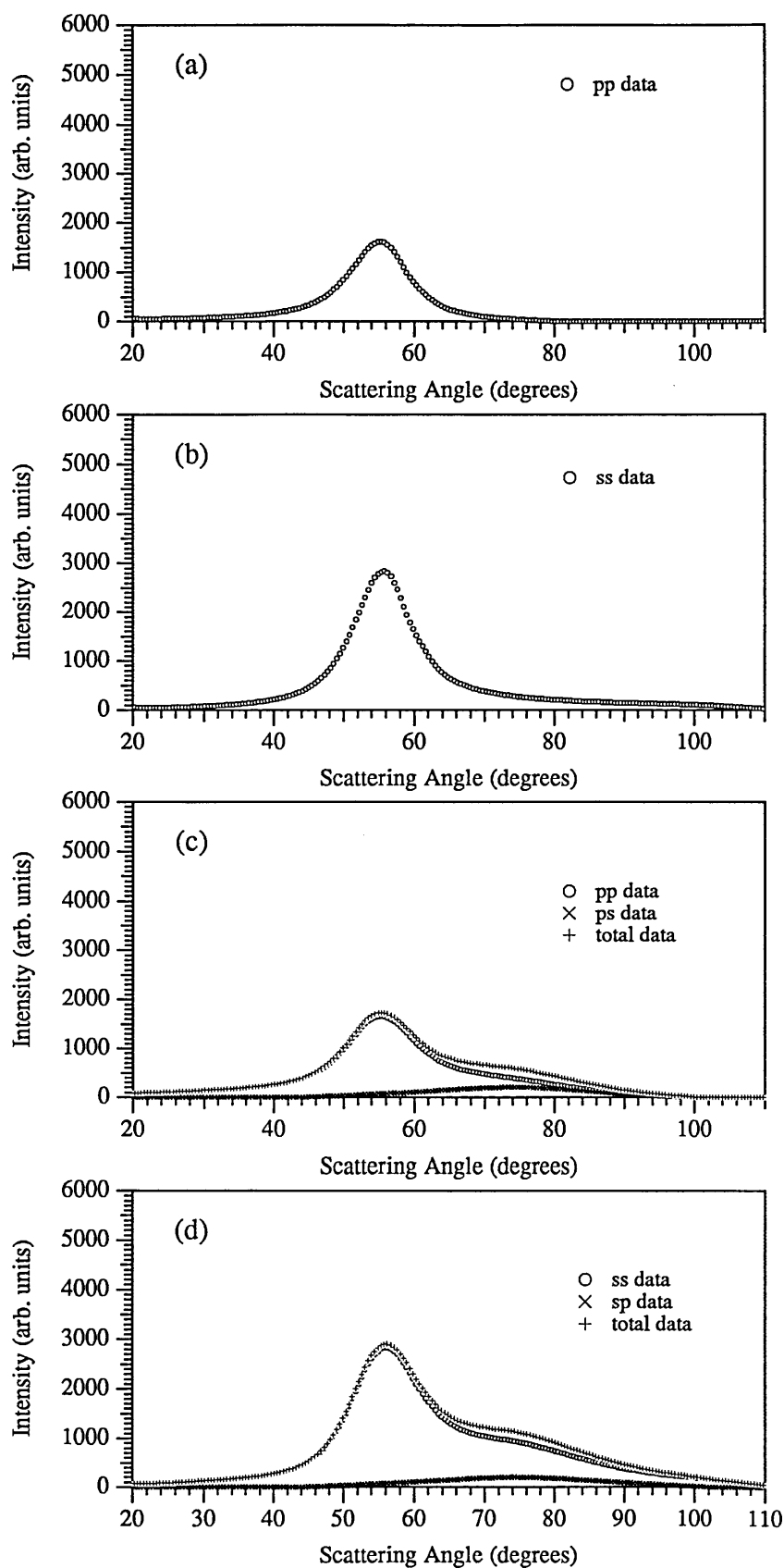


Figure 5.26: Goniophotometric curves from a single layer surface of dark brown hairs after treatment: (a) sample L, p -polarized light incident; (b) sample L, s -polarized light incident; (c) sample M, p -polarized light incident; and (d) sample M, s -polarized light incident.

Table 5.14: Summary of parameters calculated from the curves produced by the surfaces of cosmetically treated hairs.

Sample & Pol ⁿ	Scale Angle α (degrees)	FWHM (degrees)	Contrast Gloss g_c (no units)	Kurtosis Index K (no units)
I (s)	$2.6 \pm .5$	$10.0 \pm .5$	$0.990 \pm .006$	8.000
I (p)	$2.6 \pm .5$	$9.8 \pm .5$	$0.975 \pm .006$	6.138
J (s)	$2.5 \pm .5$	$14.5 \pm .5$	$0.915 \pm .006$	3.433
J (p)	$2.6 \pm .5$	$15.3 \pm .5$	$0.851 \pm .006$	3.171
L (s)	$2.1 \pm .5$	$10.1 \pm .5$	$0.972 \pm .006$	5.989
L (p)	$2.3 \pm .5$	$9.8 \pm .5$	$0.953 \pm .006$	5.965
M (s)	$2.3 \pm .5$	$14.8 \pm .5$	$0.957 \pm .006$	3.596
M (p)	$2.3 \pm .5$	$14.9 \pm .5$	$0.919 \pm .006$	3.216

oxidizing agent in an alkaline pH. The simplest alkaline bleach system contains hydrogen peroxide and ammonia or ammonium carbonate. Side reactions result in the hair keratin also being mechanically altered by the reaction with alkaline hydrogen peroxide, leaving it with an increased porosity. On a chemical level the changes are mainly due to the cleavage of the disulphide bond in cystine, and the formation of cysteic acid as the end product. The oxidative scission of disulphide bonds results in decreasing the crosslink density of the protein and provides extra anionic sites in the form of cysteic acid residues. Both the increase in hydrophilicity and the reduction in crosslink density contribute to an increase in liquid retention, alkali solubility, and sorption of polymers and a decrease in strength.

In the treatment of permanent waving, a permanent curl is achieved by altering the molecular configuration of the hair [95, 99]. Thioglycolate, a strong reducing agent, is used to break the disulphide bonds, the hair is then wound on curlers, and an oxidizing agent (sodium bromate or hydrogen peroxide) is applied to rebuild the disulphide crosslinks. The hair structure is weakened by this treatment [100] as not all the disulphide links are re-formed, making it more vulnerable to fracture under stress forces. Sample L, treated with a proprietary perming solution and neutralizer (for 15 minutes and 10 minutes respectively), did not visually appear very different from the control sample I. This is consistent with its FWHM parameter, which was found to be comparable to that of sample I. However, the kurtosis index, contrast gloss, and average scale angle for sample L all indicate that changes have taken place; the reduction in α suggests that the cuticle layers have been damaged, scattering more light diffusely out of the plane of incidence and resulting in an overall reduction

in the total amount of light detected in the plane of incidence.

The combined effects of permanent waving and then bleaching were investigated using sample M. In colour, this sample looked very similar to sample J, and this was corroborated by the similarities in shape of their light-scattering envelopes. In terms of the characterizing parameters, this sample shared features in common with both samples J (g_c , K , and FWHM) and L (α). In conclusion, it was felt that, in order to see the real effects of the cosmetic treatments on them, the hair samples should each be subjected to a programme of grooming and weathering and then re-examined.

As an alternative, it was decided to select a few strands of hair from sample L, wet them thoroughly, and then subject them to vigorous combing (in both directions) for a period of 30 minutes. After towel-drying one strand was selected from this treated batch and, together with a fibre from sample I, profiled using the Talystep device described in chapter four. The resulting profiles and corresponding frequency distributions of slope angles are shown in figure 5.27. Table 5.15 summarizes the statistical parameters of these profiles. From the profiled lengths of hair, after

Table 5.15: Statistical parameters calculated from the Talystep profiles of hair samples I and L.

Hair Sample	Mean Slope μ Av. Scale Angle	Standard Deviation σ_D
I	2.44 ± 0.50	7.03
L (after grooming)	0.67 ± 0.50	10.05

grooming and treatment, the mean scale angle was found to decrease significantly whilst the range of existing scale angles increased. This produces a broader, flatter spread for the Gaussian distribution for the permed sample than for the control.

