# **Reflection Infrared Spectral Signatures of Vehicle Paints**

Peeling Back the Effects of Photo-Physical Phenomena to Unveil Absorbance Spectra from Reflection Infrared Micro-Spectroscopy Measurements

Caroline Lee O'Driscoll BSc (Hons)

Thesis submitted for the fulfilment of the degree of **Doctor of Philosophy** within the College of Science and Engineering 1<sup>st</sup> March 2019



Supervised By:

Professor K. Paul Kirkbride Dr Jason R. Gascooke Associate Professor Rachel S. Popelka-Filcoff

# **Declaration**

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that, to the best of my knowledge and belief, it does not contain any material previously published or written by another person except where due reference is made in the text.

Signed,

Caroline O'Driscoll

# Acknowledgements

'Be a scientist. Save the world.'

I heard these words in the opening plenary of the 2017 RACI Centenary Congress. I think what struck me was not only the call for a scientist to look outward but that so many people would say 'change the world' and yet here was a call to *save* it. I thought about these words for a long time.

In my annual re-watch of the greatest television drama ever created, *The West Wing*, I am drawn to an exchange between two characters:

'The Federal Government shouldn't be directing scientific research.' 'Why?' 'Because you stink at it. 'If it was up to the NIH to cure polio through a centrally directed program ... you'd have the best iron lung in the world but not a polio vaccine." 'When did you get an M.D.?' 'I was just quoting Samuel Broder, the former director of the National Cancer Institute.'

Instead, we search for practical solutions to problems, which is admirable, but blinkers us to a world of unknowns, of possibilities, of discovery.

'That's because great achievement has no road map. The X-ray's pretty good. So is penicillin. Neither were discovered with a practical objective in mind. I mean, when the electron was discovered in 1897, it was useless. And now, we have an entire world run by electronics. Haydn and Mozart never studied the classics. They couldn't. They invented them.'

Scientific research is a discipline of unknown unknowns. We could fly to the moon because we knew what we were up against, but we can't yet know how to solve problems that are undefined. So, instead, we search for new information, for greater understanding, because we know someday what we don't understand now will inform the work of those who come after us.

In a discipline of unknown unknowns, I am proud to be a scientist and everyday a scientist works to save the world, one small spectrum at a time.

What can I say? I'm an idealist...

I would like to take this opportunity to thank and acknowledge the people who have saved me, checked my sanity and loved me.

First, to my supervisors and my teachers, Paul, Rachel and Jason. Paul, I can't believe how lucky I am to have had you as a supervisor, your enthusiasm inspires me and your knowledge is incredible. Jason, thank you for trawling through all those papers with me, I wouldn't have been able to complete this work without your advice, explanations and connections. Rachel, you're the best role model I could have asked for, you held the bar high and always reminded me to look forward when I was stuck in

the minutiae. I am so lucky to have had three diverse supervisors who have all contributed in different but essential ways to my research and my development as a researcher. Thank you for taking me in, teaching me, guiding me. I look up to you, I hope I never let you down.

Thank you also to all those who went on their own PhD journeys alongside mine. Nick, thank you for having my back, I trust your opinion more than my own and one day, when you're the head scientist of a high calibre forensic science centre, I might ask you for a job. Eliza, you taught me courage, self-respect and feminism, you are more brilliant and powerful than you will ever know, make the world worthy of you. Kelsey, your kindness speaks volumes, you have reminded me to stay positive, don't be afraid to shine. Kimmi, I don't know how to put into words how much you've helped me through our whole time at Flinders, I only hope that I have been as good to you as you have been to me.

To my mum and my sister, and to those who are as close as family, Dean and Di, Claire, and so many others, thank you for your support, for challenging me when I became unfocused, for helping me in big and small ways. I have needed you, I have leant on you, and you have held me up and held me together.

For Ryan, I have no words. You have sat with me in the dark and you held my hand through it all. I love you, always.

A PhD is hard work, I heard once that it's the worst research you'll ever do, but I believe it inspires the desire to do the best research. I believe the world *can* be the way it *should* be. I'm a scientist and one day I will help to save the world.

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# List of Commonly Used Acronyms

- EDX Energy Dispersive X-Ray Spectroscopy
- EFSW Electric Field Standing Wave
- IR Infrared
- IR-MSP Infrared Micro-spectroscopy
- KK Kramers-Kronig (transform)
- NIR Near Infrared
- OEM Original Equipment Manufacturer
- SEM Scanning Electron Microscopy
- SEM-EDX Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy
- R-IR-MSP Reflection Infrared Micro-spectroscopy

# Abstract

Infrared spectroscopy has long been used as a technique for the identification and classification of vehicle paints. Vibrational spectroscopy allows for identification of the chemical components of paint formulations, particularly the organic binders. For forensic analyses, this is of particular importance as it allows for the comparison and exclusion of paint evidence. For the defence sector and law enforcement, measuring the spectral signature of a vehicle paint is a useful capability for comparison and identification of unknown vehicles. For such applications reflection is the only viable method of spectral acquisition as there is a requirement for passive sampling.

Reflection infrared micro-spectroscopy could allow for non-destructive analysis of paint samples with the potential for further development to stand-off techniques for in-situ measurements – an advantage over the destructive transmission techniques which require dissection of the paint layers prior to analysis. However, the nature of layered samples and reflection techniques means a number of photophysical phenomena can complicate and 'contaminate' the original signature of the paint, distorting the appearance of reflection spectra.

This dissertation describes the reflection system for multi-layered, absorbing and reflecting paint samples and then outlines a number of the photo-physical phenomena present in reflection infrared micro-spectroscopy measurements. The dissertation then outlines a correction sequence that models and corrects for the contaminations that most strongly affect the spectra of vehicle paints. While the correction sequence is successful for a number of paints analysed, there are some residual anomalies which show that describing the effects present in reflection measurements is a crucial step to the further understanding and development of reflection infrared spectroscopy techniques.

# 1. Introduction Part I – Vehicle Paint Analysis

Vehicle paints are the first thing a person notices when they see a car and the apparent colour of the paint is what is most often used to identify and describe the vehicle. Despite somewhat simplistic identifications, red, blue, metallic, matte, etc., vehicle paints are really a many-layered, complex coating system.

Vehicle paint and paint flakes are often found or used as evidence in forensic investigations. The classic case involves a chip, flake or scrape of vehicle paint left at the scene. Traditionally a forensic investigation involving vehicle paint consists of either a comparison of known and unknown paint samples to identify or exclude a common source, or, an attempt to identify the type of vehicle from which a sample originated [1, 2]. In both cases the paint evidence is collected and can then be analysed in a laboratory by a number of different analytical techniques, generally falling into two categories, chemical and physical tests (See Section 1.3 Forensic Analysis Techniques). Additionally, modern stand-off infrared equipment can be used by both the defence sector and law enforcement to identify a target vehicle using reflected spectral signatures. The vehicle's spectral signature can be compared to known spectral signatures, similar to methods used in a forensic investigation. For defence and law enforcement, determining 'friend or foe' is a particularly important function and using spectrometry as a passive surveillance technique is therefore valuable. Passive sampling of spectral signatures is certainly a realistic capability of modern reflection infrared spectroscopy equipment.

This thesis will outline the beginnings of an investigation into the possibility of reflection infrared micro-spectroscopy (R-IR-MSP) as a forensic analysis method for vehicle paints and a potential indicator for evaluating the potential of differentiating vehicle paints using stand-off infrared spectroscopy techniques. R-IR-MSP was chosen as it is non-destructive, potentially easier to implement than classical infrared spectroscopy techniques and is a relatively simple model for predicting the feasibility of standoff infrared techniques. The thesis begins by describing vehicle paints physically and chemically, describing the complexities of R-IR-MSP measurements, describing the reflection system of infrared spectral signatures of vehicle paints, moving through an in-depth description of vehicle paint reflection measurements, and finally beginning the process of interpreting and analysing R-IR-MSP signatures of vehicle paints. As a result of working towards these aims, the research presented in this dissertation will contribute to knowledge of the applications of R-IR-MSP and the suitability of R-IR-MSP to vehicle paint analysis.

# **1.1. Paint Composition**

Fundamentally speaking, there are two reasons to coat a vehicle in paint. One is to prevent corrosion, and the other is to create an appearance that is aesthetic to a potential buyer [3]. These two considerations are responsible for many components of vehicle paint formulations, especially additives, as vehicle manufacturers strive to make their paints protect the vehicle for longer and appeal more to the buyer. Specifically, vehicle paints are formulated to have high gloss, resistance to environmental etching, mar resistance and a unique appearance [3]. In order to achieve these goals, the coatings have highly complex chemical compositions.

Aside from the specific purpose, vehicle paints are essentially the same as all coatings; they are a nonhomogeneous suspension [4] comprised of four basic component categories:

- 1) binders (often polymers that polymerise during the curing stage)
- 2) pigments
- 3) additives
- 4) solvents (usually a volatile compound).

Most paints are complex mixtures of many substances from each of these four categories, and therefore there is an almost limitless number of formulations [3]. Vehicle coatings, are then a number of paint formulations applied one after the other in a layered structure.

# **1.1.1. Binder Chemistry**

Binders are one of the four basic component categories in paint formulations. Their chemistry is fundamental to understanding paint formulations and for differentiating between coatings. Binders (or resins) are polymers that form the matrix that holds together paint formulations, binding particles such as pigments and additives in place, as well as allowing adhesion to the substrate and forming a strong film when dry [5]. Acrylics, alkyds, urethanes, epoxies, and polyesters are all binders used in modern vehicle paint formulations [5]. These binders are used as they form a durable finish on the rigid metal substrate of vehicle panels. Plastic substrates are more flexible than metal substrates and bumper panels, in particular, take advantage of this flexibility to avoid damage from minor collisions. The coatings on bumper panels must therefore be different from the hard and durable acrylic or alkyd based formulations often used on the metal panels [5]. Additional polymers can be used in formulations for plastic panels to ensure the coatings are not so brittle that they would crack instead of flexing as the bumper deforms [3, 5]. Furthermore, unlike other areas of a vehicle, plastic panels are often coated in paint formulations that cure at lower temperatures to prevent damage of the polymer substrates of the panels.

Binder polymers are made up of repeating units called monomers. The repeating units can be the same, forming homopolymers, or different, forming co-polymers. The polymer chains formed by the monomers may be linked, branched, cross-linked, or any combination of each of these. Each polymer chain can form covalent bonds creating block-copolymers, or, simply be together in the same matrix but without being covalently bonded [5].

The particular co-polymer blend chosen depends on the properties desired for the coating. Highly cross-linked films are generally more durable but increasing the molecular weight of linear co-polymer binders can also create coatings that are just as tough [6]. However, linear co-polymers tend to be more brittle and crystalline, so cross-links are included in the co-polymer, and spaced out appropriately, to create an 'open cage work of molecules' allowing the binders to be more flexible [6].

The acrylic melamine binder is one of the most common automotive paint binders and is formed with an acrylic co-polymer backbone and methylated, butylated or iso-butylated melamine formaldehyde cross-linker [1, 5]. Normally no more than five acrylic monomers are found in a single co-polymer, although that is not the limit on the number of different acrylic monomers used across formulations (Figure 1) [5]. Common co-polymers used in original equipment manufacturer (OEM) finishes include methyl methacrylate, butyl methacrylate, butyl acrylate, 2-ethyl-hexyl acrylate, acrylonitrile, styrene, and hydroxyl substituted monomers. Blends of methyl- and butyl- substituted methacrylates are used in different proportions to adjust the hardness of the coatings by changing the molecular weight of the co-polymer binders. Hydroxyl-ethyl acrylates and other hydroxyl- substituted monomers provide polar sites for increased crosslinking [1].



Figure 1 – Example of an acrylic melamine co-polymer with eight different monomers included to illustrate the variety used in OEM finishes, reproduced directly from [5]

Polymer formulations are chosen to offer specific properties to the final coating, including hardness, durability, adhesion, gloss, corrosion resistance among others; and many of these properties are determined by the specific co-polymers used as well as the extent of cross-linking in the polymer matrix [1, 5]. For example, in acrylic melamine polymer formulations, acrylonitrile is used to improve hardness, mar resistance and grease resistance [1].

OEM finishes are cured by baking (as thermosetting polymers are used) which promotes cross-linking through the polymer matrix, strengthening the coating and increasing the final gloss [5]. Aftermarket refinishes or repairs cannot be cured at the high temperatures used for OEM coatings, as the vehicle cannot be baked with its non-metallic componentry in place, and therefore the binders used are usually acrylic/alkyd enamels containing polyurethane.

#### 1.1.2. Pigments

Pigments are generally added to paint formulations for decorative purposes, such as to provide colour and to hide the colour of primers and the vehicle substrates, but they can also improve the properties of the paint, such as increased protection against corrosion [6]. Pigments are fine particles dispersed in paint and defined as 'any material that is coloured, black or white, organic or inorganic, that retains a crystalline form in paint' [7]. That is, pigments retain their crystalline form in liquid paint and in the solidified final film, which is what distinguishes them from dyes [8]. Pigments are also insoluble in the solvent used for the paint itself [5]. Many additives could thus be defined as pigments; however, the generally accepted use of the term 'pigment' indicates a component of the paint that imparts colour, opacity or other visually aesthetic characteristics, while an 'additive' is added to improve other properties of the coating [5].

Vehicle paint formulations encompass a wide range of hues and tones, and high pigment concentrations are often used to achieve vivid colour finishes [9]. It is important to note that paints with similar colours are not always formulated with the same pigments [10]. In fact, the same coloured pigments are not even always used in finish coats with the same apparent colour [11]. For example, yellow pigments are often used in combination with other pigments to produce brown, orange, off-white or green appearances [12]. Additionally, even paints that have the same colour profile, that is, the same absorbance spectrum for the visible region of the spectrum, do not always contain the same pigments. Similar colour profiles can be achieved using different pigments, or different proportions of the same pigments [11]. Sometimes the difference in formulations is significant enough to be detected and characterised through analytical instrumentation.

There are many different classes of pigments used in vehicle paint formulations; the major categories are inorganic and organic pigments. Inorganic and organic pigments produce colour through different means; inorganic pigments are often transition metal complexes or metallic oxides so the electronic transitions of electrons in valence shells (usually d-orbitals) dictate their visible absorptions, whereas organic pigments are usually planar highly conjugated organic molecules where  $\pi$ -electron transitions give rise to light absorption [5].

#### **Organic Pigments**

Organic pigments are usually planar molecules with a number of  $\pi$ -bonds that absorb light and lead to electronic transitions [5]. There are several groups of organic pigments and each group, or 'family', is based on the same chromophore [11]. Within these groups, the main chromophore remains the same but different structural modifications, or substituted functional groups, account for slight differences in pigment properties [11]. Not every pigment within a group is suitable for use in vehicle paint formulations due to both industry's desire for certain appearances and the need to cope with the application processes used in the automotive industry [11].