Coated Hairs

In the world of cosmetics and toiletries, much emphasis has been placed on producing products which would enhance the shiny appearance of hair. One way of doing this might be to coat the hair with a thin layer of a material having a higher refractive index, this would also negate the effects of the hair scales, which spread the specularly reflected light over a relatively large range of angles (typically 12°). A well-known hair gel/cream is the product Brylcreem. When this compound is

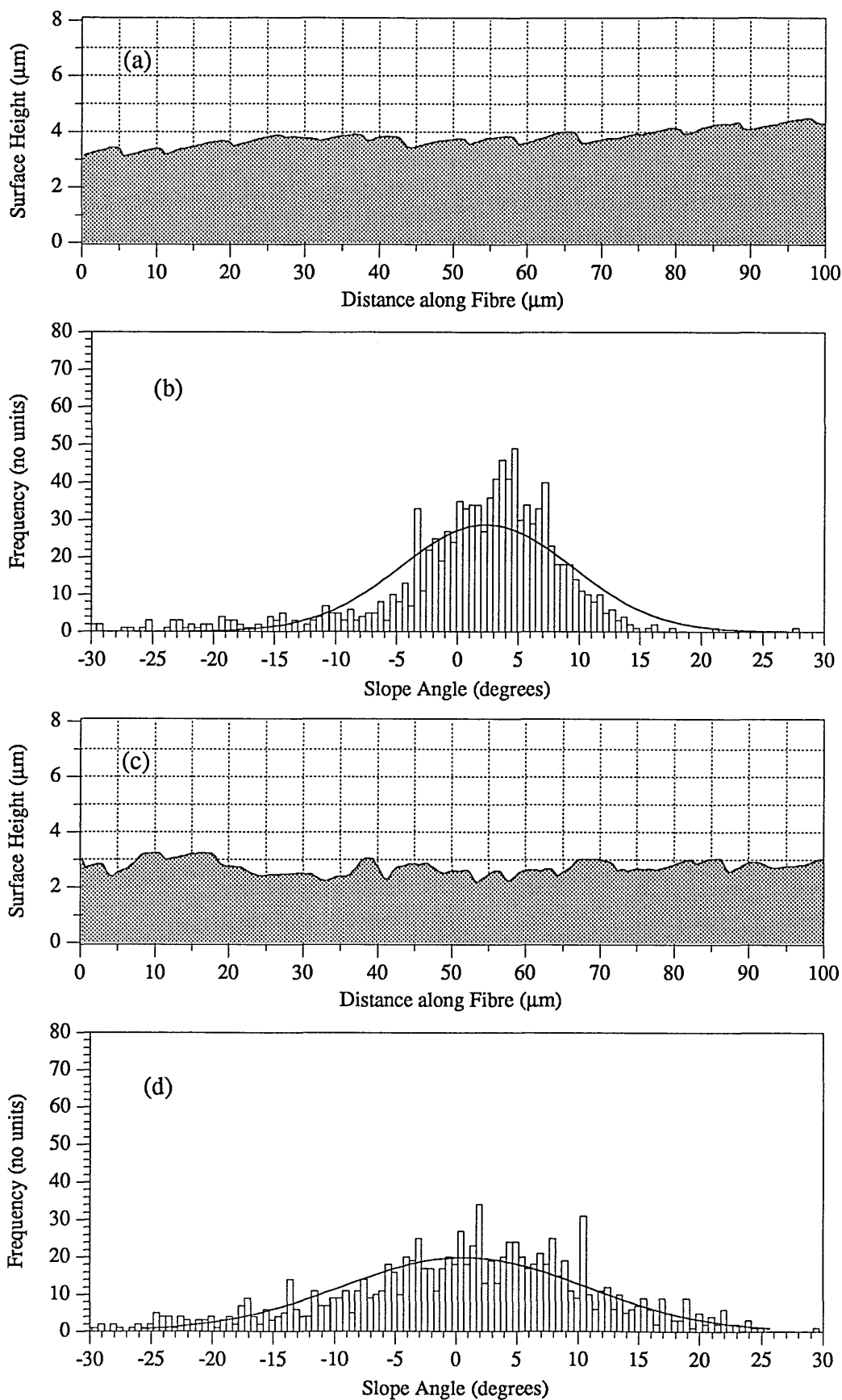


Figure 5.27: Graphs (a) and (c) show respectively the results of Talystep-profiling a Caucasian brown hair and a hair from the same sample after permanent waving. Histograms (b) and (d) illustrate the corresponding frequency distribution of slope angles present along that section of surface.

applied to a head of hair, the hair does appear shiny but not natural, as it also sticks together. To investigate the effects of Brylcreem on the light-scattering distributions of hair, two surfaces were strung from the tress of dark-brown hair (washed with a mild herbal shampoo only) used in the previous experiment. One of the hair surfaces was then coated with a layer of regular Brylcreem and the other with a layer of medicated Brylcreem. Excess cream was carefully wiped off before mounting the samples on the scattering-rig. It was decided to record a set of results immediately, whilst the compound was still wet, and then another set 24 hours later, after the samples had dried. Overnight they were placed in a sealed atmosphere to prevent them becoming contaminated by dust, etc. Polarized-light measurements at 30° incidence were taken from each surface and the results are given in figure 5.28 for the regular Brylcreem and in figure 5.29 for the medicated. The light-scattering envelopes for the control sample of dark-brown hair (sample I) are given in figure 5.25 but for the purposes of comparison with this experiment, the intensity values of these results must be divided by a factor of 2.6 to take into account the different sensitivity scale on the high-voltage supply of the photomultiplier tube used for the coated-hair experiment.

From the light-scattering measurements it can be seen that both regular and medicated Brylcreem provided a coating sufficiently thick to negate the optical effects of the scales and produce almost symmetrical curves. Indeed, on average the maximum intensity reflection was found to be at twice the angle of incidence, i.e. at the mirror angle of reflection. It was also found that the magnitude of the specular reflection was greater while the Brylcreem (regular and medicated) was still wet. Surprisingly the medicated sample produced very broad specular peaks compared to the regular, which must be due to its different composition. Table 5.16 contains the characterization parameters calculated for these hair surfaces. With respect to the control sample (see table 5.14), only the recently applied coating of regular Brylcreem increased the contrast gloss and kurtosis index of the hair, Indeed, when the Brylcreem had dried on the hair, the samples looked dull and were subjectively assessed to have a lower gloss than sample I, the control. Considering the colour (dark brown) of this hair, these visual assessments were corroborated by the g_c and K values for the medicated sample and, to a lesser extent, for the regular.