#### Inorganic Pigments

Inorganic pigments are usually transition metal complexes or metallic oxides that provide colour through d-electron absorption [5]. Inorganic pigments tend to have low tinctorial strengths and therefore higher pigment volume concentrations (essentially the ratio of pigment volume to binder volume in a paint formulation) are required to achieve desirable and vivid colours [13]. In monocoat systems, high pigment volume concentrations can reduce the gloss of the finish coat, so inorganic

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pigments are less favoured in formulations using this layer system as compared to clearcoat/basecoat formulations where gloss is achieved with the application of the clearcoat [13].

Many inorganic pigments can occur in several different crystal structures (polymorphism) that often have different colour appearances [5]. The most common inorganic pigment (and the most common pigment used in vehicle paint formulations [14]) is titanium dioxide, which occurs in three different crystal structures, rutile, anatase and brookite [5]. Rutile and anatase are both used extensively in vehicle paints, but rutile is the more common of the two, due to a slightly higher refractive index and greater durability [5].

#### **Chromatic Pigments**

Chromatic paints are coloured paints that contain pigments designed to impart colour to the paint formulation. It is important to understand how these pigments produce coloured appearances, especially when investigating their spectral signatures. As mentioned above, organic and inorganic chromatic pigments produce coloured appearances through different electron transitions relating to their  $\pi$ -bonds or valence shells respectively [5]. Despite the particulars, these transitions essentially create colour in the same way; photons of particular wavelengths will be absorbed due to these transitions and others will be reflected or transmitted [4]. The reflected photons are the ones that reach the human eye and result in the observable colour of the paint. For example, a pigment in a paint that appears blue is reflecting photons of that particular blue wavelength and absorbing complementary wavelengths [4]. The mixture of pigments used in the paint formulation, and therefore the combination of all reflected photons, results in the final observed colour of the vehicle.

Different wavelengths of light reflect and refract slightly differently and changes to paint formulations must be made to account for these differences across the visible (colour) spectrum. Yellow, orange and red pigments absorb short wavelengths of visible light (the blue and green wavelengths), and have high indices of refraction for the longer, reflected wavelengths [12]. Blue and green pigments absorb longer wavelengths of visible light and have high indices of refraction for wavelengths in the nearinfrared region [12]. Since scattering is dependent on the wavelength of the reflected light  $(\frac{1}{\lambda^4})$ , compared to blue and green pigments, yellow, orange and red pigments are more effective in scattering visible light. More scattering decreases the penetration depth of the incident light and results in fainter observable colours [12]. Therefore, higher pigment volume concentrations are used for yellow, orange and red paint formulations than for blue and green paint formulations [12].

#### Achromatic Pigments

Achromatic paints are black, white, neutral grey and silver paints that have no apparent colour in their appearance [4]. White appearances are a result of the reflection of all (or nearly all) visible

wavelengths, while black appearances are the result of absorption of all wavelengths so no visible light is reflected back to the observer [4]. Black and white pigments are used to create achromatic appearances, where neutral greys are a combination of both.

Black paints normally contain predominantly carbon black pigments that absorb most wavelengths of light and do not reflect an observable colour [15]. Carbon based pigments are usually the products of partial combustion of petroleum or natural gas [4]. Since combustion products are either carbon or simple carbon chains, differentiating between different black paint formulations is difficult and generally relies on binder composition [15].

Some achromatic pigments have minor absorptions in areas of the spectrum, which results in a slightly coloured appearance. Sometimes, secondary pigments are used to counter slight chromatic tints in achromatic systems creating unique paint formulations [4]. Titanium dioxide is the most common white pigment but it does have an absorption band in the violet region which results in minor yellowish tints in some white paint formulations [3, 4]. To counter the yellow, secondary pigments, such as Carbazole violet, are used to reflect in the region that titanium dioxide absorbs, resulting in an achromatic final appearance sometimes with a faintly visible colour effect [4]. The subtle chromatic effect is often highly appealing and unique to a certain manufacturer.

## **1.1.3. Effect Pigments**

For the purposes of this dissertation, it is important to consider effect pigments in detail and separately from pigments in the general sense. Effect pigments are pigments used to create non-matte colours by taking advantage of light interference to cause colour-shifting effects [3, 5]. There are several different colour effects that can be created using effect pigments, such as metallic or pearlescent finishes. Effect pigments are generally contained in the basecoat in clearcoat/basecoat formulations or in between the two in tricoats [8].

Some effect pigments are used to mimic the iridescence of naturally occurring materials, such as pearls or butterfly wings [5]. Colour-shifting paint formulations often contain refractive particles that act as miniature diffraction gratings when oriented parallel to the substrate [5]. Metallic and pearlescent finishes are achieved by adding particles to basecoat formulations. These particles are often aluminium flake (for metallic finishes) or mica particles with any of a few coatings, such as titanium dioxide, of controlled thickness. Effect pigments provide lustre based on reflective properties combined with interference, rather than absorption like chromatic pigments [16].

Effect finishes are unique finishes as their appearance is different depending on the angle of observation [3, 16]. The extent to which the colour changes with the angle is called the degree of colour flop [3]. There are two major types of effect finishes in paints, metallic and pearlescent.

The final appearance of metallic finish paint formulations is a delicate balance between opacity and the desired metallic effect [8]. Metallic finish coat formulations must be applied as a thin film, usually 15  $\mu$ m, so that the aluminium flakes are oriented parallel to the surface of the paint and offer a 'high degree of sparkle' [8]. Additionally, metallic finish coat formulations must have a semi-transparent finish so that the sparkle of the aluminium flakes can be seen [5]. Often, organic pigments are used to achieve a tinted yet semi-transparent finish as they are more transparent than inorganic pigments [5].

Pearl effect pigments are usually contained in a separate, transparent, layer between the clearcoat and the opaque, pigmented basecoat [8]. Mica is often used to create the popular pearlescent finishes especially when coated with titanium dioxide (or similar inorganic pigments) as they can produce different coloured effects depending on the thickness of the coatings [8, 16]. Mica particles are semitransparent, unlike aluminium flake, and therefore do not increase the opacity of the paint formulation (opacity provided by pigments is often referred to as 'hiding power'), which means they must be used in conjunction with other pigments even if the mica is coloured [16]. This is why pearl finishes can be vivid, as the effect pigments do not hide the basecoat colour like the metallic finishes do.

Older paint formulations may include bismuth oxychloride (BiOCI) which was developed 50 years ago as the first synthetic pearlescent additive [16]. In the 1990s particles of bismuth oxychloride were coated with cerium hydroxide (Ce(OH)<sub>3</sub>) making the particles much more stable when exposed to light, and therefore more suitable for use in vehicle paint formulations. The light-stable particles were first used in some 1998 OEM finish coats and were most suitable for use in darker finishes to produce a bright metallic lustre but had only limited popularity [16]. Bismuth oxychloride gives paint an appearance similar to that of mica-based pearlescent finishes but reflects twice as much light as mica particles due to a smoother surface texture. The uniform thickness and layer structure of the crystals also allow bismuth oxychloride to produce iridescence effects, where the paint appears to be different colours when viewed from different angles [16].

In the future, analysis of vehicle paints is only going to become more complex as new pigments are developed to create unique colours and appearances. Iridescent pigments and coatings that use thin film interference effects are already present in the market although not widely popular. Lexus have also developed a new pigment to be brought into production in 2018. The new Structural Blue has

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been inspired by the wings of the American Morpho butterfly, whose wings appear blue but are actually colourless [17]. The blue colour is 'created by light interference on the microscopic lattice surface structure of the butterfly's wings' which lead Lexus to develop a new pigment manufactured as a series of thin layers with no blue components, creating a series of nano-structures. Structural Blue is applied as a '15 micrometre layer between the primer and clearcoats' as a basecoat. The development of pigments which take advantage of optical effects highlights the complex nature of the interactions of light and coatings right across the spectrum.

#### 1.1.4. Additives

Additives are compounds added to the paint formulation for a functional purpose, usually to improve or change the properties of the coating. They are often used to improve the weather resistance of the coating but can also be used to improve appearance and ease of application.

#### **Extender** Pigments

Some pigments don't only add colour to a paint formulation but can also act as additives, changing the properties of the paint formulation. For example, pigments that add bulk to a paint formulation and increase its opacity, or 'hiding power', and are called 'extender pigments'. Many extender pigments will not produce optical effects as they have the same index of refraction as the paint binder [5]. Extenders also can be used to slightly modify physical or chemical properties of paint formulations, including altering gloss, surface texture, viscosity, strength properties and chemical or abrasion resistance [5]. For example, rutile serves to make a paint formulation appear opaque due to strong absorptions in the near-ultraviolet range [5, 12]. Titanium dioxide polymorphs appear white and are therefore often used alongside other pigments, in light coloured formulations, such as light blue, pink, yellow, and off-white or beige shades [14].

Talc, diatomaceous silica, crystalline silica (quartz) and synthetic silica are extender pigments that are used as flattening agents to create semi-gloss or matte finishes, in particular flat, black non-metallic finishes in monocoat formulations [14, 16]. Synthetic silica can also be used in primers to promote adhesion or as a viscosity control agent in finish coats with low pigment volume concentrations [16]. Barium sulphate is another extender pigment used to increase the viscosity of basecoat formulations to prevent paints sprayed on vertical surfaces from sagging [16]. Barium sulphate is unsuitable for increasing the viscosity of clearcoat formulations as the large particle sizes reduce transparency and can therefore reduce gloss.

#### **Photo-Stabilisers**

Arguably, the most important additives in vehicle paint formulations are those designed to resist the effects of environmental degradation. The most common processes that lead to the degradation of

vehicle paints are photo-initiated oxidation and hydrolysis, both of which are a result of exposure to sunlight, air and water [3]. Hydrolysis and photo-initiated oxidation are interrelated processes and can be accelerated in high humidity or high temperatures [3]. Additives which resist weathering are called photo-stabilisers (light stabilisers) and usually fit into one of two categories, hindered amine light stabilisers (HALs) or UV absorbers [3, 8]. Both types of photo-stabilisers can be used in primer formulations as well as finish coat formulations and may also migrate through the paint layers if not covalently bonded to the binders [3, 8].

UV absorbers are organic molecules that work to reduce the UV absorption of the polymer binders [3, 8]. There are two main types of UV absorbers, those that directly absorb sunlight and those that quench the binder molecules that have been excited by UV absorption (see reaction equations below) [3]. Direct absorbers (A) absorb sunlight, move into an excited state then release the excess energy as heat. Quenchers (Q) absorb the excess energy from polymer binders (P) that have been excited by sunlight, before also releasing that energy as heat. Both types of UV absorbers act as a 'sun block' for the polymer binders [8].

A + sunlight  $\rightarrow A^* \rightarrow A$  + heat P + sunlight  $\rightarrow P^*$  P\* + Q  $\rightarrow$  P + Q\* Q\*  $\rightarrow$  Q + heat

Hindered amine light stabilisers (HALs) are usually amines with two methyl functional groups on each of the two carbon atoms bearing the nitrogen (Figure 2) [3]. HALs quench free radicals that are produced when UV light breaks down compounds in paint formulations and can regenerate after doing so, but will eventually break down themselves [8].



Figure 2 – A representation of HALs molecules showing the amine structure with two methyl groups on each carbon adjacent to the nitrogen. R groups can be hydrogens, or variants on alkyl functional groups (recreated from [3]

Combinations of HALs and UV absorbers are best for long lasting coatings as they act in concert to protect the coating from photo-degradation [3].

Inorganic pigments are often coated with stabilisers to improve weather resistance; for example, bismuth vanadate pigments are usually coated with silicates, calcium phosphate, zinc phosphate, or

aluminium oxide [9]. Similarly, chromate based pigments are often coated with silica to prevent reactions with the paint binder due to oxidising properties [14].

#### Viscosity Modifiers

Vehicle paints are vulnerable to sagging as the coatings are relatively thick and often spray-applied to vertical substrates [3]. Generally, the higher the molecular weight of the polymer binders, the higher the viscosity of the paint formulation [3]. Thus, adjusting the molecular weight of the co-polymers is a method for changing the viscosity of the paint formulation. However, a delicate balance must be struck between increasing molecular weight to reduce sagging and allowing the paint to be fluid enough for even spray application.

Additionally, viscosity-modifying components may be added to the paint formulation separate to the formation of co-polymers and binders. Such modifiers are still present after the curing stages and therefore have refractive indexes similar to those of the acrylic binders in the clearcoat so as not to reduce gloss [3]. Increasing the viscosity of a paint formulation using modifiers serves two purposes. The first is to reduce sagging as the paint cures and the second is to prevent the settling of pigments and inhomogeneity of the paint formulation during storage [3]. Historically, small particles of silica (SiO<sub>2</sub>) have been used as viscosity modifiers in many coatings.

#### *Plasticisers*

The polymer binders used in paint formulations form a durable and hard finish on the rigid metal substrate of vehicle panels, but this is not always desirable. Plasticisers may be added to formulations, such as those applied to more flexible substrates like bumpers, to ensure the paint does not crack with the small impacts that the bumper is designed to cope with [5]. Binder formulations that are mostly linear polymers are also made less brittle with the addition of plasticisers, which enable the polymer molecules to 'slide past one another more easily', creating a flexible coating [6].

Plasticisers are small molecules, often esters, added to fill the spaces between the large polymer binders to allow movement and flow [5]. They create effects similar to solvents and allow the coatings to flow and move even when cured. Modern vehicle paint formulations rely more on cross-linking and binder chemistry to create flexibility and therefore tend not to have as many plasticisers as older lacquers [8].

## 1.1.5. Solvents

Solvents allow the other paint components to remain in a liquid suspension, thus facilitating spray application to the vehicle panels, but will evaporate during the curing stages and are therefore not present for detection for long after curing. Paint solvents are often volatile organic compounds but there is also a drive to use water-based coatings where water is used as an evaporative solvent in order to reduce toxicity [5]. The need for solvents drives the development of coatings, determining the maximum thickness for the layers and the methods of drying, curing and application.

While solvents evaporate during the curing stages of paint application, some residual solvent can be present, trapped in the coating after curing and can be detected using analytical techniques. However, since solvents are generally not present in the cured coating they cannot be detected using infrared spectroscopy (although pyrolysis gas-chromatography mass-spectrometry has some capability for detecting small amounts of solvent still present in cured coatings, particularly in non-OEM finishes), and thus are not discussed further in this dissertation as they are outside the context of this work.

It is worth noting here that butanol might be detected in paint formulations but not because it is used as a solvent. Rather, butanol can be formed during the curing process when butoxylated melamine is used in the paint formulations. During curing, the melamine forms cross-links and the butoxy moiety is lost as butanol [18]. Most is lost to vaporisation during curing but some can be trapped within the paint.

#### **1.2.Vehicle Paint Layer Systems**

Vehicle paints are applied to the panels of a vehicle in sequential layers creating complex coating systems. Several different coating systems are common amongst vehicle manufacturers and they are most often defined by their different finishing layers. Monocoats, clearcoat/basecoat, and tricoat systems are the most common and all include at least one layer of primer on the substrate surface before the characteristic finish layers [5]. The electrocoat primer and primer surfacer are present for corrosion resistance, and to smooth the surface of the steel panels allowing for an even finish, respectively [19]. There are two or three finish coats, including the pigmented basecoat and the clearcoat. Applying a clearcoat over a coloured basecoat achieves a higher gloss finish [3].

Clearcoats were first introduced to the vehicle paint industry in the 1970s and since then monocoat systems have almost disappeared entirely in favour of clearcoat/basecoat systems [19, 20]. In the past, clearcoats were not used in vehicle paint systems because the cost of an extra coating layer was prohibitive, especially when the durability of available clearcoats was inadequate [3]. With the development of binder technology and the introduction of light stabilisers, clearcoats became much more durable in the long term and therefore the more desirable option [3].

Most modern vehicle paints are now tricoat or clearcoat/basecoat systems (Figure 3) and can be easily identified by a visual inspection of the layers under and optical microscope or by investigating a cross section using scanning electron microscopy (Figure 4).

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#### Reflection Infrared Spectral Signatures of Vehicle Paints - Caroline L. O'Driscoll



Figure 3 – The most common original finish paint systems for automotive paints, reproduced directly from [5]



Figure 4 - Scanning electron microscope image (backscatter electron) of an exemplar vehicle paint sample illustrating the tri-coat system (with a gap between the mounting resin and the clearcoat of the paint sample)

The total thickness of a clearcoat/basecoat coating system is only slightly more than a monocoat system due to the high pigment volume concentration (PVC) of the basecoat [3]. Because the basecoat does not need to be glossy (the clearcoat will give gloss to the final appearance of the vehicle) roughly twice the PVC of a monocoat is used which dramatically increases the hiding power and means a thinner pigment layer can be applied [3]. Typically, a 12-20 µm basecoat and a 40-50 µm clearcoat will give a high gloss and long-term durability that exceeds that of a 50 µm monocoat finish coat [3].

Historically, physical identification of the number of layers was held in such high confidence that one forensic analyst, Fredrich Klug, stated 'Identity in the form of certainty is considered to be established

when six or more layers of paint, layer for layer, are in complete agreement in colour, texture layer sequence, chemical reactivity and elemental composition' (quoted in [18] from personal communication). Later, Gothard's studies of Australian vehicle paints found that in a collection of 500 samples, there were 232 unique layer sequences and every vehicle with six or more layers was unique [21, 22]. It is still reasonable to say that as the number of paint layers increases, the chance of finding that sequence of layers on multiple vehicles decreases, because a respray either at factory or aftermarket is involved. However, modern mass production reduces variation between individual vehicles as factory assembly procedures have allowed for innumerable vehicles to be coated with exactly the same paint system, which means assuming only one vehicle could have been responsible for the unknown sample is not correct [18]. Therefore, forensic investigations often require multiple analyses and methods to confirm certainty of identification to further differentiate samples.

#### **1.2.1. Basecoats**

Pigmented basecoats (colour coats) are opaque and hide the less desirable colours of the primer materials as well as sometimes incorporating effect pigments, such as pearlescent flakes [5]. Monocoat systems consist only of opaque layers with a thick pigmented layer, whereas clearcoat/basecoat systems and tricoat systems both utilise a colourless clearcoat to impart a glossy finish to the overall appearance of the paint [5].

Basecoats are pigmented layers where effect pigments (such as aluminium flakes for metallic effects or mica particles for pearlescent effects) can be added and are therefore the layer that gives the vehicle its colour and initial appearance [23]. A small amount of wax, zinc stearate, or cellulose acetobutyrate is often added to the basecoat formulation in order to minimise the distortion of the basecoat when the clearcoat is applied [3]. The clearcoat is spray applied over a still-wet basecoat as it is more economical to bake the vehicle panels (in order to cure the binders) just once [3], although this can lead to diffusion of components across the layers and unclear layer interfaces (see also Section 5.1.1 Layer Identification).

## **1.2.2. Clearcoats**

The primary purpose of clearcoats is to improve the gloss of the vehicle coatings [3]. Clearcoats also improve the durability of the coating system as they must maintain appearance for as long as possible [3]. To fulfil their purpose, clearcoats are usually quite thick (40-50  $\mu$ m) [3], un-pigmented and designed to provide high gloss, hardness, physical protection from scratching or mechanical impact, and protection from UV degradation and weathering [19, 24]. Over time, there have been significant changes to the binder formulations in clearcoats [23].

Clearcoat formulations are ever-changing as new technology and new chemistry come to the forefront of industry. Different binder formulations are constantly under development and manufacturers are always adapting to changes in environmental standards and industry regulations [20]. In the past, all clearcoats were acrylic based, but recently many manufacturers have changed to acrylic urethanes, or two-component urethanes for refinish formulations [23]. Currently, most modern OEM clearcoats fall into one of two formulations: a formulation combining melamine, acrylic and styrene polymers, or, a formulation combining melamine, acrylic, styrene and urethane polymers [20]. Although these formulations are highly similar, the proportions of these polymer components, as well as the particular acrylic monomers included in the formulation, are what differentiate between different manufacturers of clearcoats. Clearcoat formulations also contain high proportions of UV absorbers and hindered amine light stabilisers, typically absorbing at 290-350 nm, to protect from UV degradation and weathering [19, 24].

#### **1.3.Forensic Analysis Techniques**

Vehicle paints are complex systems therefore a variety of analysis techniques, working in concert, are often required to properly characterise paints for forensic investigations. Historically, optical microscopy was the main method of investigation and was used to compare the visual appearance and layer structure of the paints. Microscopy investigations were then followed by micro-chemical testing, involving solvent tests on the various layers, with the aim of identifying different binders and resins by their solubility and reactions [18, 24].

This approach was used by Gothard in two surveys, each of 500 vehicles, one in 1975 and the other in 1996. Gothard describes a process of comparison and elimination that enabled clear differentiation of all but four and six vehicles respectively [21, 22]. Optical microscopy was the main differentiator with micro-chemical tests easily producing differentiating comparisons of the majority of samples remaining. Only a very few samples were then further tested using analytical instrumentation as they could not be differentiated prior to further testing. However, despite the ability to differentiate between vehicle paint samples, the tests performed in the Gothard surveys did not provide identifying information for the chemical composition of all the paint samples tested (with the exemption of a few pairs of samples tested using analytical instrumentation). For more complete identification of the samples, further descriptive and analytical analysis must be performed.

In modern times, traditional micro-chemical analysis has been superseded by the more descriptive instrumental techniques including pyrolysis gas chromatography mass spectrometry (py-GC-MS), Raman spectroscopy and infrared spectroscopy [24]. Additionally, newer methods work with small samples or are entirely non-destructive which is advantageous because, as with many areas of modern

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analytical chemistry, a non-invasive, non-destructive technique is ideal for forensically relevant samples.

The table below (Table 1) summarises a number of techniques commonly and historically applied to the forensic investigation of vehicle paints. While there are a number of techniques evolving in literature, including hyperspectral techniques such as the work by Ferreira [25] and photo-acoustic IR [26], the most commonly applied techniques accepted by forensic science laboratories are listed in the summary. These techniques have been documented in numerous textbooks and are an accepted standard in forensic laboratories [2, 5, 18]. Guidelines specifically relating to the evaluation of paint as forensic evidence, such as the American Society for Testing and Materials [27] also outline the accepted practice.

Technique	Method	Paint Component or Property Observed	Advantages and Disadvantages
Optical Microscopy	<ul> <li>Varied lighting conditions used to visualise the paint under optical zoom</li> <li>Fluorescence techniques</li> </ul>	<ul> <li>Layer structure</li> <li>Texture</li> <li>Colour</li> <li>Presence of effect or large pigment flakes</li> <li>Thickness of layers</li> </ul>	<ul> <li>Non-destructive (unless flake removed from bulk paints)</li> </ul>
Micro-chemical Tests	<ul> <li>Reaction with acetone, sulphuric acid etc. to observe colour reaction or dispersion on agitation</li> <li>Can be done layer by layer</li> </ul>	<ul> <li>Preliminary chemical composition</li> </ul>	<ul> <li>Destructive</li> <li>Non-specific, classifies by type/class of paint</li> <li>No molecular information</li> <li>Usually used as a discriminatory technique</li> </ul>
UV-Vis Spectroscopy	<ul> <li>Reflection measurements of bulk paint samples using an integrating sphere (for bulk samples) or micro- spectrophotometry</li> <li>Transmission measurements taken of solution, colour coats digested in acid</li> </ul>	<ul> <li>Colour profile</li> <li>Possible identification of pigments based on colour profile</li> </ul>	<ul> <li>Non-destructive in bulk, destructive in solution</li> <li>Qualitative (unless chromaticity coordinates are calculated)</li> </ul>
Infrared Spectroscopy	<ul> <li>Traditionally samples prepared as KBr discs</li> <li>Modern investigations use ATR or diamond cell</li> <li>Either transmission or reflection (measured in absorbance)</li> <li>IR-micro-spectroscopy or beam condenser</li> </ul>	<ul> <li>Organic compounds</li> <li>Binders and resins</li> <li>Some inorganic pigments</li> </ul>	<ul> <li>Highly specific</li> <li>Destructive if using KBr discs</li> <li>Layer by layer investigations</li> </ul>

### Table 1 - Summary of analysis techniques applied to vehicle paint samples [2, 5, 18]

Raman	<ul> <li>Historically single layer dissected and mounted</li> <li>Cross sections</li> <li>Depth-profiling cabability</li> </ul>	<ul> <li>Molecular structure of binders</li> <li>Organic pigments</li> </ul>	Complementary to infrared spectroscopy
Pyrolysis Gas-chromatography	<ul> <li>Solid sample directly pyrolized or treated with thermal hydrolysis-alkylation reagents</li> </ul>	<ul> <li>Binder monomers</li> <li>Plasticisers</li> <li>Organic additives</li> <li>Residual solvents</li> <li>Fatty acid profiles and extent of cross-inking (alkyd resins)</li> </ul>	<ul> <li>Sensitive to low concentrations</li> <li>High discrimination power</li> <li>Destructive</li> </ul>
Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM- EDX)	<ul> <li>Historically single layer dissected and mounted</li> <li>Whole sample mounted as cross section</li> <li>SEM imaging with EDX elemental profiling</li> </ul>	<ul> <li>Elemental profile of all layers</li> <li>Elemental analysis of individual pigment particles</li> </ul>	<ul> <li>Destructive as sample is lost once mounted and carbon coated, however, sample still available for further analysis</li> <li>Information on all layers available quickly</li> <li>Qualitative</li> </ul>
Inductively coupled plasma mass spectrometry (ICPMS)	Depth profiling	Metallic elements	<ul> <li>Elemental concentrations</li> <li>Isotope ratios</li> <li>Depth profiling possible with laser ablation</li> <li>Destructive</li> </ul>
LIBS	<ul> <li>Bulk paint sample</li> <li>Emission spectra obtained through plasma excitation induced by high laser powers</li> </ul>	Metallic elements	<ul> <li>Qualitative</li> <li>Destructive</li> <li>Layer profiles possible through successive firing of the laser</li> </ul>
XRD	<ul> <li>Single layers or whole sample (total content analysed)</li> </ul>	Inorganic pigments	Destructive
XRF	Bulk paint sample analysed	<ul> <li>Elemental analysis</li> <li>Inorganic pigment identification</li> </ul>	Non-destructive

# **1.3.1. Forensic Investigations and Examinations**

There are numerous crime situations that might result in the need to examine paint evidence [2]. For vehicle paints, the most common situation is a vehicle collision, either with another vehicle or with an object. In such cases, vehicle paint may be transferred from one surface to another, in either a one-way or two-way transfer. In any crime situation, vehicle paint evidence can come in the form of chips, flakes or smears.

The most conclusive type of paint examination is a physical match [2, 27]. This examination involves comparing a chip or flake of paint to a possible source and if the paint 'fits' the source, the conclusion is that the paint has originated from that source. For example, the shape of a recovered paint chip might match the damage observed on a vehicle belonging to a person of interest and therefore the conclusion might be that the vehicle was part of an incident under investigation. If a physical match cannot be found, either because the paint has transferred as a smear or because there is no source comparison, further examinations must be conducted [2, 8].

Paint examinations where a physical match cannot be determined usually aim to compare two paints to determine if they could share a common source. In such a case a paint of 'known' origin (a reference sample) is analysed using the same methods as the 'unknown' forensic sample (a paint of questioned origin obtained as trace evidence in a forensic investigation). If the samples can be differentiated by any of the analysis methods (usually those listed in Table 1) the conclusion is that the two paints cannot have come from the same source [2]. Alternatively, if the two paints cannot be differentiated they may share a common source. Either conclusion is useful to law enforcement and forensic investigations.

If there is no reference sample for comparison, a database can be used to potentially identify a vehicle type as the source of the forensic item. The Royal Canadian Mounted Police maintains a vehicle paint database known as the paint data query (PDQ) database which contains information on the chemical formulations and layer structures of thousands of vehicles [28, 29]. Databases can be used to compare an unknown vehicle paint with a large number of known paint formulations in order to narrow down the possible source vehicle types [2]. Again, this information is useful to law enforcement and can inform forensic investigations.

## **1.4.Infrared Spectroscopy**

Infrared spectroscopy is of particular interest for vehicle paint analysis as it is a quick, non-destructive method of chemical analysis and can be used to characterise organic molecules based on the wavelength of light absorbed by the molecules, and is one of the best methods for paint binder

identification [18]. Infrared spectroscopy is a popular technique in analytical chemistry, and in the forensic science industry, due to its non-destructive nature and high sensitivity to molecular structure.

Traditional infrared spectroscopy involves preparing a thin film, solution or pressed disc containing the analyte of interest and illuminating the sample with an infrared source. Some of this light will be absorbed by the sample and the rest transmitted and detected. From this transmitted light, the absorbed wavelengths can be identified. The absorbed light is characteristic of certain bonds present in the sample, and thus the spectrum is characteristic of the sample's chemical composition. There are several forms of IR spectrophotometric analysis that are now common in analytical chemistry, including transmission, attenuated total reflectance (ATR), and micro-spectroscopy when small samples are involved.

IR spectroscopy is highly discriminatory but it does have limitations. Minor differences between chemical structures can be hard to identify and so can minor concentration differences between samples [2, 18]. In mixtures, chemical components present in quantities of less than 5% by weight can be difficult to detect [18].