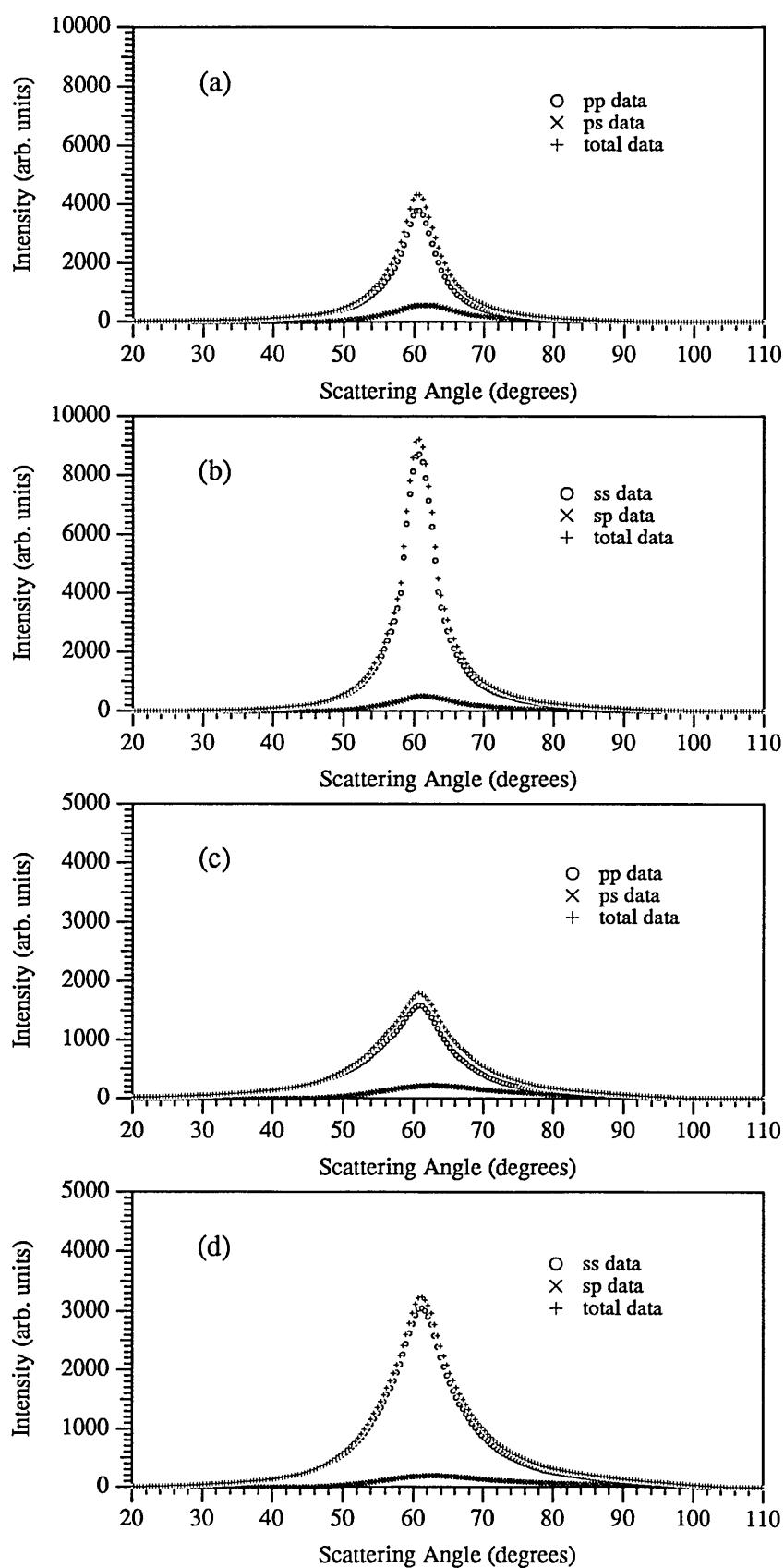


Figure 5.28: Goniophotometric curves from a single-layer surface of dark-brown hairs after treatment with regular Brylcreem: (a) wet, *p*-polarized light incident; (b) wet, *s*-polarized light incident; (c) dry, *p*-polarized light incident; and (d) dry, *s*-polarized light incident.

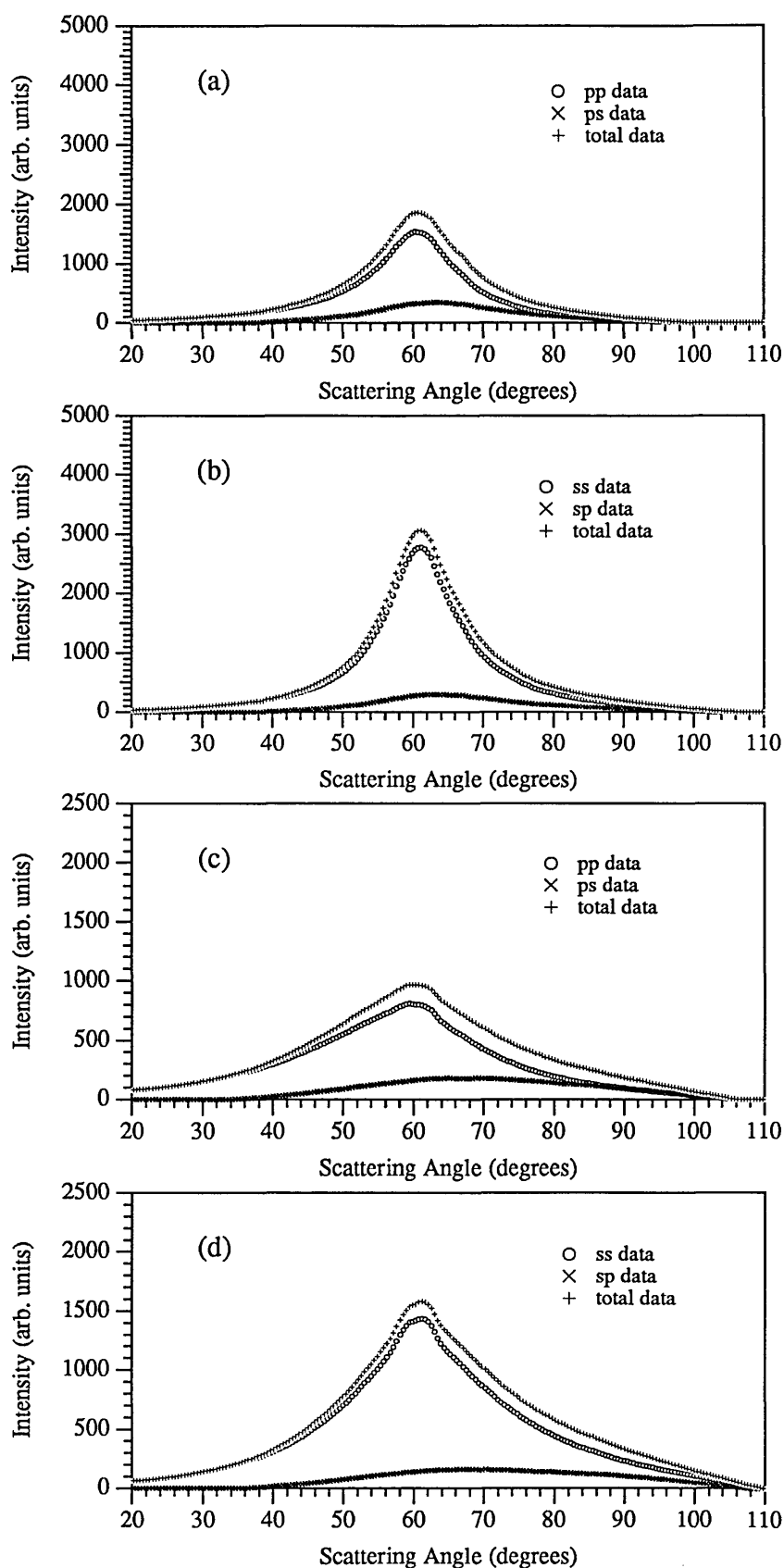


Figure 5.29: Goniophotometric curves from a single-layer surface of dark-brown hairs after treatment with medicated Brylcreem: (a) wet, *p*-polarized light incident; (b) wet, *s*-polarized light incident; (c) dry, *p*-polarized light incident; and (d) dry, *s*-polarized light incident.

Table 5.16: Summary of parameters calculated from the curves produced by the surfaces of Brylcreem-coated hairs.

Sample & Polarization	Specular Angle θ_s (degrees)	FWHM (degrees)	Contrast Gloss g_c (no units)	Kurtosis K (no units)
Regular wet (s)	$60.8 \pm .5$	$5.2 \pm .5$	$0.998 \pm .006$	8.311
Regular wet (p)	$60.8 \pm .5$	$8.9 \pm .5$	$0.991 \pm .006$	7.566
Regular dry (s)	$61.2 \pm .5$	$10.6 \pm .5$	$0.989 \pm .006$	5.963
Regular dry (p)	$60.8 \pm .5$	$11.9 \pm .5$	$0.972 \pm .006$	5.509
Medicated wet (s)	$61.2 \pm .5$	$13.1 \pm .5$	$0.971 \pm .006$	5.438
Medicated wet (p)	$60.7 \pm .5$	$15.1 \pm .5$	$0.949 \pm .006$	5.045
Medicated dry (s)	$61.2 \pm .5$	$23.8 \pm .5$	$0.911 \pm .006$	4.128
Medicated dry (p)	$59.4 \pm .5$	$28.4 \pm .5$	$0.841 \pm .006$	3.917

General Conclusions on Characterization Methods

In assessing the usefulness and appropriateness of the different methods of characterizing goniophotometric curves, two main points need to be considered. The first is a method's degree of correlation with visual assessments of the same samples, and the second is the time it takes to make each calculation, since, in commercial circumstances, many samples would need to be classified rapidly.

The calculation of simple contrast gloss, g_c , has the advantage that it is relatively quick and easy to perform, but the disadvantage is that it relies on only two data points and therefore takes no account of the shape of the rest of the curve. Also, if the value of diffuse measurement, d , falls below the resolution of the measuring equipment then two hairs with very different appearance but low scattering in the direction of d will be calculated to have the same contrast gloss value of unity. Indeed, it can be seen from table 5.4 and reference [70] that there is very little variation in the values of simple gloss for dark hairs. Generally, all the values were found to be concentrated in the top six per cent of the full range.