# 1.4.1. Molecular Vibrational Spectroscopy

Infrared spectroscopy identifies and characterises molecules based on the wavelengths of IR light that are absorbed by intramolecular bonds. Every molecule has bonds, and the movement of atoms within the molecule (e.g. stretching or bending of these bonds) gives rise to the different vibrational modes present in the molecule [30]. Some vibrational modes are very localised, i.e. C-H or C=O stretches, whereas others involve the concurrent motion of several atoms. These vibrational modes are quantised and result in absorption bands in IR spectroscopy that correspond to the energies of the vibrational modes in the molecule. A change in vibrational state (the energy of these vibrational modes) can be initiated by the absorption or emission of infrared photons corresponding to the amount of energy required to change the vibrational state. However, for a change in vibration to be induced by infrared light (i.e. be IR active) the vibration must produce a change in dipole moment within the molecule (Figure 5). Importantly, the electric field vector of the incident light and of the oscillating dipole must be oriented in the same plane for absorption to occur [30, 31].



Figure 5 - Molecular structure of a methacrylate monomer indicating the electric dipole moment of the carbonyl bond. The vibrational energy corresponding to this stretching motion is 1731 cm<sup>-1</sup>.

Vehicle paints have a number of components with vibrational modes that show clear absorption peaks in infrared spectra, particularly organic binders. Acrylates and urethanes often display clear carbonyl vibrations at 1731 cm<sup>-1</sup> (Figure 5) and 1690 cm<sup>-1</sup> respectively [15]. A series of C-O stretches around 1300-1000 cm<sup>-1</sup> are generally due to the acrylic binders and thus the region is often termed the acrylic 'fingerprint' region [8, 20]. The presence of melamine is inferred when peaks corresponding to the inplane triazine ring expansion (1550 cm<sup>-1</sup>) and out of plane C-H vibrations (815 cm<sup>-1</sup>) are present together [8, 20]. Inorganic pigments can also produce strong, characteristic absorbance bands in the infrared region; for example, kaolin ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ) often presents with a characteristic double peak at 3650 cm<sup>-1</sup> and 3670 cm<sup>-1</sup>(Figure 6).



Figure 6 - Transmission spectra for the clearcoat and basecoat of a typical car paint sample (CPS011) showing, in particular, characteristic kaolin peaks in the basecoat spectrum

## **1.4.2. Fourier Transform Infrared Spectroscopy**

This section is a brief overview of the methodology and theory behind Fourier transform infrared (FTIR) spectroscopy. More complete explanations can be found elsewhere but key ideas are crucial to understanding further chapters of this dissertation. FTIR spectroscopy works through the use of a

Michelson Interferometer which allows a measurement of the difference between the spectrum of the infrared source and the detected light after interaction with the sample.

#### The Michelson Interferometer

The Michelson interferometer divides the beam from the incident light source into two paths via a beamsplitter and then recombines the two beams after a path difference has been introduced. Recombination creates interference between the two beams and the variation of intensity of the recombined beam, as a result of the interference, is measured as a function of the path difference by the instrument's detector [31]. Path length is varied using a moveable mirror (Figure 7) resulting in a varied amount of interference depending on the distance the mirror moves. The detector in an interferometer measures only the power (intensity) of the light, as it interferes, as a function of the path length difference.



Figure 7 - Diagrammatic representation of the Michelson Interferometer, illustrating the mixed and movable mirrors, and the beam paths before recombination

If any particular wavelength is considered, when the path length is varied by half a wavelength (as a result of moving the mirror) then the original intensity is produced, as the optical path length difference is now a full wavelength. Thus, the wavelength of the incident light can be determined from the distance the mirror was moved between each signal intensity maxima. For a continuum source, such as the globar used in infrared spectroscopy, there will be a point where all wavelengths constructively interfere, creating a single large, sharp peak in the interferogram. This is called the 'centre burst' and the interferogram is symmetrical around this centre burst as the optical path length difference varies. Using these principles, and a Fourier transformation of the interferogram, the interferometer can resolve the incident wavelengths and measure them all simultaneously and the
amount of absorption at each wavelength by measuring the power of the recombined beam at thousands of mirror displacements.

Interferograms are measured with and without a sample in the path of the recombined beams. These interferograms are converted to spectra by applying a Fourier transform (see below). The ratio of these two spectra determines the absorption spectrum of the sample.

#### The Fourier Transform

The mathematics of the Fourier transform are able to deconvolute a function (an interferogram in the case of FTIR spectroscopy) into a series of sine and cosine functions. For a continuum, as is used in modern infrared spectroscopy, the Fourier transform becomes an integral over the continuum. The mathematics is further complicated when the interferogram is not symmetrical and a complex (in the mathematical sense of complex numbers) Fourier transform must be used [31].

In practise, it is only important to understand the transform as a series of alternations between the spectral domain and the optical path length domain. Interferograms are measured as a function of the change in path length as the mirror moves and thus reside in the optical path length domain, whereas spectra are measured as a function of the frequency of the detected light (measured and reported in wavenumbers).

In the spectral domain, real and imaginary components must be separated to generate reflection and absorption spectra respectively, as is dictated by the complex refractive index. Generally, infrared spectroscopy does not concern itself with the components separately as absorbance measurements are taken to be the sum of the real and imaginary components. In practise, analytical chemists do not require both components to be separate as most analytes will be either absorbing or reflective (discussed further in sections 2.7 Light Interactions with Absorbing and Reflection Samples and 2.7.3 Anomalous Dispersion). It is only when these two traits combine at the same wavelength of IR light that spectral data require further processing.

#### Advantages of FTIR Spectroscopy

There are a number of advantages to using Fourier transforms and interferometers for spectrometry, and in fact, for infrared spectroscopy, FT instruments are the norm. Perhaps the greatest advantage is the ability to detect and measure a broad range of wavelengths simultaneously rather than selecting one incident wavelength at a time and moving through a spectral range successively. This is also known as Fellgett's advantage and makes FT instruments much quicker than their dispersive counterparts.

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Additionally, due to the Michelson Interferometer, wavelength calibration is easier and quicker on an FT instrument. Usually calibration is performed internally with a laser source of known wavelength, often a helium-neon laser. Since the wavelength of the laser is known, the optical path length difference can be calibrated by inspection of the interferogram of the incident laser light. This method of internal calibration for FT instruments is also known as Conne's advantage.

FTIR instruments do not require slits to control the bandwidth of the incident IR beam, which means that there is no loss of the throughput of the beam compared to dispersive instruments. This is called Jacquinot's advantage and is the reason why micro-spectroscopy and ATR are possible in FTIR spectroscopy.

Combining Jacquinot's advantage with Fellgett's advantage means that FTIR spectrometers can achieve the same (or better) signal-to-noise ratio as dispersive spectrometers. Additionally, Fellgett's advantage is not applicable for UV-Vis techniques UV detectors are shot noise limited.

# **1.4.3. Attenuated Total Reflectance**

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR, hereafter referred to only as ATR) is an IR spectroscopy technique that uses a reflectance crystal to obtain IR spectra of a sample surface. ATR is essentially a non-destructive IR technique, as the sample can be recovered and analysed further by other techniques. However, some sample preparation methods may be semi-destructive; for example, using a flake of vehicle paint will mean taking that flake from a bulk sample [5]. While ATR can easily measure the clearcoat without dissection of the sample (or indeed a primer if removed carefully from substrate), if spectra from each layer are desired, the vehicle paint sample will need to be dissected. Additionally, it is worth noting that the compression required for analysis may 'squash' the sample.

Despite some semi-destructive aspects of sample collection, ATR minimises the need for any physical sample preparation due to the use of the reflectance crystal [18]. All that is required for ATR analysis is contact of the sample surface with the reflectance crystal [20, 24]. Unlike external reflection spectroscopy, smooth surface properties are not required and ATR can be performed on any sample surface that can contact the crystal [5]. ATR crystals can be many different materials, such as ZnSe (refractive index 2.4) or Ge (refractive index 4.0) but are preferentially diamond (refractive index 2.4) as diamond is more durable [5]. The ATR crystal does absorb some IR wavelengths but applying a general background subtraction will subtract the crystal spectrum to obtain clean sample spectra; however, these spectra will have low signal in regions of high absorbance by the crystal.

In ATR the IR excitation beam is passed through a reflectance crystal (Figure 8). This is an IR transmitting crystal with a high refractive index. The IR beam is incident at an angle that causes internal reflection of the beam through the ATR crystal one or more times [5]. Each time it contacts the sample-crystal interface, the IR beam is transmitted into the sample in the form of an evanescent wave [20]. The evanescent wave created by the internal reflection of the IR excitation beam is absorbed and attenuated by the sample as per the wavelengths absorbed by the molecule's vibrational modes, creating an ATR spectrum [5].



Figure 8 - A schematic representation of the incident IR beam passing from the source through the ATR crystal (single bounce shown) and producing the evanescent wave that penetrates into the sample

The evanescent wave will only penetrate 1-2  $\mu$ m into the sample surface, making ATR a surfacesensitive technique and perfect for analysis of uncontaminated vehicle paint surfaces and clearcoats [18]. Penetration depth is described by the formula below, where  $\lambda$  is the wavelength of the incident light, n<sub>1</sub> is the refractive index of the ATR crystal, n<sub>2</sub> is the refractive index of the sample, and  $\Phi$  is the angle of incidence [32].

$$depth = \frac{\lambda}{2\pi n_1 \left(sin^2 \Phi - \left(\frac{n_2}{n_1}\right)^2\right)^{1/2}}$$

Since penetration depth is proportional to wavelength, the relative intensities of absorption bands as well as some wavelength maxima will be different for ATR and transmission spectra [15, 18, 32]. Therefore, ATR and transmission data should only be compared for general qualitative purposes with this difference in mind [5]. However, there are corrections available that will adjust absorbance values as a function of the penetration depth of the evanescent wave, following on from the above formula [33].

Such correction are readily accepted in forensic applications. For example, Ryland et al directly compared ATR with transmission measurements from traditional FTIR in a study published in 2001 [15]. They observed, as expected, that uncorrected ATR measurements resulted in the absorption bands at long wavelengths having increased relative intensities when compared with transmission

measurements of the same samples, since longer wavelengths penetrate slightly deeper into the sample and therefore undergo more interaction with the sample's chemical components [15]. ATR spectra are therefore often subjected to correction as part of post-processing in order to make comparisons to transmission IR spectra. ATR spectral correction is important in this dissertation as it shows precedent that different styles of IR measurement will create different spectra due to optical and physical effects.

# **1.4.4. Infrared Micro-spectroscopy (IR-MSP)**

FTIR can be combined with an optical microscope, using reflecting optics, for the analysis of small samples in either transmission or reflection modes. In contrast to classic FTIR, the collimated beam does not directly illuminate the sample, but instead is focused through a Cassegrain objective. While focusing allows a smaller area of the sample to be interrogated, it also introduces optical complexities [34, 35]. The inclusion of the microscope also allows visual selection of the area for analysis.

IR-MSP is advantageous in forensic applications since trace evidence by nature, is usually very small. In forensic laboratories, infrared micro-spectroscopy (IR-MSP) is often used for the analysis of vehicle paints. Small flakes of paint, as are usually encountered as evidence, can be directly analysed without preparation of a disc or solvent as in traditional FTIR.

The absorption of light by a sample cannot be measured directly and can only be inferred by the measurement of other optical effects using various instrumentation and optical geometries. There are two main geometries for instrumentation in infrared-micro-spectroscopy (IR-MSP); the first is transmission and the second, reflection. There are some distinct differences in the optics of these geometries that must be understood in order to analyse samples appropriately and to understand the optical contributions to the spectra obtained.

#### **Transmission**

Transmission measurements in IR microscopy involve a reasonable amount of sample preparation. Samples must be thin enough to allow transmission of the incident beam in order to measure the absorbance by the sample. Essentially, however, transmission in IR-MSP is not dissimilar in concept to transmission in classic FTIR instruments.

In transmission mode, incident light is focused through the objective onto the surface of the sample, through the stage and into a second set of optics that collects the transmitted light and directs it to the detector. A thin section of the sample must be dissected and placed on a window to allow the IR beam to pass directly through the sample. Samples are usually mounted on an IR-transparent slide, such as a diamond cell or salt disc in the stage. Thicker samples must be thinned prior to transmission

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measurements, often in a diamond cell, to make them optically thin enough to transmit IR light and avoid complete absorption (usually 5-20  $\mu$ m).

In a simplified description, the transmission geometry measures the light that passes through a thin sample and thus the assumption is that the light not detected has been absorbed. This can be represented mathematically as;

#### *Absorbance* = *Incident Light* - *Transmitted Light*

There are some losses due to reflection and scattering effects but generally, with simple samples (optically thin, homogeneous) these can be considered negligible. Thus, the sum of absorbance and transmittance is equal to the incident light. This assumption is not always correct and can result in measured Christiansen effects and rising baselines. However, it is fair to say that these are often ignored or countered with sample preparation and baseline subtraction. In either case the transmitted light is detected by the instrument and therefore absorbance can be calculated and converted into spectral data. At the very least, these losses are not dissimilar across instruments and geometries and therefore are accepted within the parameters of infrared spectroscopy in the literature.

In an infrared microscope, a Cassegrain objective is used to focus the infrared light from the source onto the sample while a second Cassegrain objective is used to focus and collect the transmitted light (Figure 9).



Figure 9 - Schematic of the microscope geometry for transmission measurement, adapted from [34]

In older styles of IR-MSP transmission illumination came from underneath the sample analogous to traditional optical microscopes. However, the instrument used throughout this dissertation uses topdown illumination for both transmission and reflection, so the focusing objective (condenser Cassegrain) is the same for both transmission and reflection (and is also used as the collection objective for reflection). A second Cassegrain underneath the sample is used for collection in transmission.

#### Reflection

Reflection modes offer potential advantages over transmission or traditional methods as, in principle, no sample preparation is necessary and therefore, samples of any thickness can, in principle, be analysed. A secondary advantage, that has directed this research, is that reflection techniques can be applied to field application or stand-off spectrometric methods used in surveillance-type scenarios. Reflection allows non-destructive, *in situ* spectral measurements with no prior preparation of the analyte.

In reflection mode, incident light is focused through the objective onto the surface of the sample, which is mounted on a reflective substrate and placed on the stage. The reflective substrate is often

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a gold mirror and mounting does not imply that the sample must be immobilised when mounted but simply placed atop the mirror. Optically flat media will show little scattering of light from the sample surface but will reflect the incident beam in two ways. The first is initial reflection from a reflective surface following the laws of reflection, and the second is the successive orders of refraction-reflection throughout the sample post absorbance-transmission.

If the sample is thin enough to allow reflection off the gold mirror after transmission through the sample, the reflected light will then be transmitted back through the sample before collection. This technique is sometimes referred to as 'transflection' as the IR beam is transmitted through the sample but also reflected from the gold mirror. Transflection is only possible with thin samples, such as deconstructed paint layers, to ensure that the IR beam reaches the reflective mirror.

As a simplification, the reflection geometry measures the light that is reflected from the sample surface and thus the assumption is that the light that is not reflected has been absorbed by the sample. This can be represented mathematically as;

#### Absorbance = Incident Light - Reflected Light

There are some losses due to transmission (where light does not return to the detector) and scattering but in the general description, these losses are considered negligible. The reality of these measurements is much more complex, but the simple description does give a general overview of the way the measurements are taken.

In an infrared microscope, a Cassegrain objective is used to focus the infrared light form the source onto the sample and the reflected light passes back through the same objective to the detector (Figure 10).



Figure 10 - Schematic of the microscope geometry for reflection measurements, showing the incident light on the left and reflected light on the right, adapted from [34]

Because both the incident and reflected light move through the same Cassegrain objective, further into the microscope are some more complex optical components to separate out the beams of light before they reach the detector and interferometer. These will not be discussed here as the method of measurement is the focus of the information in this chapter rather than the workings of the spectrometer.

#### **Transflection**

Transflection is not, in the strictest sense, a different geometry of measurement in IR-MSP as the instrument is set exactly the same way as in reflection measurements (Figure 10). The incident IR light is focused through the Cassegrain objective and the detected light collected via the same objective [33, 36]. The difference between reflection and transflection is really in the geometry of the sample and the way the incident light interacts with the sample. In both scenarios the sample is mounted on a reflective substrate, such as a gold mirror or reflective slide, and a background spectrum is collected off that substrate prior to analysing the sample, as shown in Figure 11 [36].

In reflection measurements the sample is optically thick and therefore any reflection from the substrate is impossible, thus the measured reflection is essentially the incident light minus anything refracted into the sample and absorbed by the vibrational modes present (Figure 11 Part B). Comparatively, transflection samples are optically thin and therefore there are two instances of reflection, first from the sample surface and then from the interface of sample and reflective substrate (Figure 11 Part C). The incident light will pass through the sample once, be reflected from the substrate, and pass through the sample again, resulting in a 2l path length (not accounting for angle of incidence) through a sample of thickness l [36]. Therefore, the spectrum measured is essentially

the same as a transmission spectrum for the same sample, with some contribution from surface reflection, but with twice the absorbance attenuation [33, 36].



Figure 11 - Schematic for the sample geometry in reflection and transflection measurements. a) the geometry for background reflection measurements, b) the geometry for reflection measurements, c) the geometry for transflection measurements. R indicates reflection, I indicated incident light and Q indicates refraction.

Importantly, in transflection, reflection still occurs on the sample surface, so there are two influences on the detected beam, reflection from the surface ( $R_1$ ) and the resulting refraction post interaction with the sample ( $Q_2$ ) as shown (Figure 11 Part C). The interference interaction of  $R_1$  and  $Q_2$  in transflection measurements is partially responsible for the complexities observed in transflection measurements.

#### **1.4.5. Comparison to Conventional Infrared Spectroscopy**

Ideally, in a general sense, IR-MSP can be considered as an augmentation of conventional IR spectrometric techniques simply looking at a smaller point on a sample [34]. Indeed, for general analysis of chemical composition for samples prepared as thin films or pressed discs, the techniques work in very similar ways and produce very similar results. However, the nature of a microscopy approach means that there are differences in the optical elements required to measure spectra for small areas, and therefore, the optical system involved is very different. Indeed, as IR-MSP is currently practised, there are a number of differences that should be considered because each of these differences contributes to the measured spectrum [34].

First, the optical elements used for IR-MSP are very different to optical elements in conventional IR spectroscopy. The Cassegrain objectives and the central obscuring element mean that a 'hollow cone' of light is incident on the sample rather than a collimated beam. The instrument used throughout this dissertation creates a cone of light where incident light has a range of angles of incidence, 16-35.5° and a numerical aperture of 0.58 [37].

Secondly, there are sample geometry considerations to be made. The nature of IR-MSP recommends it as a technique for very small samples, samples that are often small compared to the beam, curved (such as untreated fibres in forensic analysis), or non-homogeneous in the x-y plane (such as cross sections or materials made from aligned polymer molecules). Small samples present particular difficulty because they can be heterogeneous on the scale of the microscope beam. Additionally, the edges of small samples can create an uneven surface and a site for diffraction.

#### 1.4.6. Advantages and Disadvantages of R-IR-MSP

There are advantages and disadvantages to all the different types of infrared spectroscopy. Classical infrared techniques for analysing solid samples (i.e. relevant to bulk paint) require mounting a sample in a window (NaCl or similar) or creating a disc (KBr or similar). Not only are these techniques cumbersome but also untenable when looking at vehicle paint samples of forensically relevant sizes. One advantage of ATR is that it can be used for very small samples, which is particularly advantageous for the forensic science sector where case samples are often very small. ATR has the additional advantage of little or no sample preparation but the disadvantage of only 1-2  $\mu$ m of sample penetration (as discussed above in 1.4.3 Attenuated Total Reflectance). For paints this means dissection of the sample is critical if analysis of any layer other than the clearcoat is desired.

R-IR-MSP for analysis of other forms of trace evidence such as hair and fibres, as microscope-based techniques offer advantages for analysis of small samples. Transmission IR-MSP, although it reliably produces excellent spectral data, has the same disadvantages as ATR when it comes to vehicle paint sample preparation. In order to analyse each layer of a vehicle paint sample, the samples must be dissected prior to transmission IR-MSP analysis. An additional disadvantage of transmission is that the dissected samples often still need to be pressed in a diamond cell to be optically thin enough to allow transmission of the IR light; otherwise the instrument will be unable to detect small differences in absorbance and will present with a saturated signal. Pressing the sample into a thin film can also introduce interference fringes, which can interfere with interpretation of the spectra and often need to be removed, resulting in either another step in post-acquisition processing, or, the need to resample.

The forensic science industry already uses transmission IR-MSP for the analysis of vehicle paints, and a technique for the preliminary examination of vehicle paints is desirable, particularly a technique that can be used as a screening method prior to dissection of paint evidence. Reflection IR-MSP (R-IR-MSP) might be the technique of choice as it offers the possibility of more significant advantages than ATR or transmission. Firstly, it requires minimal sample preparation and allows collection of spectral data from deeper into the sample without the need to thin the sample. No sample preparation also means

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that the sample is intact for further analysis by complementary techniques, such as Raman or SEM-EDX. Additionally, the depth of penetration for incident light is unknown for vehicle paint samples in R-IR-MSP. This means it is possible that the light will penetrate through the clearcoat and into the basecoat as well which may allow for data collection relating to both the clearcoat and the basecoat in one spectrum. Collecting information from both the clearcoat and basecoat in one spectrum could be advantageous in forensic applications where two samples are being compared to determine or exclude a common source. In such circumstances acquiring information from two paint layers at once may increase the discrimination power of the technique which may allow R-IR-MSP to be used as a screening tool to indicate if further analysis and dissection of the paint samples is necessary. If R-IR-MSP could be used as a screening tool there may be no real need to determine which peaks in the spectrum correspond to components of the clearcoat or basecoat, comparison of the spectral signatures would be enough to screen the samples. A screening technique could indicate early on if destructive methods will be necessary and therefore possibly reduce the number of tests required. Not only does this save the inconvenience of dissecting a very small paint flake under an optical microscope with a scalpel, but it also means that measuring and comparing the thickness of the layers via interpretation of the reflection spectra is a possibility.

In addition to the advantages of R-IR-MSP, reflection is the only geometry of IR spectroscopy that can be adapted into a stand-off technique and used for surveillance or rapid, non-invasive surveying of vehicles and paints *in situ*. Stand-off is particularly useful when laboratory methods cannot be applied and can be used to supplement traditional surveillance techniques. This is particularly relevant to surveillance or intelligence investigations where there is a need to be both covert and non-destructive. Stand-off IR techniques are already used in other applications such as the analysis of gases or hazardous materials [38]. Further development could allow modern stand-off infrared instrumentation to be used by both the defence sector and law enforcement to identify a target vehicle using reflected spectral signatures. The vehicle's spectral signatures can be compared to known spectra, similar to methods used in a forensic investigation, to inform surveillance or intelligence outcomes. R-IR-MSP offers a laboratory-based mechanism to model and assess reflectionbased infrared spectroscopy which can inform further development of stand-off techniques and their application to vehicle paints.

Despite having a number of advantages over classical infrared spectroscopy techniques, there is relatively little literature describing applications of R-IR-MSP in analytical chemistry and none readily available on the application of R-IR-MSP to vehicle paint analysis. Such a literature gap is likely because R-IR-MSP involves a complex spectrometric geometry which can cause a number of reflection

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phenomena resulting in spectra that are often difficult to interpret. R-IR-MSP data does not always present the 'usual' absorption peaks and flat baseline that analytical chemists might be used to interpreting. This is because R-IR-MSP is a multifaceted technique with many spectroscopic complexities resulting in a large number of photo-physical phenomena which can distort absorption spectra and make peak matching difficult. But, if the spectra are repeatable, then identification and evaluation of present photo-physical phenomena offer a workable innovation for screening and standoff applications. In order to comprehensively interpret and use the results from R-IR-MSP measurements such complexities must be understood so the presence of photo-physical effects in spectra can be identified and interpreted. The next chapter describes the reflection of light as well as a number of photo-physical phenomena present in R-IR-MSP.

# 2. Introduction Part II – Photo-physical Phenomena in R-IR-MSP

There are three major areas of information that must be compiled and investigated before describing the reflection system. First, it is important to outline the geometries of the measurements taken in IR-MSP to provide context for the interaction theory (this has already been done in 1.4.4 Infrared Microspectroscopy (IR-MSP)). Second, it is important to thoroughly appreciate the wave behaviour of light and how it interacts with matter. Third, it is imperative to understand the impact of complex light interactions on the resultant measured spectra. Through these three things, it is possible to understand and describe the different effects possible when light interacts with light, and more complex photo-physical phenomena apparent in reflection, and indeed transflection, measurements.

## 2.1.Interactions of Light and Matter

Generally, there are four ways that light can interact with matter, transmission, reflection, absorption and scattering (Figure 12). Importantly, both absorbed and transmitted light are actually results of refraction through the sample and therefore, are assumed to obey Snell's law of refraction (when travelling through isotropic media) [39-41].



Figure 12 - Light interactions with a sample. Incident light (I<sub>0</sub>) is reflected (R<sub>1</sub>), refracted and absorbed (A<sub>1</sub>), transmitted (T<sub>1</sub>) and scattered (S<sub>1</sub>)

Conservation of energy dictates that the intensity of light for each of these four modes of interaction should sum to the intensity of the incident light. Therefore;

$$I_0 = A_1 + R_1 + T_1 + S_1$$

Each of the four intensities will contain information about the way that mode of light has interacted with the sample and therefore, with correct interpretation, will deliver information on the sample. For chemical investigations absorption is typically the most important quantity because this is directly related to the chemical composition and vibrational modes present in the sample. However, absorption cannot be measured directly and is usually inferred by measuring spectral transmittance (transmission) or reflectance (reflection) [30, 41].

Molecular vibrational modes are quantised and absorption of photons of corresponding energies creates changes in the vibrational mode if the vibration also produces a change in the dipole moment within the molecule [30]. Additionally, the electric field vector of the incident light and of the oscillating dipole must be oriented in the same plane for such absorption to occur [30]. Therefore, for absorption interactions is it important to consider light as an electromagnetic wave.

#### 2.2.Electromagnetic Waves and the Spectrum

In the mid-1800s, Maxwell opened the field of optics as a branch of electromagnetism though characterising and proving the behaviour of light as an electromagnetic wave [41]. Maxwell also developed the description of the electromagnetic spectrum, a continuous spectrum where light is described by frequency and wavelength, and Maxwell's equations became the fundamental laws of electromagnetism.

Electromagnetic waves are a form of transverse wave as the electric and magnetic fields propagate perpendicular to each other. The direction of propagation is perpendicular to both and accurately characterised as the cross product of the electric and magnetic field vectors. The electric and magnetic fields oscillate in a sinusoidal fashion, in phase with each other with the same frequency and therefore wavelength. Thus, the electric (E) and magnetic (B) fields are each a component of the electromagnetic wave and can be described as sinusoidal functions of the position along the path of the wave (x) and the time of measurement (t);

$$E = E_m \sin(kx - \omega t)$$
$$B = B_m \sin(kx - \omega t)$$

where  $E_m$  and  $B_m$  represent the amplitudes of the electric and magnetic fields respectively [41]. The wavefunctions also account for the angular frequency ( $\omega$ ) and angular wave number (k) of each oscillating field. Generally, the electromagnetic wave is represented as a 'beam' or 'ray' of light shown as an arrow in the direction of propagation.

Light can be classified on a scale, the electromagnetic spectrum, depending on the frequency or wavelength of the electromagnetic wave. Visible light falls in the wavelength range 400-700 nm and can be detected and interpreted by the human eye (Figure 13). Infrared light is classified as light with a longer wavelength than visible red light, generally 700-1,000,000 nm (approx. 14,000-10 cm<sup>-1</sup>).





# 2.2.1. Plane Waves

In classical physics, the motion of waves is described by the wave equation. The wave equation can be solved for a number of different circumstances, including one, two and three-dimensional space and considering the nature and environment of the wave in question. Solving this equation for the simplest electromagnetic wave results in the description of a plane wave [39]. A plane wave description indicates that at each point along the direction of propagation, the electromagnetic wave can be described as a wave with wavefronts that are infinite parallel planes normal to the direction of propagation.

Importantly, when a plane wave is incident on the boundary between two homogeneous media with different optical properties (such as the interface of two paint layers) the wave will split into two waves; one reflected, which will propagate back into the first medium and the other refracted, to be transmitted through the second medium [39]. Thus, the plane wave model supports the model of reflection and refraction contributing to the complex nature of R-IR-MSP measurements.

#### 2.3. Polarisation and Isotropy

Light is an electromagnetic wave, meaning that is has both an electric and magnetic field, for spectroscopy the electric field and the plane in which it oscillates are particularly important. If all the planes of oscillation for a beam of incident light are oriented to be the same, this is referred to as linearly polarised light.

Most light sources are not polarised, meaning there is no control over the direction of the electric field; sometimes this is referred to as random polarisation [5, 43]. In an infrared microscope, there may be some residual polarisation due to reflection on the internal optics of the microscope but the light source is not usually deliberately polarised. If the incident infrared light does have residual polarisation (or indeed, is deliberately polarised), then the orientation of the sample becomes crucial

for absorption. For absorption of infrared wavelengths to occur, the electric field vector of the incident light *and* the electric field of the molecular bond's oscillating dipole must be oriented in the same plane [30, 31]. Hence, if all the absorbing molecules in a sample are randomly distributed then even with polarised light, absorption will be the same regardless of the sample's orientation relative to the plane of oscillation of the electric field. Such a sample is referred to as isotropic because it shows the same absorption properties in all directions [41]. If the opposite is true, and there is alignment of the molecules in a sample, the sample is anisotropic, as it will show different absorption characteristics depending on its orientation with the incident electric field [41]. Sample anisotropy is often highlighted in the forensic investigation of polymer fibres, as the orientation of the polymer molecules means a different absorption spectrum is obtained using polarised incident light when the sample is oriented in different directions [44].