This contrast gloss measurement has been found to be critically dependent on the angle of incidence, as was found in an earlier subsection. Stamm et al. reported the simple gloss measurement to have a lower reliability than the integrated gloss values which were based on all the data points. This method of evaluation of the goniophotometric data has the advantage that it does take into account the full scattering distribution, but again it is very dependent on the value of d . If d is measured to be very small or below the measurement resolution then $G_c = 1$, since D will also be zero. Alternatively, if the sample is highly transparent, e.g. for the

white hair in table 5.4, then d is large and the integrated value D is larger than the integrated value of S . This produces a negative value for G_c which is difficult to interpret physically. Clearly the transparency of the sample has a large effect on this method of assessment and is out of proportion to that estimated by a visual observer.

Measurement of the FWHM has been found to take into account variations in surface condition and also degree of transparency of hair samples, both of which affect the appearance of hair, but alone it does not unambiguously represent a set of samples because it is difficult to separate the two contributions in the final result.

The skewness index was found to be useful in supporting the observed trend towards greater asymmetry of the light-scattering envelope as the hair samples become more transparent.

The kurtosis index seemed in many ways to be the best method of assessing the results. It uses all the data points and has a strong statistical (mathematical) basis, in contrast to the ad hoc methods of calculating D , for instance, invented by different workers [58, 59]. It was also found to be sensitive to small changes in the distribution of the scattered light and was in general agreement with visual estimations of shine for a set of hair samples (treated and untreated).

5.3.2 Hair Surfaces Orientated Vertically

This experiment investigated the light-scattering envelopes produced by single-layer surfaces of hairs (strung from the six basis samples) orientated vertically as shown in figure 5.2(b), and illuminated with the quartz halogen lamp. As before, the surfaces were illuminated at angles of 0° and 30° . The results produced with linearly polarized light by the black, blond, and white hairs are given in figures 5.30 and 5.31. The results of this experiment will be compared and contrasted to those obtained in sections 3.2.2, 3.3.2, and 5.2.2, which examined individual hairs (laser and white light illumination) and surfaces (laser illumination) orientated vertically. Note: in these experiments the angle of scatter was measured with respect to the outward normal from the surface, and the gap in the data points in the direction of backward scatter corresponds to those angles over which the detector blocked the incident beam during a scan.

As with the other vertically orientated experiments on hairs, the light-scattering envelopes were divided into two types of results — those for the dark hairs and

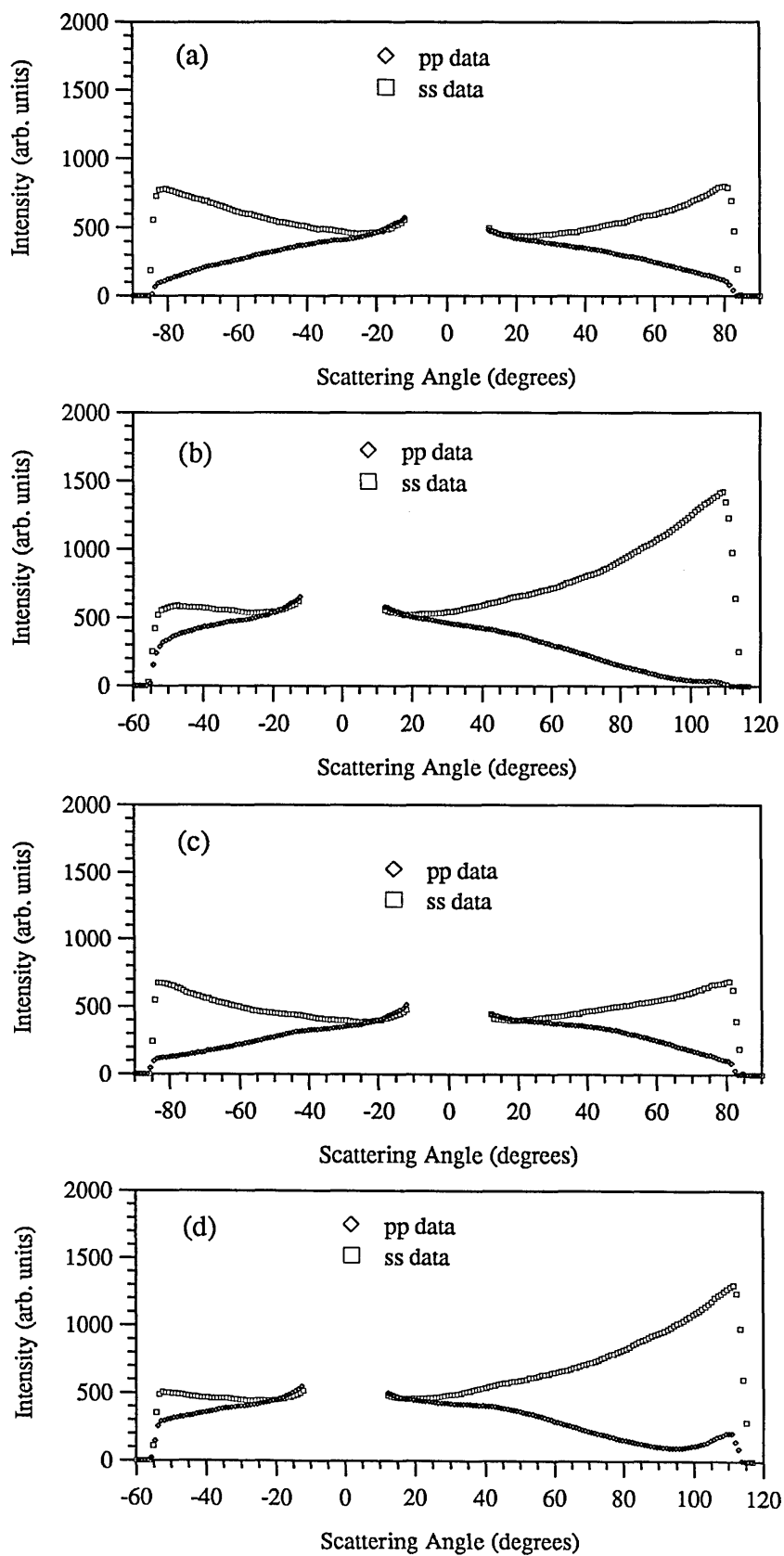


Figure 5.30: Goniophotometric curves from a single-layer surface of black hairs at (a) normal incidence and (b) 30° incidence, and from a single-layer surface of brown hairs at (c) normal incidence and (d) 30° incidence.