Vehicle paints are essentially homogenous in chemical and physical nature and are therefore isotropic when considering each layer independently and in a top down fashion. More precisely the samples show 'transverse translational invariance' meaning that spectrum of the sample is the same even if it is rotated [45]. As an aside, cross-sectioned vehicle paint samples are not isotropic as there is some alignment of the polymer binders in the vertical space, as they 'settle' in the curing phase [3]. This means that in a vertical cross-section, along with compositional differences of the different layers, there is significant anisotropy of the molecular electric fields and therefore different absorption properties depending on the orientation of the sample with respect to the polarisation of the incident light. Additionally, migration of chemical components through various layers has been observed and documented in literature [19].

The isotropic nature of vehicle paints indicates that their orientation in R-IR-MSP measurements does not change the absorption properties of the sample, but the implications are important in understanding and assessing the reflection and absorbance of the samples. It is important to acknowledge the alignment of the electric fields of the paint and incident light, because this relationship has great implications for the physics and spectroscopic interactions.

#### 2.4. The Optics of Reflection and Refraction

When light is incident on a surface, some light is reflected from the surface as though it had 'bounced' off it. Specular reflection results when that surface is smooth and therefore each ray of light is reflected at the sample angle (equal to the angle of incidence) relative to the surface normal (the normal is perpendicular to the sample surface or interface) [30, 40]. If the surface is rough, the reflected light will be scattered in a number of difference directions and is described as diffuse

reflection [30, 40]. Specular reflection is the ideal case and is considered here as vehicle paints have a smooth polished surface.

Additionally, if the reflective surface happens to be the interface of two transparent media, that is media through which the light can travel, some incident light will be transmitted through the surface interface and will continue to travel through the second medium [40]. Such transmission is termed refraction and occurs at any interface of two transparent media where the light is incident at some given angle.

The angle of incidence, the angle at which the light is reflected, and the angle at which the light is refracted are all related. By convention, these angles are measured relative to the surface normal. The Law of Reflection states that the angle of incidence is equal to the angle of reflection. The Law of Refraction states that refracted light will have an angle of refraction related to both the angle of incidence and the refractive indices of the two media [39-41]. The mathematical relationship for the Law of Refraction is called Snell's Law and is as follows;

$$n_1 \sin(\theta_1) = n_2 \sin(\theta_2)$$

Where  $n_1$  is the refractive index of the incident medium,  $n_2$  is the refractive index of the second medium,  $\theta_1$  is the angle of incidence and  $\theta_2$  is the angle of refraction. Additionally, both Laws state that the reflected and refracted beams will be in the same plane as the incident beam, the plane of incidence [39-41]. The figure below (Figure 14) shows a diagrammatic description of the Laws of Reflection and Refraction.



Figure 14 - Reflection (R) and refraction (Q) at the interface of two media with the same refractive index (a), where refractive index n2 is greater than n1 (b) and where refractive index n2 is less than refractive index n1 (c) adapted from [41]

The refractive index of a medium  $(n_x)$  is the ratio of the speed of light in a vacuum to that in the medium [40]. The refractive index is complex  $(n = \hat{n} + \kappa i)$  if the medium is absorptive as well as

reflective (the complex refractive index is discussed further below). The real component is the factor of speed reduction in the light and the imaginary part, the absorptive index ( $\kappa$ ), describes the medium's absorption properties [36]. As shown, if the refractive index  $n_2$  is greater than  $n_1$ , the light is refracted towards the normal and the angle of refraction is smaller than the angle of incidence. If the refractive index  $n_2$  is less than  $n_1$ , the opposite is true. If the refractive indices match, so do the angles of incidence and refraction.

#### 2.4.1. The Electric Field and Polarisation by Reflection

Polarised light is light travelling in one direction where all the oscillating electric fields are oriented the same way. If light has random electric field orientation, it is therefore unpolarised.

When light is incident on a surface, the oscillating electric field can be resolved into two components, parallel (symbol *p*) and perpendicular (symbol *s* from the German 'senkrecht') to the plane of incidence [46]. Fully polarised light will have an electric field aligned in only one particular direction. Unpolarised light, light with random electric field orientation, statistically has an equal magnitude for components parallel or perpendicular to the surface. When unpolarised light is reflected from a surface, the two components will not be reflected with equal magnitudes and thus the reflected light will be partially polarised [41]. However, the angle of incidence plays an important role in the partial polarisation. For every dielectric medium, there is an incident angle, termed the Brewster Angle, where reflected light is fully polarised in the perpendicular direction and all parallel components are refracted into the medium [41, 46]. Additionally, at the Brewster angle, reflected and refracted rays are perpendicular to each other, mathematically;

# angle of reflection + angle of refraction = $90^{\circ}$

This relationship can be combined with Snell's Law of reflection to show that the angles are related to the refractive index of the media,

angle of reflection = 
$$tan^{-1}\frac{n_2}{n_1}$$

#### **2.5.Interference**

The principle of superposition states that, 'when several effects occur simultaneously, their net effect is the sum of the individual effects' [41]. When considering two waves travelling in the same direction through the same medium, the principle of superposition applies and therefore indicates that the effect on the medium is the sum of the effect of each individual wave. Thus, waves travelling through the same region will add algebraically to produce a 'resultant wave' but without any alteration to the travel of each wave on its own [41]. This phenomenon of combination of waves is called interference. If the waves are completely in phase, they will undergo fully constructive interference and the amplitude of the resulting wave will be the sum of the amplitudes of the interfering waves. If the waves are completely out of phase, they will undergo fully destructive interference and result in the cancellation of the wave. If the waves are somewhere between exactly in and out of phase, the resulting interference is intermediate, neither fully constructive nor fully destructive [41]. Additionally, when the interfering waves are travelling in the same direction, the resulting wave is also travelling and, in any interference scenario, the resultant wave is also sinusoidal and only the resultant wave can be observed.

# 2.5.1. Interference of Electromagnetic Waves

Since electromagnetic waves are made up of oscillating electric and magnetic fields, each oscillating field can be described separately when considering interference of electromagnetic waves. That is, the electric fields will interfere and combine as per the principle of superposition and the magnetic fields will do the same. Thus, the effect of the electric field will be the combination of the electric fields of each interfering wave.

This is important when considering the effect of the combined electric field (particularly the orientation of the resultant electric field) on the absorption properties of a medium when light is experiencing interference within that medium. Absorbance is proportional to the square of the net electric field strength so a change in electric field impacts directly on the absorbance of the sample.

#### **2.5.2. Thin Film Interference**

In reflection, samples that are optically thin can create a unique interference pattern in the spectra. Interestingly, very thin films actually reduce interference as the interference pattern becomes merely a shift in the baseline of the spectrum. However, there are difficulties with preparing samples thin enough to reduce interference in this manner and it is not always feasible for forensic applications where the aim is to prevent any destruction of, or alteration to the sample.

The simplest thin film system can be imagined as a three-phase system, the surrounding medium, the thin film and then the surrounding medium again [40, 41, 47]. In the figure below (Figure 15) this is imagined as a thin section of a sample surrounded by air. Just as light is reflected and refracted from the first surface interface, at the front of the sample, so is the refracted beam then reflected and refracted from the second interface after transmission through the film. Thus, some light is reflected off the surface taking path 1 (P<sub>1</sub>) and some travels through the film, taking path 2 (P<sub>2</sub>), meaning that each beam has now travelled a different distance creating a phase difference between the waves. The two reflected beams will meet again in the surrounding medium (once the beam on path 2 has left

the film) and interfere constructively or destructively depending on their respective phases [40, 47]. The interference effect is therefore observed with detection of these two reflected beams.



Figure 15 - Simple schematic describing the interaction of an incident beam of light on a thin film

Reflection from an interface can also create a phase change in the wave depending on the refractive indices of the two-media meeting at the interface. If the light is travelling through a high refractive index medium and meets a medium of lower refractive index no phase change occurs. If the light is travelling through a low refractive index medium and meets a high refractive index medium any transmitted light will remain in the same phase as the incident light, but the reflected light will undergo a phase change of  $\pi$  radians, (or 180°) corresponding to half a wavelength again [40, 41]. Such a phase shift can contribute to the interference between the two reflected waves in a thin film system.

Phase differences and multiple reflections create significant interference in thin film spectra. Interference in spectra creates a 'fringe' pattern present throughout the spectrum. Fringe effects are frequently observed in transmission and reflection spectra of thin films due to the interference of multiple reflections [48]. The fringe pattern presents as periodic (sinusoidal) peaks and troughs across the spectrum, with maxima occurring when  $k\lambda = 2nt \cos \theta$  (where k is an integer,  $\lambda$  is the wavelength, n is the refractive index, t is the thickness of the film, and  $\theta$  is the angle between the normal to the film and the direction in which radiation is propagated though it) in transmission spectra [48]. In reflection spectra, minima occur for the same conditions.

In addition to thin film interference, the thickness of the film does change the relative amounts of reflection and absorption present in a spectrum. Thicker films have more surface reflection contribution to the spectrum as much of the absorbed and transmitted light is lost as it either loses energy within the sample and does not reach the detector, or, is transmitted through the sample and never reflected back from the surface of the sample. Thinner films show clearer (and relatively

stronger, higher signal-to-noise) absorption peaks in transmission because the non-absorbed light is transmitted with lower losses.

# 2.5.3. Electric Field Standing Waves

Interference occurs as a result of the superposition of two waves with the same properties meeting and interacting while travelling in the same direction. If, however, the two waves are travelling in opposite directions, a different, but not dissimilar effect takes place (Figure 16). This effect is also due to the principle of superposition but rather than resulting in a travelling wave, instead results in a standing wave [41]. In a standing wave there are places, called nodes, where the wave is always at a minimum and halfway between these nodes are antinodes where the amplitude of the resulting wave is always at a maximum. Rather than these nodes and antinodes travelling and propagating the wave, instead the location of the nodes and antinodes does not change [41]. Thus, the amplitude of a standing wave is not constant across location and, at any point, is determined by the location of that point relative to the nodes and antinodes.



Figure 16 - Schematic describing the combination of two waves travelling in opposite directions creating a standing wave (reproduced directly from [49])

In reflection, incident and reflected waves with the same properties can interact and combine to create a standing wave. In particular, for electromagnetic waves, the oscillating electric fields can interact and create an electric field with the amplitude properties of a standing wave.

In a transflection style measurement (or for similar reflection measurements) reflected light from the substrate undergoes a phase shift of  $\pi$  before travelling back through the sample in the opposite direction [50]. Therefore, the incident (or more specifically the light which is initially refracted and then transmitted through the sample, to then be incident on the reflective substrate) and reflected light have the same wave properties but are now out of phase and travelling in opposite directions. Interference between these two waves creates a standing wave within the sample which has a node at the surface of the reflective substrate. The wavelength of this standing wave is dependent on both the refractive index of the sample and the wavelength of the incident light [51, 52]. In particular, the electric fields of the light rays experience interference and create an electric field standing wave (EFSW). Because of this interference, and the principle of superposition, the electric field experienced by the sample is actually the combination of the electric fields of the incident light [51, 52]. The magnitude of the standing wave represents this electric field strength.

Since there is always a node at the reflective surface, the thickness of the sample film determines the magnitude of the EFSW and therefore the electric field at the sample surface [51, 52]. Depending on sample thickness, the sample surface could correspond to a node, antinode or somewhere in-between as determined by the level of interference of the incident and reflected waves at this point in the phase of the EFSW. If the EFSW has an antinode at the surface, then the electric field is maximised at this point and therefore there is an increase in absorption [51, 52]. If the EFSW has a node at the surface, then the electric field is negated at the surface and reflection is enhanced. Therefore, for each incident wavelength there is an effect on the absorption properties of the sample because of the strength of the EFSW at the sample surface [51, 52]. The EFSW causes altered peak intensity ratios and shifts in peak positions dependent on the incident wavelength and the thickness of the sample [53].

While some literature suggests that the interface of air at the sample surface is responsible for the spectral distortions rather than an EFSW effect [54], there is more support for the presence of standing waves in transflection measurements where a thin layer on a smooth interface can be described as a Fabry-Pérot etalon [53]. A Fabry-Pérot etalon is a transparent (and absorbing in the case of samples for spectroscopic analysis) layer with two reflective surfaces, which is consistent with transflection and reflection measurement geometry [53]. Interestingly, the EFSW effect has also been observed and described in ATR spectroscopy [55].

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#### **2.6.Refractive Index**

Electromagnetic waves do not require a medium to travel through and all electromagnetic waves, and therefore all wavelengths of light, travel at the same speed, approximately 2.998 x  $10^8$  ms<sup>-1</sup>, when moving through a vacuum. However, when moving through different media, the speed of travel is altered. The wave speed (*c*) and the electric (*E*) and magnetic (*B*) fields are related by;

$$\frac{E_m}{B_m} = \frac{E}{B} = c$$

where the ratios of the amplitudes and magnitudes (respectively) of the electric and magnetic fields are equal to the speed of the wave, that is, the speed of light [39, 41].

Since the refractive index for a medium is equal to  $\frac{c_0}{c_1}$ , where  $c_0$  is the speed of light in a vacuum and  $c_1$  is the speed of the same light in that medium, the refractive index 'encountered by light in any medium except vacuum depends on the wavelength of that light' [41]. This dependence implies that when light of many wavelengths, for example a white light source or infrared source, is incident on a surface interface, the refracted light will undergo chromatic dispersion meaning each wavelength will display a different angle of refraction. Chromatic dispersion can easily be observed in the classic experiment where a beam of white light is incident on a glass surface or prism and the result is a refracted rainbow of colours displaying the full range of the visible spectrum. Generally speaking, while refractive index is medium specific, smaller wavelengths of light will encounter a greater refractive index of any medium is wavelength specific. That the index of refraction is wavelength ( $\lambda$ ) dependent is well known, if not commonly recalled in spectrometry. It is also not well documented, particularly not for the mid-IR region, however crucial it may be for spectrometric investigation via reflection.

In the special case where the refractive index of the second medium,  $n_2$ , is less than the refractive index of the incident medium,  $n_1$ , and the angle of incidence is large enough, incident light will not undergo refraction at all and instead will be completely reflected. Such a case is called total internal reflection and occurs at angles of incidence greater or equal to the critical angle ( $\theta_c$ ), determined by  $\theta_c = sin^{-1}\frac{n_2}{n_1}$  [41].

# 2.6.1. The Complex Refractive Index

Reflection from a surface is dependent on both the absorption and reflection functions of the surface medium. For a medium that can both absorb and reflect light, these optical functions combine and the refractive index will have two components, one defined by reflection and the other defined by absorbance, specifically the molar extinction coefficient [56]. In other words, the component of the refractive index which describes reflectivity is mathematically 'real', and the component of the refractive index which describes absorption is mathematically 'imaginary'. Thus, the true refractive index of a medium that both reflects and absorbs light is complex. Classical physics also comes to this conclusion by following the consequences of Maxwell's equations [39, 57].

Classic optics describes the real refractive index (*n*) as a dispersive factor, responsible for reflection and scattering effects (the factor for the change of speed in the wave as it travels through different media [36]), and the imaginary part of the refractive index as an absorptivity index ( $\kappa$ ), describing absorption. Reflection will occur at the surface of the medium (for example, the air-sample interface) while absorption will occur within the sample [45]. Mathematically, the complex refractive index ( $\eta$ ) can be expressed as a function of these two phenomena;

$$η = n - \kappa i$$

Since the absorptivity index is a function of the molar extinction coefficient ( $\varepsilon(\lambda)$ ), it is also a function of wavelength, indicating again, this time mathematically, that the complex refractive index is wavelength dependent [45]. This links wavelength dependence to anomalous dispersion.

#### 2.7.Light Interactions with Absorbing and Reflection Samples

The relationship between reflection and absorption for a particular medium is intricately linked to the definitions of reflectivity and transmissivity for that medium, and defined by the angle of incidence, wavelength and extent of polarisation of the incident light [58]. Reflectivity and transmissivity, and therefore absorptivity, can be described using the Fresnel equations, by applying classical electromagnetic theory for the interaction of a plane wave with a reflecting and absorbing medium, the properties of which can be described by the complex refractive index [58].

Because transmission and absorption are reliant on the orientation of electric fields (both of the medium, and the incident light), it is much simpler to consider isotropic media (see section 2.3 Polarisation and Isotropy for more information), although the interactions and definitions can be extrapolated and extended to include anisotropic samples. The two orientations of particular importance are the electric fields parallel and perpendicular to the plane of incidence. Each of these will have a fraction of light transmitted and a fraction reflected, as defined by the Fresnel coefficients [58].

#### 2.7.1. Fresnel Equations

The Fresnel equations describe coefficients for transmissivity (t) and reflectivity (r) at the interface of two media (defined by the subscript notation). These coefficients are defined by the magnitude of the

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incident electric field ( $E_{inc}$ ), and reflected or transmitted electric fields [36]. For the interface of air and the sample interface the coefficients can be expressed as:

$$r_{12} = \frac{E_{ref}}{E_{inc}}; \ t_{12} = \frac{E_{trans}}{E_{inc}}$$

Assuming that all incident light is either transmitted or reflected (simplifying and considering the conservation of energy), the coefficients are also directly related. However, the reflection coefficient is dependent on the polarisation of the electric field. Thus, Bassan [36] defined the coefficients mathematically as below for perpendicular and parallel electric field polarisation respectively:

$$t_{12} = 1 - r_{12}$$
$$t_{12} = (1 - r_{12}) \frac{\cos \theta_1}{\cos \theta_2}$$

For media that are also absorbing, the reflection coefficient is complex, as reflectivity is related to the complex refractive index both as a definition of reflectivity and through Snell's law, which relates refractive index to the angle of reflection [36].

The forms of the Fresnel equations vary according to the system they are being used to describe; for example, a four-phase system where reflection and transmission is occurring at the interfaces for all four phases will require a different form of the equations than when describing transmission through a thin film surrounded only by air [58].

#### 2.7.2. Multiple Layer Systems

In a sample or system of multiple layers, and therefore multiple interfaces, light detected as 'reflection' will actually be the additive sum of all successive orders of reflection and refraction at each of the interfaces. Thus, the form of the Fresnel equations and the description of the reflection system for multiple layered systems are highly intricate. This can be complicated further of course, when the media involved are absorbing and therefore the refractive indices are complex.

In general, however, the Fresnel equations and electromagnetic theory can still describe multiple layer reflection, particularly with the additional application of Snell's law of reflection. The reflection coefficient for a multiple layer system then becomes the composite of all light beams reflected and transmitted [36]. Each transmitted beam then becomes the incident light for the layer beneath and is considered as such in the composite coefficient calculations.

Bassan [36] has described the reflection coefficients for a three-layer system (for example, air or vacuum, thin layer sample and substrate) taking into account a term for the phase change

encountered upon reflection – the beta( $\beta$ ) terms. Interference must also be accounted for, as must the two transmission coefficients, from the first and second interfaces respectively. The exponential term also takes into account the lost intensity due to absorption [36]. The process for multilayered systems essentially begins with expressing the reflectivity and transmissivity coefficients for each interface and then combining all terms.

Firstly, considering the two transmission coefficients:

$$t_{12}t_{21} = (1 - r_{12})^2$$

For a three-layer system, the resulting reflection coefficient is mathematically described as below:

$$r_{123} = r_{12} + \frac{(1 - r_{12})r_{23}e^{(-2i\beta_2)}}{1 + r_{12}r_{23}e^{(-2i\beta_2)}} = \frac{r_{12} + r_{23}e^{(-2i\beta_2)}}{1 + r_{12}r_{23}e^{(-2i\beta_2)}}$$

Repeating this process, determining the various contributions to the reflection coefficient from each interface, theoretically allows for the determination and calculation of the Fresnel coefficients for a system of essentially infinite layers [36]. Considering the complex refractive index for each layer will account for phase changes and absorption from each layer.

The complexities of multiple layer interactions can be mathematically described and modelled, but the resultant spectra can only be predicted and calculated, as by Bassan [36] if all the terms are known. For real world samples, such as vehicle paints, there is no simple way to calculate the effects of reflectivity and the complex refractive index upon the spectrum. However, understanding the interaction of multiple orders of reflection and refraction is crucial to qualitatively understanding the reflection system because the interface of each layer will provide a new place for reflection to occur within the sample.

#### 2.7.3. Anomalous Dispersion

As described above, the refractive index of a medium is dependent on the wavelength of light incident on that medium. The refractive index changes with wavelength and this phenomenon is termed 'dispersion' [39]. Dispersion is best described by deep discussion of atomic theory as it relates to electric fields of molecules and their interaction with light (absorption) with particular attention to the generation of dipole moments [39].

In simplified terms, at wavelengths corresponding to the energies of vibrational modes within the sample, the absorptivity index ( $\kappa$ ) peaks. The real refractive index (n) will therefore undergo a sudden change and this is termed 'anomalous dispersion' [33, 45]. Anomalous dispersion creates 'dispersive line shapes' in reflection spectra, as shown in Figure 17 [33]. Since reflection is governed by the real

refractive index, the sudden change due to an absorption peak distorts the reflection spectrum [45]. When reflection is plotted in absorbance units, as is common in infrared spectroscopy studies, the anomalous dispersion is easily observed as 'dispersive line shapes' in the spectrum peaks. These dispersive line shapes can often appear very similar to first derivative spectra.



Fig. 2. Schematic absorption and dispersion line shapes due to the imaginary and real part of the refractive index, respectively.

Figure 17 - Line shapes for absorption (top) and anomalous dispersion (below) as in reflection spectra of absorbing samples. Reproduced directly from [33]

The more complex explanation (which will only be briefly stated here) starts with the description of the angular frequency of the incident field ( $\omega$ ) where, at the resonance (or absorbance) frequency ( $\omega_0$ ), electrons will oscillate in the incident field [39]. At the resonance frequency, damping becomes a particularly important factor 'as the vibrating of electrons emit[s] electromagnetic waves which carry away energy' [39]. Since each electron contributes to polarizability, damping must be taken into account by representing a resistant force into the mathematical consideration of the motion of the system. Working this through, polarization becomes a complex quantity [39]. The modulus of this complex function is a curve with a sharp maximum at a frequency slightly smaller than the resonance frequency, and a minimum at a frequency slightly greater. Thus, between these two frequencies, there is a region where the curve decreases and this is described as a region of anomalous dispersion (Figure 18).



Fig. 2.3. Dispersion curves.

# Full curve: effect of damping neglected. Broken curve: effect of damping taken into account. (The ordinates now represent the real parts of $n^2$ and of $4\pi N\alpha$ .)

#### Figure 18 - Dispersion curves reproduced from [39]

Therefore, light with shorter wavelengths than the resonance frequency is refracted less than light with longer wavelengths [39]. Importantly, different regions of light with absorption frequencies relating to different vibrational modes (molecular, atomic etc.) must be considered of equal importance. For instance, since the absorption frequencies for free atoms correspond to ultra-violet wavelengths, investigations of free atoms in the visible region do not need to consider anomalous dispersion [39]. For molecular vibrational modes, it is important to consider anomalous dispersion as investigations of molecular structure rely on identifying molecular absorbance peaks in the infrared region.

#### 2.7.4. The Christiansen Effect

Infrared spectra of crystalline powders embedded in solid, liquid or air matrixes can show an anomalous transmittance peak within an absorption band which can sometimes be attributed to the Christiansen effect. The Christiansen effect occurs as an increase of the transmittance of crystalline powders at wavelengths where the powder and the matrix refractive indices are equal [59]. This wavelength is known as the Christiansen wavelength ( $\lambda_{Chr}$ ) and the transmittance peak is known as the Christiansen peak. The Christiansen peak alters the profile of absorption bands present across Christensen wavelengths [59]. The Christiansen effect is related to anomalous dispersion (described above) but limited to certain wavelengths rather than across the spectrum. As with anomalous dispersion, there are two distinct effects on peak shape; the first is the change in the absorption band profile and the section is a significant shift in the absorption maximum for that band. Unlike anomalous dispersion, but similar to Mie scattering (described below) the particle size of the crystalline powder is a contributing factor to the manifestation of the Christiansen effect.

#### 2.7.5. The Kramers-Kronig Transform

Pure absorption and reflection effects are governed by the complex refractive index and are related by the Kramers-Kronig transform [33]. The Kramers-Kronig (KK) transform is a mathematical relation summarised by the following equations:

$$n(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon(\omega)}{\omega - \omega_0} d\omega$$

$$\varepsilon(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{n(\omega)}{\omega - \omega_0} d\omega$$

Where  $\omega$  is the angular frequency of light (and  $\omega_0$  the angular frequency at an absorption maximum),  $\varepsilon$  is the molar extinction coefficient (related to the absorptive part of the complex refractive index) and n is the real part of the complex refractive index (the reflective part of the complex refractive index) [45]. These equations can be used to separate the absorptive and reflective contributions in a spectrum.

Application of the KK transform corrects anomalous line shapes in reflection spectra by acknowledging both the real (reflective) and imaginary (absorptive) components of the refractive index. The KK transform is accepted practise in the use of R-IR-MSP and can be performed by spectral acquisition software without the need for external or post-processing. However, the KK transform can only correct spectra that are purely the result of reflection by changes in the real component of the refractive index [33, 45, 60].

#### 2.8.Mie Scattering

Mie scattering has been reported as responsible for undulations in the baseline of infrared spectra. It has also been reported that Mie scattering from spherical (or near-spherical) particles in the sample can also mix reflective and absorptive band shapes [45, 61]. In investigations of human cells, such effects are not unexpected considering the size of the nucleus of cells is in the same order as the wavelength of the incident light,  $1-10 \mu m$  [61, 62].

Described first by Mie in 1908, dielectric spheres will scatter electromagnetic radiation of a wavelength comparable to the size of the sphere [63]. The size of the particles dictates the appearance of the baseline oscillations. In some literature, it has been reported that *resonant* Mie scattering could also be responsible for the peak shape distortions generally attributed to anomalous dispersion [64]. In these reports, the resonant Mie scattering can display either a 'positive' or 'negative' dispersion artefact where the shape of the distorted peak can have the maximum on either side of the resonance frequency (absorption maximum) which has been correlated with the gradient of the Mie scattering efficiency curve [64]. However, it is reported that the resonant Mie scattering effect will occur in both transmission and transflection measurements [64].

# **2.9.Sample Thickness**

Vehicle paints are layered systems where each layer can be tens of microns thick [3, 65](see also 1.2 Vehicle Paint Layer Systems). The literature on the above described photo-physical phenomena reports on samples that are much thinner than even one layer of a vehicle paint. Typically, the samples where such phenomena have been observed are on the order of tens of nanometres thick, such as tissue and cellular material [51, 61]. Mayerhofer investigated interference-based effects in samples between 500-900 nm [53]. Work by Allara looked at polymer films up to 2 µm in thickness [58].

Since vehicle paints are several orders of magnitude thicker than other samples reported in literature it is not unreasonable to expect that they would be more absorbing and therefore might have fewer (and/or weaker) reflection effects. At the very least, their behaviour cannot be easily inferred from previous investigations.

## 2.10. Research Aims

Considering both the advantages of R-IR-MSP for forensic analysis, and the potential to use R-IR-MSP to demonstrate the capability of other reflection modes when applied to vehicle paints (see also 1.4.6 Advantages and Disadvantages of R-IR-MSP), the research presented in this dissertation aims to inform the defence and forensic industries of the potential/capability of R-IR techniques for laboratory or stand-off characterisation of vehicle paints. The results will be presented in the context of the complex nature of R-IR-MSP measurements with reference to the requirements of forensic analysis and the properties of vehicle paint samples.

In order to achieve the broader research aim, this dissertation aims to:

- 1) Document the reflection infrared spectral signatures of vehicle paints with comparison to other infrared spectroscopy techniques
- 2) Describe how vehicle paints act spectroscopically when subjected to R-IR-MSP analysis

- 3) Identify any characteristics of the reflection infrared spectral signatures of vehicle paints which might occur as a result of reflection measurement geometry
  - a) If any previously described photo-physical phenomena can be identified in R-IR-MSP measurements for vehicle paints, model and attempt to remove the influence of these effects

Each aim will be addressed in a chapter to follow, once the methods of instrumentation and sampling have been described.

# 3. Instrumentation and Sampling

Several different instruments were used to conduct this research and are described below. The main instrument used for the most significant portion of the data was the Nicolet Continuµm FT-IR Imaging Microscope. Paint samples were sourced from a variety of locations and catalogued using scanning electron microscopy (SEM) prior to investigative analysis. All raw data, including SEM images and energy dispersive x-ray spectroscopy (EDX or EDS) scans is included in the appendices (Chapter 9 Appendices).