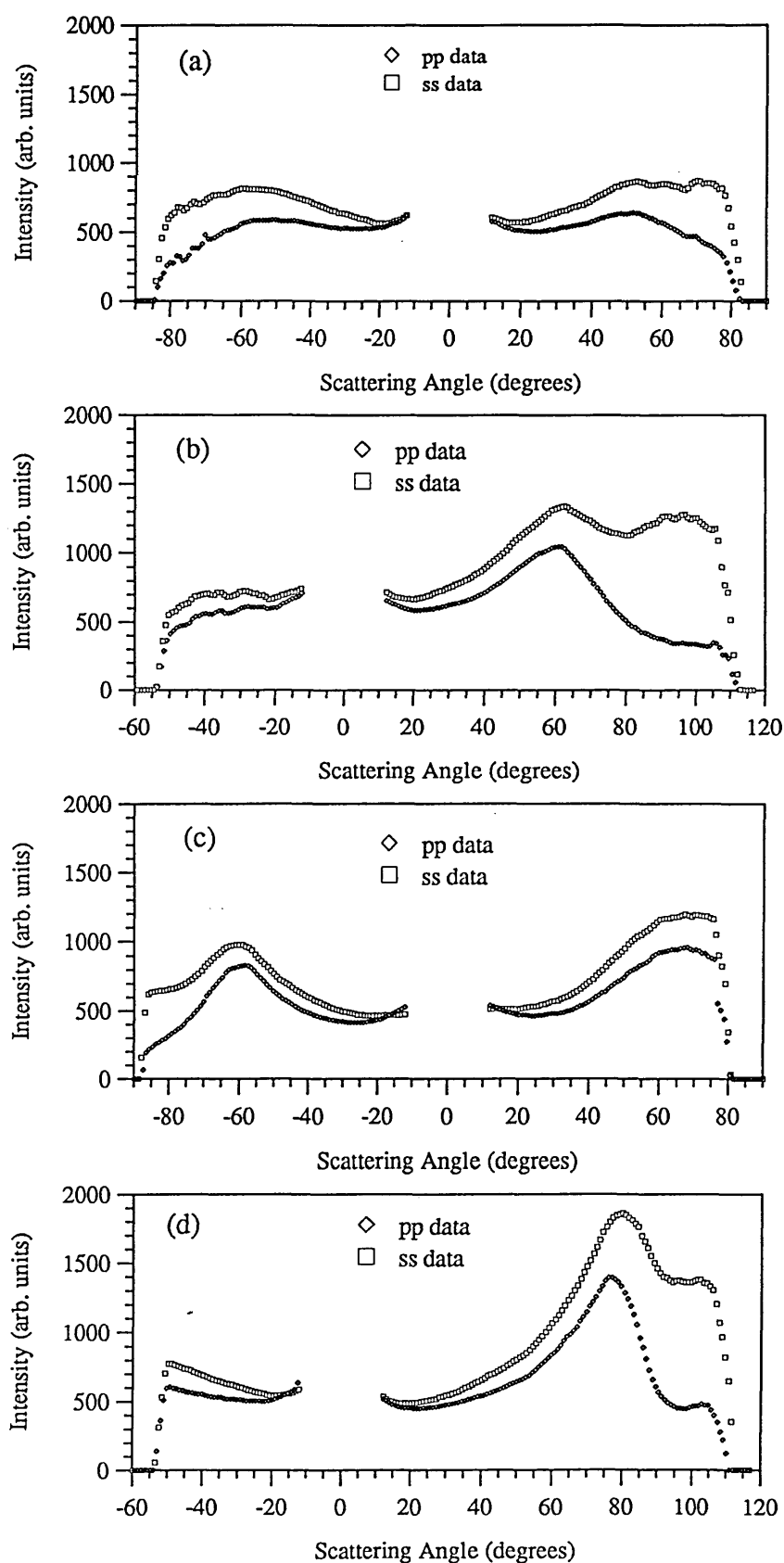


Figure 5.31: Goniophotometric curves from a single-layer surface of blond hairs at (a) normal incidence and (b) 30° incidence, and from a single-layer surface of white hairs at (c) normal incidence and (d) 30° incidence.

those for the light (almost transparent). Considering first the results for a surface of black hairs at normal incidence, it can be seen that the shapes of the *s*- and *p*-polarized curves in figure 5.30(a) are very similar to those that were obtained for a single black hair with the same illumination source, the main difference being that the intensity of the surface scans drops to zero at $\pm 90^\circ$ for both polarizations. This effect may be explained in purely geometric terms: the apparent size of the illumination spot alters as the detector rotates about the surface until at $\pm 90^\circ$ the detector can no longer see the illuminated area and records a scattered intensity of zero. For an explanation of the other features of the light-scattering envelope, the reader is referred to section 3.2.2. Similarly, the light-coloured (almost transparent) hair samples gave results which have the same general form as those reported for the same surfaces when illuminated by a laser source, as described in section 5.2.2. For all the hair samples investigated, the curves produced by halogen illumination were found to be smoother (no speckle pattern), but otherwise the same analysis as given in section 5.2.2 may be invoked to explain the shapes of the curves.

Chapter 6

Conclusions and General Comments

6.1 Introduction

This final chapter serves as a way of consolidating the results of the thesis and highlighting any important comments and conclusions. It also contains ideas for further work in this area, both experimental and computer modelling.

6.2 Individual Hair Fibres

The investigation into the light-scattering envelopes produced by individual hairs revealed a number of points.

First was that the intensity of reflection in the specular direction follows the Fresnel reflection formulae. This was evidenced by the results of the investigations into the effects of varying the angle of incidence of the incident beam in the horizontally orientated fibre experiments, and by the shape of the light-scattering envelope produced by a dark hair fibre orientated vertically to the planes of incidence and detection.

Second, that the shape of the light-scattering envelopes depends on the level of pigmentation (colour) of the hair. This was further analysed via polarization measurements, which indicated that two main processes dominate the total light-scattering envelope: specular reflectance from the front surface of the fibre (independent of colour), and light that had undergone one or more internal reflections before scattering (dependent on type and concentration of pigment granules). Confirmation was presented by the results of scanning a blond (partially transparent) hair before and after gold-coating it.

Third, the shape of the light-scattering envelope — particularly the definition of the specular peak — was found to be linked to the surface condition of a hair,

and thus could be used to monitor changes in the general condition of a hair caused by treatments such as brushing and combing. Also, localized mechanical damage to a hair may be identified via large-scale changes to the shape of the light-scattering envelope produced when a hair was illuminated at that damaged region.

Fourth, for hair orientated vertically, widely different light-scattering envelopes were found to be produced by light and dark hairs. It was noted for the light-coloured hairs (blond and white) that their light-scattering envelopes included peaks of high intensity. The angular positions of the latter were observed to vary with the orientation of the cross-section of the hair with respect to the incident beam. The absence of any such peaks for dark-coloured hairs indicated that they must be formed by the component of light scattered after one or more internal reflections. Also, the widths of the peaks detected were found to correlate with the degree of inhomogeneities included in the hair shaft.

In view of the results from these individual fibre experiments, and because of the cyclic nature of hair growth (see section 5.1), this means that a single hair chosen from a sample need not be representative of the average condition of the sample, it was decided to leave the assessment of glossiness of hair to the experiments conducted on planar arrays of hair, strung parallel at regular intervals.

6.3 Raytracing Results

From the refractive-index measurements it seemed a reasonable assumption to conclude, for the purposes of undertaking a raytracing through an optical model of a hair, that the cortex region of hair has a uniform refractive index. Indeed, the average refractive index of hair was measured to be 1.545 at a wavelength of 550 nm, and this value was used in all the computer simulations, although at a later stage an absorption factor was also included to take account of the presence of pigment granules.

The model of a vertically orientated hair was able to explain all the features in the light-scattering envelopes that were recorded experimentally. For the dark-coloured hairs, the general shape of the light-scattering envelopes could be explained in terms of the light scattered from the front face of the cylinder. The peaks observed for the light-coloured hairs were determined to be due to the formation of singularities in the geometric light field which are called caustics. Using cylinders with elliptical cross-sections of varying indices of ellipticity and orientation to the incident beam,

it was possible to simulate the variations in angular position of the caustic peaks found in the experimental results.

The model of a horizontally orientated hair consisted of a series of flat-top cones each with a different cone angle. Each cone angle was assigned a probability weighting according to the frequency of occurrence of the corresponding scale angle on the surface of a hair as recorded by a Talystep profiling device. The computer simulation was able to account for the differences in the shape of the light-scattering envelope due to variations in pigment level and surface condition of a hair. However, one of the assumptions used in the model — that the near and far sides of the cone were inclined at the same angle to a central long axis — meant that, away from normal incidence, the model broke down. Further work to improve this optical model of a hair should include the introduction of a medulla region and the addition of flexibility in being able to change the angle of inclination of the near and far sides of the conic unit independently.

6.4 Planar Arrays of Hair

When working with planar arrays of hair, it was rapidly realised that, for the results to be valid and meaningful, all the hairs must be orientated in the same direction, i.e. all root ends to the right or all to the left.

Variations in the shape of the light-scattering envelopes produced by arrays of hair illuminated at three different visible wavelengths were studied. From the results, it was concluded that only those hairs which contained the pigment phæmelanin exhibited a wavelength dependence in their scattering distributions. Hair samples containing this red pigment were found to show increased absorption of light at short wavelengths (in the blue and green regions of the visible spectrum).

Enhancement of intensity in the backscatter direction was observed for arrays of hairs orientated vertically to the plane of incidence and detection. This feature of enhancement was found to be restricted to single layers of light-coloured (partially transparent) hair and double layers of hair of all colours. From this, it was concluded that two slightly different scattering mechanisms were responsible: for the partially transparent hairs, the possibility exists for retroreflection of light inside a hair; and for the double layers of dark hairs, light may follow identical but reversed paths by bouncing off the fibres as illustrated in figure 5.13 — both mechanisms creating forward and time-reversed paths and hence constructive addition of the scattered

light waves.

In terms of further work, one obvious extension would be to conduct experiments on arrays of hair many layers deep and on arrays of hair where the inter-fibre distance (i.e. distance of separation of hairs in the single- and double-layer surfaces) was varied. In this way, it may eventually be possible to simulate experimentally the salon situation of a full head of hair.

Although attempts to develop hair-care products which can restore the original properties of a hair after it has been damaged have been numerous, they have also been largely unsuccessful. Nevertheless, a desire exists in the toiletry industry to monitor and quantify the effects of both damage and restoratives on the appearance of hair. From the results in this thesis, it can be concluded that the kurtosis index, K , and the calculation of simple contrast gloss, g_c , provide the most appropriate objective methods of assessment. The kurtosis index has a sound statistical basis, uses all the data points in a goniophotometric scan, and is sensitive to small changes in appearance. It has also been found to give good agreement with visual estimations of shine for a given set of hair samples. However, neither evaluation method is able to cope with changes in hair colour; consistently predicting, independent of hair condition, that light-coloured hairs are less glossy than dark.

Thus, it might be of use to determine any changes in the chromaticity co-ordinates of a hair sample before and after treatment and include this in the objective methods of assessment. Indeed, from the variation-of-wavelength investigations, it was demonstrated that the chromaticity co-ordinates of hair colour may be calculated from data extracted from the goniophotometric scans.

Appendices

Appendix 1

The most important stage in the interfacing equipment was the pre-amplifier used to convert the current signal from the photomultiplier tube into a voltage and then to amplify it so that it would lie in the range (0 – 1.8 volts) accepted by the analogue-to-digital converter input port of the computer. The circuit design for this stage is shown in figure 6.1. The RSAD524AD is a precision monolithic instrumentation

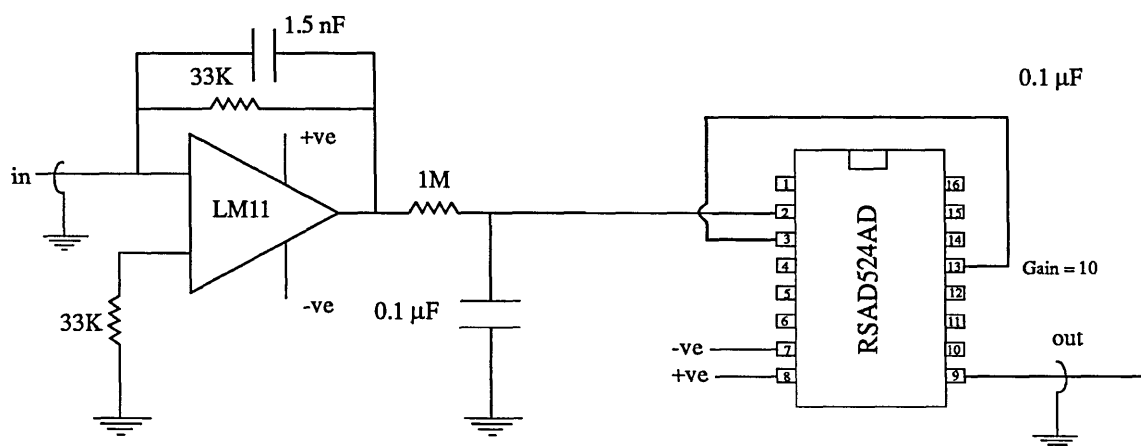


Figure 6.1: Circuit diagram of pre-amplifier stage.

amplifier specifically designed for data acquisition applications which require high accuracy under worst case operating conditions. It has a variable gain, low offset-voltage drift, and low noise. Further information on this item may be obtained from RS data sheet no. 4793.

The amplifier circuit was designed so that the input should be a virtual earth, since a current source such as a photomultiplier tube, should always be fed into an 'earth' to conserve current. Two 9v PP3 batteries were used to provide the $\pm$ supply rails. The LM11 op-amp chip was chosen (minimum supply voltage of $\pm 2.5V$) as it requires only a few picoamps to operate, i.e. it has a low input bias current $I_b \sim 25pA$. The first stage is essentially a current-to-voltage converter. The capacitors are included to smooth out the signal and reduce the effects of noise.

The other pre-amplifier used between the user port of the computer and the stepper motor driver circuit is of a much simpler construction, having a fixed gain of

approximately two. A CLN11 op-amp is used in a negative-feedback loop to amplify the output signal from the computer (≈ 5 volts on high) so that as it pulses the input of driver chip (RSSAA1027) the voltage is greater than the 7.5 volts required.

Appendix 2

The embedding medium used for mounting hair samples prior to sectioning was observed to be almost transparent. Thus, it was possible for the real part of the refractive index of O.C.T. compound, in its liquid state, to be calculated from reflectance data measured over the visible wavelength region of the electromagnetic spectrum, using the equipment detailed in reference [101] by Dr. Cacoullis. A summary of the results is given in the following table.

Table 6.1: Refractive index of O.C.T. compound measured over the wavelength range 400–710nm.

Wavelength (nm)	Refractive Index (no units)	Wavelength (nm)	Refractive Index (no units)
400	1.404 ± 0.028	410	1.401 ± 0.028
420	1.401 ± 0.028	430	1.399 ± 0.028
440	1.398 ± 0.028	450	1.396 ± 0.027
460	1.395 ± 0.027	470	1.394 ± 0.027
480	1.395 ± 0.027	490	1.394 ± 0.027
500	1.396 ± 0.027	510	1.397 ± 0.027
520	1.396 ± 0.027	530	1.396 ± 0.027
540	1.396 ± 0.027	550	1.396 ± 0.027
560	1.397 ± 0.027	570	1.396 ± 0.027
580	1.396 ± 0.027	590	1.395 ± 0.027
600	1.395 ± 0.027	610	1.395 ± 0.027
620	1.396 ± 0.027	630	1.395 ± 0.027
640	1.396 ± 0.027	650	1.395 ± 0.027
660	1.395 ± 0.027	670	1.395 ± 0.027
680	1.395 ± 0.027	690	1.395 ± 0.027
700	1.396 ± 0.027	710	1.398 ± 0.028

Appendix 3

The conversion of a colour, C , measured in terms of 3 reference stimuli (R), (G), and (B) into the C.I.E. tristimulus set of reference stimuli, (X), (Y), and (Z), is as follows:

In the experiment detailed here, the reference stimuli were at wavelengths $\lambda_R = 633\text{nm}$, $\lambda_G = 514\text{nm}$, and $\lambda_B = 456\text{nm}$ respectively. Now,

$$(C) = r(R) + g(G) + b(B)$$

where $r = \frac{R}{R+G+B}$, etc., and R , G , and B are the actual amounts of red, green, and blue light that are measured in the experiment to have been scattered by the colour, C .

From Wright [67], the reference stimuli wavelengths have C.I.E. chromaticity co-ordinates as given in table 6.2.

Table 6.2: Chromaticity co-ordinates of the reference stimuli wavelengths.

Wavelength(λ)	x	y	z
633 nm	0.7140	0.2859	0.0001
514 nm	0.0389	0.8120	0.1491
456 nm	0.1440	0.0297	0.8263

In general, the chromaticity co-ordinates, x_c , y_c , and z_c , of a colour, C , may be related to the amount of light it scatters at the reference wavelengths by:-

$$\begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix} = \begin{pmatrix} x_r & y_r & z_r \\ x_g & y_g & z_g \\ x_b & y_b & z_b \end{pmatrix} \begin{pmatrix} r_c \\ g_c \\ b_c \end{pmatrix}$$

where the elements of the transformation matrix may be calculated from the chromaticity co-ordinates of the pure spectrum colours at the reference wavelengths. For example, substituting for pure red (R) gives,

$$\begin{pmatrix} 0.7140 \\ 0.2859 \\ 0.0001 \end{pmatrix} = \begin{pmatrix} x_r & y_r & z_r \\ x_g & y_g & z_g \\ x_b & y_b & z_b \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

thus, $x_r = 0.7140$, $x_g = 0.2859$, and $x_b = 0.0001$. The other elements may be deduced in a similar manner by substituting for the green and blue wavelengths.

Thus, knowing R , G , and B it is possible to calculate, via r , g , and b , and the transformation matrix, the amounts of light scattered by a colour, C , in terms of the C.I.E. tristimulus co-ordinates.

Bibliography

- [1] Lundgren, H. P. and Ward, W. H., *Ultra-structure of Protein Fibres*, 39–117, Academic Press., New York (1963).
- [2] Brown, A. C. and Swift, J. A., *Hair breakage: the scanning electron microscope as a diagnostic tool*, J. Soc. Cos. Chem., **26**, 289–297 (1975).
- [3] Mackean, D. and Jones, B., *Introduction to Human and Social Biology*, 96–97, John Murray (1976).
- [4] Ryder, M., *Hair: Studies in Biology No. 41*, Edward Arnold Ltd. (1973).
- [5] Leon, N. H., *Structural aspects of keratin fibres*, J. Soc. Cos. Chem., **23**, 427–445 (1972).
- [6] Robbins, C. R., *Chemical and Physical Behaviour of Human Hair*, V. N. R. (1979).
- [7] Wolfram, L. J. and Lindemann, M. K. O., *Some observations on the hair cuticle*, J. Soc. Cos. Chem., **22**, 839–850 (1971).
- [8] Kassenbeck, P., *Morphology and fine structure of hair*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 52–64 Springer-Verlag, (1981).
- [9] Rebenfeld, L., Weigmann, H. D., and Dansizer, C., *Temperature dependence of the mechanical properties of human hair in relation to structure*, J. Soc. Cos. Chem., **17**, 525–538 (1966).
- [10] Mercer, E. H., *The heterogeneity of the keratin fibers*, Text. Res. J., **23**, 388–397 (1953).
- [11] A., E. Hecht and Zajac, *Optics*, Addison-Wesley (1974).

- [12] Wolfram, L. J. and Albrecht, L., *Chemical- and photo-bleaching of brown and red hair*, J. Soc. Cos. Chem., **82**, 179–191 (1987).
- [13] Schwartz, A. M. and Knowles, D. C., *Frictional effects in human hair*, J. Soc. Cos. Chem., **14**, 455–463 (1963).
- [14] Tolgyesi, E., *Weathering of hair*, J. Cos. & Toil., **29**, 29–33 (1983).
- [15] Swift, J. A. and Brown, A. C., *The critical determination of fine changes in the surface architecture of human hair due to cosmetic treatment*, J. Soc. Cos. Chem., **23**, 695–702 (1972).
- [16] Robinson, V. N. E., *A study of damaged hair*, J. Soc. Cos. Chem., **27**, 155–161 (1976).
- [17] Fair, N. B. and Gupta, B. S., *The chlorine-hair interaction. I. Review of mechanisms and changes in properties of keratin fibers*, J. Soc. Cos. Chem., **38**, 359–370 (1987).
- [18] Fair, N. B. and Gupta, B. S., *The chlorine-hair interaction. II. Review of mechanisms and changes in properties of keratin fibers*, J. Soc. Cos. Chem., **38**, 371–384 (1987).
- [19] Kelly, S. E. and Robinson, V. N. E., *The effect of grooming on the hair cuticle*, J. Soc. Cos. Chem., **33**, 203–215 (1982).
- [20] Wall, R. A. and Hunter, L. D., *Normal adult hair - structure and properties*, Cosmet. and Perf., **89**, 31–36 (1974).
- [21] Kaplin, I. J., Schwan, A., and Zahn, H., *Effects of cosmetic treatments on the ultrastructure of hair*, J. Cos. & Toil., **97**, 22–26 (1982).
- [22] Robinson, V. N. E., *Split ends — a scientific study of a hair*, Cosmet. and Perf., **90**, 25–30 (1975).
- [23] Robbins, C. R. and Bahl, M. K., *Analysis of hair by electron spectroscopy for chemical analysis*, J. Soc. Cos. Chem., **35**, 379–390 (1984).
- [24] Gardner, B. B. and MacAdam, D. L., *Colorimetric analysis of hair colour*, Am. J. Phys. Anthro., **19** (2), 187–201 (1934).

- [25] Trotter, M., *Anthropometry: classifications of hair colour*, Am. J. Phys. Anthro., **25** (2), 237–260 (1939).
- [26] Beste, M. Den and Moyer, A., *An instrumental description and classification of natural hair colour*, J. Soc. Cos. Chem., **19**, 595–609 (1968).
- [27] Gerrard, W. A., *The measurement of hair colour*, Int. J. Cos. Sci., **11**, 97–101 (1989).
- [28] Wyszecki, G., *Uniform colour spaces*, In *Golden Jubilee of Colour in the CIE, 53-78* The Society of Dyers and Colourists, England, (1981).
- [29] Dupre, A. and Bonalfe, J. L., *Polarized light microscopy. Its interest in the study of congenital hair defects*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 414–419 Springer-Verlag, (1981).
- [30] Garn, S. M., *The examination of hair under the polarizing microscope*, Ann. New York Acad. Sci., **53**, 649–652 (1951).
- [31] Fraser, R. D. B., *Birefringence and elasticity in keratin fibres*, Nature, **172**, 675–676 (1953).
- [32] Curtis, R. K. and Tyson, D. R., *Birefringence: polarization microscopy as a quantitative technique of human hair analysis*, J. Soc. Cos. Chem., **27**, 411–431 (1976).
- [33] Gould, J. and Sneath, R. L., *Electron microscopy image analysis; quantification of ultrastructural changes in hair fiber cross-section as a result of cosmetic treatments*, J. Soc. Cos. Chem., **36**, 53–59 (1985).
- [34] Dobb, M. G. and Johnson, F. R., *Morphology of the cuticle layer in wool fibres and other animal hairs*, J. Tex. Inst., **52** (4), 153–163 (1961).
- [35] DiBianca, S. P., *Innovative scanning electron microscopic techniques for evaluating hair care products*, J. Soc. Cos. Chem., **24**, 609–622 (1973).
- [36] Swift, J. A., *New development in electron microscopy*, J. Soc. Cos. Chem., **22**, 477–486 (1971).
- [37] Swift, J. A., *The hair surface*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 65–72 Springer-Verlag, (1981).

- [38] Gerdes, R. J. and Brown, A. C., *Analysis of hair surface structure for product evaluation*, In *First Human Hair Symposium*, 302–316, (1978).
- [39] Mahrle, G., Sterry, W., and Orfanos, C. E., *The use of scanning electron microscope to assess damage of hair*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 524–528 Springer-Verlag, (1981).
- [40] Raman, C. V. and Bhat, M. R., *The structure and optical behaviour of some natural and synthetic fibres*, Proc. Indian Acad. Sci., **39A**, 101–116 (1954).
- [41] Lundberg, J. L., *Light scattering from large fibers at normal incidence*, J. Colloid. and Interface Sci., **29** (3), 565–583 (1969).
- [42] Edmonds, I. R., *A diffraction method for the estimation of average diameter and standard deviation of diameter in a fibre sample*, J. Tex. Inst., **60**, 161–164 (1969).
- [43] Onions, W. J. and Ellingham, B., *Measurement of fibre diameter variation by optical diffraction*, Brit. J. of App. Phys., **10**, 328–332 (1959).
- [44] Lynch, L. J. and Thomas, N., *Optical diffraction profiles of single fibers*, Text. Res. J., **41**, 568–572 (1971).
- [45] Lynch, L. J., *The use of light-scattering profiles of single fibers to measure and compare the within-fiber diameter variability of wool tops*, Text. Res. J., **44**, 203–205 (1974).
- [46] Lynch, L. J., *A study of the relationship between the light-scattering profiles of single wool fibres*, Text. Res. J., **44**, 446–448 (1974).
- [47] Brancik, J. and Datyner, A., *The measurement of swelling of wool fibers in solvent by laser beam diffraction*, Text. Res. J., **47**, 662–665 (1977).
- [48] Buras, E., Fookson, A., and Breuer, M., *Precise measurement of humidity effects on human scalp hair diameter*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 634–637 Springer-Verlag, (1981).
- [49] Hunter, R. S., *Methods of determining gloss*, J. Res. Nat. Bur. Standards (U.S.), **18**, 19–39 (1937), (RP 958).

- [50] Nickerson, D., *A new cotton lustermeter for yarns and fibers*, Text. Res. J., **27**, 111–123 (1957).
- [51] Nimeroff, I., *Analysis of goniophotometric reflection curves*, J. Opt. Soc. Amer., **42**, 579–583 (1952).
- [52] Christie, J. S., *An instrument for the geometric attributes of metallic appearance*, Appl. Opt., **8**, 1777–1785 (1969).
- [53] Walsh, J. W. T., *Photometry*, Constable and Company Ltd., 2nd edition (1953).
- [54] Harrison, V. G. W., *Definition and measurement of gloss*, The Printing and Allied Trades Research Association, Cambridge, England (1945).
- [55] Keitz, H. A. E., *Light calculations and measurements*, Philips' Technical Library (1955).
- [56] Lavin, E. P., *Monographs on applied optics no. 2. Specular reflection*, Adam Hilger Ltd. (1971).
- [57] Stamm, R. F., Garcia, M. L., and Fuchs, J. J., *The optical properties of human hair I. Fundamental considerations and goniophotometric curves*, J. Soc. Cos. Chem., **28**, 571–599 (1977).
- [58] Stamm, R. F., Garcia, M. L., and Fuchs, J. J., *The optical properties of human hair II. The luster of hair fibers*, J. Soc. Cos. Chem., **28**, 601–609 (1977).
- [59] Guiolet, A., Garson, J. C., and Levecque, J. L., *Study of the optical properties of human hair*, Int. J. Cos. Sci., **9**, 111–124 (1987).
- [60] Goodman, J. W., Fookson, A., and Breuer, M., *Statistical properties of laser speckle patterns*, Dainty, J. C., editor, *Topics in Applied Optics*, 9–75 Springer-Verlag, 2nd edition, (1984).
- [61] O'Donnell, K. A. and Mendez, E. R., *Experimental study of scattering from characterized random surfaces*, J. Opt. Soc. Amer., **A**, **4** (7), 1194–1205 (1987).

- [62] Kim, M-J., Dainty, J. C., Friberg, A. T., and Sant, A. J., *Experimental study of enhanced backscattering from one- and two-dimensional random rough surfaces*, J. Opt. Soc. Amer., **A**, 7 (4), 569-577 (1990).
- [63] Beyak, R., Meyer, C. F., and Kass, G. S., *Elasticity and tensile properties of human hair. I. single fiber test method*, J. Soc. Cosmet. Chem., **20**, 615-626 (1969).
- [64] Busch, P. and Thiele, K., *Contributions to the elastic behaviour of hair fibres and hair strands*, In Orfanos, Montagna, and Stuttgart, editors, *Hair Research*, 623-628 Springer-Verlag, (1981).
- [65] Nicodemus, F. E., *Directional reflectance and emissivity of an opaque surface*, App. Opt., **4** (7), 767-773 (1965).
- [66] Nicodemus, F. E., *Reflectance nomenclature and directional reflectance and emissivity*, App. Opt., **9** (6), 1474-1475 (1970).
- [67] Wright, W. D., *The measurement of colour*, Hilger & Watts Ltd., 2nd edition (1958).
- [68] Sant, A. J., *Variations with wavelength of light scattered from identical, randomly rough metal and dielectric diffusers*, In *Conference Summaries*, Garmisch-Partenkirchen, FRG, (1990) ICO-15.
- [69] Yin, N. E., Kissinger, R. H., Tolgyesi, W. S., and Cottington, E. M., *The effect of fiber diameter on the cosmetic aspects of hair*, J. Soc. Cos. Chem., **28**, 139-150 (1977).
- [70] Bustard, H. K. and Smith, R. W., *Studies of factors affecting light scattering by individual human hair fibres*, J. Soc. Cos. Chem., **12**, 121-133 (1990).
- [71] Bustard, H. K. and Smith, R. W., *Investigation into the scattering of light by human hair*, Applied Optics, **30**, No. 24, 3485 - 3491 (1991).
- [72] Faust, R. C., *Optical properties*, In Meredith, R. and Hearle, J. W. S., editors, *Physical Methods of Investigating Textiles*, 320-345 Textile Book Publishers, (1959).

- [73] Allen, M., *Practical Refractometry by means of the microscope*, R. P. Cargille Laboratories, Inc., 2nd edition (1962).
- [74] Rohner, P. and Brunner, J., *The thin section method for cross-sections of textile fibres*, Struers Metallographic News, 16–17 (1987).
- [75] Strzlecka, T., *A hypothetical structure of melanin and its relation to biology*, *Physiol. Chem. Phys.*, **14**, 233–237 (1982).
- [76] Bohren, C. F. and Huffman, D. R., *Absorption and Scattering of Light by Small Particles*, Wiley, Chichester and New York, 1st edition (1983).
- [77] Dolan, M. B., *The Infrared Optical Constants of Powders and Liquids*, PhD thesis, Imperial College, University of London, February 1987.
- [78] Wolfe, W. L. and Zissis, G. J., editors, *The Infrared Handbook*, Office of Naval Research, Washington D.C., 1st edition (1978).
- [79] Cooke, D. D. and Kerker, M., *Light scattering from long thin glass cylinders at oblique incidence*, *J. O. S. A.*, **59** (1), 43–59 (1969).
- [80] Holboke, L. E. and Berriman, L. P., *A study of the effects of cotton fiber structure on luster*, *J. Tex. Res.*, **33**, 205–217 (1963).
- [81] Richmond, J. H., *Scattering by a dielectric cylinder of arbitrary cross section shape*, *I.E.E.E. Transactions on Antennas and Propagation*, **5**, 334–341 (1965).
- [82] Welford, W. T., *Aberrations of Optical Systems*, Adam Hilger Ltd., Boston and Bristol, 1st edition (1986).
- [83] Boas, M. L., *Mathematical Methods in the Physical Sciences*, Wiley, Boston and Bristol, 2nd edition (1983).
- [84] Keller, J. B., *Geometrical theory of diffraction*, *J. Opt. Soc. Amer.*, **52**, 116–130 (1962).
- [85] Sommerfeld, A., *Optics*, New York Academic Press (1954).
- [86] Born, M. and Wolf, E., *Principles of Optics*, Pergamon Press, 6th edition (1983).

- [87] Tolgyesi, E., Coble, D. W., Fang, F. S., and Kairinen, E. O., *A comparative study of beard and scalp hair*, J. Soc. Cosmet. Chem., **34**, 361–382 (1983).
- [88] Hammond, H. K. and Nimeroff, I., *Measurement of sixty-degree specular gloss*, J. Res. Nat. Bur. Standards (U.S.), **44**, 585–598 (1950), (RP 2105).
- [89] Beyak, R., Kass, G. S., and Meyer, C. F., *Elasticity and tensile properties of human hair. II. light radiation effects*, J. Soc. Cosmet. Chem., **22**, 667–678 (1971).
- [90] Persad, S., Menon, A., and Haberman, H. F., *Comparisons of the effects of uv-visible irradiation of melanins and melanin-hematoporphyrin complexes from human black and red hair*, Photochemistry and Photobiology, **37** (1), 63–68 (1983).
- [91] Edman, W. and Marti, M. E., *Properties of peroxide-bleached hair*, J. Soc. Cosmet. Chem., **12**, 133–145 (1961).
- [92] Kollias, N. and Baqer, A. H., *The role of human melanin in providing photoprotection from solar mid-ultraviolet radiation (280–320 nm)*, J. Soc. Cos. Chem., **39**, 347–354 (1988).
- [93] Tronnier, H., *Methods for testing the hair and scalp*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 607–622 Springer-Verlag, (1981).
- [94] Wolfram, L. J., *Reactivity of human hair*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 482–485 Springer-Verlag, (1981).
- [95] Jachowicz, J., *Hair damage and attempts at its repair*, J. Soc. Cos. Chem., **38**, 263–286 (1987).
- [96] Jachowicz, J., Wissurel, G., and Garcia, M. L., *Relationship between triboelectric charging and surface modifications of human hair*, J. Soc. Cos. Chem., **36**, 189–212 (1985).
- [97] Cannell, D., *Split ends and their repair*, J. Cos. & Toil., **79**, 29–31 (1979).
- [98] Lindo, S. D. and Spoor, H. J., *Hair processing and conditioning*, In *First Human Hair Symposium*, 135–144, (1978).

- [99] Price, V. H., *The role of hair care products*, In Orfanos, Montagna, and Stuttgen, editors, *Hair Research*, 501–506 Springer-Verlag, (1981).
- [100] Deem, D. E. and Reiger, M. M., *Mechanical hysteresis of chemically modified hair*, J. Soc. Cos. Chem., **19**, 395–403 (1968).
- [101] Cacoullis, S., *Infrared Optical Constants of Volatile Liquids*, PhD thesis, Imperial College, University of London, September 1988.