# 3.1. Thermo Nicolet FT-IR Spectrometer

Most spectra in this dissertation were obtained using a Thermo Nicolet Nexus 870 FT-IR (ThermoFisher Scientific Inc., Massachusetts, USA), equipped with an extended range KBr beam splitter, and the OMNIC<sup>™</sup> software. This instrument was used to obtain both Attenuated Total Reflectance (ATR) and infrared micro-spectroscopy (IR-MSP) spectra through the use of two different accessories.

# **3.1.1. Attenuated Total Reflectance**

ATR measurements were taken using the single bounce Smart Orbit ATR accessory utilising a diamond crystal and DTGSTEC detector. All ATR spectra were the result of 16 accumulated scans at 4 cm<sup>-1</sup> resolution over the spectral range 7000-525 cm<sup>-1</sup>. ATR spectra were processed using the OMNIC software, applying a Happ-Genzel apodization function and Mertz phase correction. ATR correction, to adjust relative peak heights, was also applied using the OMNIC<sup>TM</sup> software.

For ATR measurements, a flake of paint was analysed with the layer structure intact, and the clearcoat contacting the ATR crystal. The flake was then held in place by the pressure arm on the ATR accessory, under appropriate pressure to achieve a spectrum with a high signal to noise ratio (judged by eye under the preview in the instrument software).

# 3.1.2. Infrared Micro-spectroscopy

For IR-MSP measurements, in both reflection and transmission modes, the Nexus was equipped with a liquid-nitrogen cooled Nicolet Continuµm FT-IR Imaging Microscope (ThermoFisher Scientific Inc., Waltham, Massachusetts, USA). All samples were measured using a 15x focusing Cassegrain objective with a numerical aperture of 0.58 and angle of incidence 16-35.5°; and detected by a MCT/A detector. Spectra were measured across the wavenumber range 7000-525 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution. The sample spectrum was collected at 128 averaged scans and the OMNIC<sup>TM</sup> software applied no corrections to the spectra, only the Norton-Beer strong apodization function and Mertz phase correction to the interferograms. Transmission measurements were taken on each layer of paint individually. The individual layers were separated from the bulk paint sample using a scalpel and pressed between two diamond windows to create a thin film. Spectra were taken of the thin film on one diamond window using the window as the 100% transmission reference. This microscope uses top down illumination for transmission so the same focusing optics are used for transmission and reflection measurements, but a second Cassegrain lens system is used for detection in transmission (Figure 19).



Figure 19 - Schematic of the IR-MSP system set up for a transmission measurement showing the incident (red) and transmitted (pink) light (received from [37])

For reflection measurements, a flake of paint, layer structure intact, was placed on a gold mirror under the microscope objective, clearcoat up. The gold mirror was used as a 100% reflectance reference for all reflection spectra. Spectra were taken by focusing the microscope on the surface of the paint flake. Reflected light is collected through the same Cassegrain objective that focuses the incident light.

# 3.2. FEI Inspect<sup>™</sup> F50 Field Emission Microscope (Scanning Electron Microscope)

The Scanning Electron Microscope used for layer investigations and characterisation of effect pigments was an FEI Inspect<sup>TM</sup> F50 Field Emission Microscope (FEI – part of ThermoFisher Scientific,

Oregon, USA) equipped with an Energy Dispersive X-ray Spectrometer (EDAX, New Jersey, USA) and the corresponding TEAM<sup>™</sup> EDS Analysis System software.

Larger flakes of paint were used to investigate the cross-section and layers system of the vehicle paint samples using Scanning Electron Microscopy (SEM). A number of polyester resin discs were prepared via the method published by Seyfang et. al. in 2015 [66]. This process involves casting thin (approximately 10-15 mm) cylinders of polyester resin (Recochem, Lytton, Queensland, Australia. Diggers<sup>™</sup> fibreglass resin treated with curing agent in the ratio of 60 mL: 1.6 mL, respectively) into 25 mm lengths of 30 mm (internal diameter) PVC tubing adhered to a flat piece of glass using laboratory grease. A hacksaw with two blades was then used to cut into the cured discs creating 5 parallel slots approximately 2 mm wide and 3 mm deep in one face. Under an optical microscope, flakes of paint approximately 4 mm by 4 mm were then placed within these slots and held there using Blutac<sup>TM</sup> as an adhesive. Care was taken to ensure the paint cross-section was visible, the top of the flake was protruding from the slot, and the flake was mounted at 90° to the disc surface, thus ensuring that a representative cross-section could be prepared. The slots were then carefully filled with Tuffleye® resin (Feather Craft Fly Fishing, St. Louis, Missouri, USA), which was then cured using a Polylight<sup>™</sup> (Rofin Forensic, Melbourne, Victoria, Australia) at 450 nm [66, 67]. The disc face with the cured slots was then polished to smooth the protruding flakes of paint, using silicon carbide abrasive paper starting at P400 and following with progressively finer grades to P1200. The prepared disc was then attached to a 13 mm aluminium SEM stub using double-sided adhesive carbon tape, carbon coated (Hitachi HUS-5GB High Vacuum Evaporator) and conductive carbon ink (Pasco Scientific, Roseville, California, USA) used to connect the resin-filled slots to the SEM stub to increase grounding.

Scanning Electron Microscopy Energy-dispersive X-ray Spectroscopy (SEM–EDS) was used to investigate the composition of each layer in the paint cross-section using a linescan mode. The linescans, as well as images, were taken using an accelerating voltage of 25 keV, working distance of 10 mm, spot size of 5, and dwell time of 200  $\mu$ s, and spatial resolution of 0.1  $\mu$ m. The images were taken in backscatter mode to visualise and measure the layer structure, since brightness in the image using this detector is proportional to effective atomic mass. Secondary electron mode was trialled but images provided much less contrast as the sample surface was smooth. The SEM was also used to measure the thickness of the paint layers visible in the cross-section by measuring the distance between layer interfaces.

#### 3.3. FieldSpec 4.0 Hi-Res Spectroradiometer

Visible/NIR reflection spectra were also obtained using an ASD Inc. (a PANalytical Company, Boulder, Colorado, USA) FieldSpec 4.0 Hi-Res Spectrophotometer. The FieldSpec 4.0 is equipped with three detectors; one near-IR and two shortwave-IR detectors, for a total detection range of 350-2500 nm.

All reflection spectra were taken using the contact probe accessory and Spectralon® white reflectance standard as the 100% reflectance reference sample. Vehicle paint samples were placed flat on the laboratory bench and the contact probe held vertically so the aperture was fully in contact with the surface of the sample. Flakes were not used for these measurements; instead the vehicle panel was used intact. Care was taken to ensure that full contact of the probe and the sample surface was achieved.

#### 3.4. Reporting Spectral Data and Spectral Processing

Throughout this dissertation all infrared spectra are reported in absorbance units, rather than transmittance, because absorbance is more linear with concentration and thickness (Beer-Lambert relation). Additionally, absorbance units allow direct comparison between reflection and transmission spectra as each technique measures different sample-light interactions.

For transmission, conversion to absorbance units is simply a transform of the measured transmittance T into absorbance A [30]. Transmittance is measured as the fraction of incident light transmitted through the sample, using the power of light detected, and is often reported as a percentage (%T). Therefore,

$$T = \frac{P}{P_0} \text{ and } \% T = \frac{P}{P_0} \times 100$$

Where  $P_0$  is the power of the incident light and P is the transmitted power [30]. The fraction of light not transmitted is considered (in a simplified model ignoring scattering and reflection) absorbed. Hence, there is an inverse relationship between measured transmittance and absorbance allowing the interconversion of these functions via

$$A = \log_{10}\left(\frac{1}{T}\right) \therefore A = -\log_{10}(T)$$

For reflection, conversion between measured reflectance and absorbance is also achieved through a logarithmic relationship between reflectance (R) and absorbance [30, 36]. Reflectance is measured as the amount of light reflected from the surface of the sample compared to a 100% reflecting standard, usually a gold mirror. Therefore,

$$R = \frac{R_{sample}}{R_{standard}}$$

The relationship between measured reflectance and absorbance in a reflection measurement is similar to the above relationship for absorbance and transmittance in a transmission measurement. The relationship also allows the interchange of reflectance and absorbance units via

$$A = -\log_{10}\left(\frac{R_{sample}}{R_{standard}}\right) = \log_{10}\left(\frac{1}{R}\right)$$

Thus, reflection spectra are reported in approximate absorbance units,  $\log_{10}\left(\frac{1}{R}\right)$ . Consistency in reporting allows comparisons between spectra from different instruments.

#### 3.4.1. Refractive Index Data

Kramers-Kronig (KK) transformations were carried out on raw reflection spectra by the instrument software (OMNIC<sup>TM</sup>) and yielded approximate refractive index data across the spectrum. In some cases, applying the KK transform resulted in higher levels of contamination of the spectrum rather than correction. This is evidenced and discussed in further chapters (particularly section 4.5.2 Applying the Kramers-Kronig Transform).

#### **3.4.2. Coding and the Proposed Correction Sequence**

All other transforms on spectral data, or models of spectral data, were carried out using a correction sequence written by the author in MATLAB (The MathWorks, Natick, Massachusetts, USA) based on published methods (see section 6.2 The Proposed Correction Sequence and 6.3 Results of the Proposed Correction Sequence for application). The applied MATLAB code can be found with annotations in 9.4 Appendix 4 – MATLAB Code for the Proposed Correction Sequence.

#### 3.5. Sample Acquisition

Vehicle paint samples were sourced from three locations. The first was a sunroof installation company (Roofrack City, Gilbert Street, Adelaide, Australia), from the portion of the roof panel that is removed during the process of installing the sunroof. The second was from the rear bumper of cars, and the third was petrol hatch covers. Both the second and third group were sourced from wrecker's car yards (U-Pull-It, Lonsdale, South Australia). Where possible, the make, model, year of manufacture, vehicle identification number (VIN) and paint codes were recorded for cross-referencing.

From the larger sample pool, 25 samples were selected for a focus group to test the suitability of R-IR-MSP to vehicle paint analysis. Samples were chosen based on colour and sample size. Blue samples were chosen as it was hoped that the pigment copper phthalocyanine ( $C_{32}H_{16}N_8Cu$ , CuPc) would be visible in the spectrum if IR penetration through the clearcoat was achieved.
As much information as possible was retrieved and recorded for each sample from the focus group (Table 2). It is worth noting that all paints in the sub-set contain an effect layer.

Sample ID	Make	Colour Specifics	Manufacturing Year	Paint Code	Car Part	Substrate
CPS001	Toyota	Bright Blue	Nov/12	8H5	Roof	Metal
CPS002	Ford	Bright Blue	Jan/13	Unknown	Roof	Metal
CPS003	Ford	Bright Blue	Unknown	Unknown	Roof	Metal
CPS004	Toyota	Bright Blue	Jan/13	8T7	Roof	Metal
CPS005	Honda	Dark Blue	Dec/12	Unknown	Roof	Metal
CPS006	Holden	Bright Green	Feb/12	7465	Roof	Metal
CPS007	Jeep	Yellow Green	Jul/12	Unknown	Roof	Metal
CPS008	Holden	Peacock Blue	Jan/13	Unknown	Roof	Metal
CPS009	Ford	Dark Blue	Feb/12	ED	Roof	Metal
CPS010	Mazda	Mid-Blue	Nov/12	41B	Roof	Metal
CPS011	Ford	Peacock Blue	Jul/06	CF	Roof	Metal
CPS012	Hyundai	Royal Purple	Nov/96	Unknown	Rear Bumper	Plastic
CPS013	Hyundai	Med-Blue	Jul/93	Unknown	Rear Bumper	Plastic
CPS014	Ford	Bright Blue	Jan/14	KN	Roof	Metal
CPS015	Holden	Bright Green	Nov/07	609R	Roof	Metal
CPS016	Ford	Dark Blue	Feb/12	VN	Roof	Metal
CPS017	Holden	Bright Blue	May/11	608R	Roof	Metal
CPS018	Holden	Dark Green	Jan/14	103X	Roof	Metal
CPS019	Ford	Mid-Blue	1996	Unknown	Petrol Hatch Cover	Metal
CPS020	Daewoo	Peacock Green	1999	Unknown	Petrol Hatch Cover	Plastic
CPS021	Holden	Dark Green	1995	Unknown	Petrol Hatch Cover	Plastic
CPS022	Mitsubishi	Grey-green	1994	Unknown	Petrol Hatch Cover	Metal
CPS023	Ford	Peacock Blue	1994	Unknown	Petrol Hatch Cover	Plastic
CPS024	Holden	Dark Blue	1991	Unknown	Petrol Hatch Cover	Plastic
CPS025	Holden	Dark Green	Jul/14	Unknown	Roof	Metal
PMMA Flake & PMMA Cast	Standard	Colourless	2015	N/A	N/A	N/A

Table 2 - Information on paint samples in the focus group, including manufacturing information for the vehicle of origin

# **3.6. Sample Preparation**

All samples were cleaned with ethanol prior to any analysis. Cleaning was ensured that no contamination was present on the surface of the paint that might influence the spectra. Waxes and polishes are often present on car surfaces but this research (and dissertation) does not take them into

consideration when analysing vehicle paint samples. Ethanol was sprayed onto a Kimwipe® and then the surface of the paint sample was wiped clean.

With the exception of spectral acquisition on the ASD FieldSpec, all analysis was done on flakes of paint. Under an optical microscope, a scalpel was used to pry the flakes of paint off the vehicle substrate (metal sheeting) ensuring that all layers, including the primer, remained together after separation from the substrate. New flakes of paint were selected for each instrumental method.

## 3.6.1. Production of the PMMA Standard

The poly(methyl methacrylate) (PMMA) standards were cast in-house by dissolving PMMA powder (Sigma Aldrich, >95% PMMA, <5% toluene, molecular weight approx. 120,000 by gel permeation chromatography) in chloroform while stirring. After 20 minutes the solution was highly viscous and clear. The solution was then placed in a sonic bath for 20 minutes to remove bubbles and assist in final mixing. The PMMA solution was then poured into a circular rubber mould (26 mm diameter). The mould was placed in a 70°C oven for 3 hours to remove the chloroform. Once the chloroform was boiled off, the mould was left at room temperature to cure overnight. Once cool, the PMMA block was removed from the rubber mould. A flake of PMMA was taken from the edge of the mould where the PMMA had cured in a thin (<1 mm) film. The final block cast PMMA was 25 mm in diameter and 4 mm thick.

# 4. Spectral Comparison

As discussed above (see section 1.4.6 Advantages and Disadvantages of R-IR-MSP for more detail), R-IR-MSP holds great potential for forensic applications, but, despite all the possible advantages, R-IR-MSP analysis of vehicle paints is an acknowledged gap in published literature. The first aim of this dissertation is to document the reflection infrared spectral signatures of vehicle paints with comparison to other infrared spectroscopy techniques. In order to address this aim, this chapter will describe the reflection spectra of vehicle paints, compare these spectra to ATR, transmission and near-IR spectra, and then apply known models to the R-IR-MSP data. The observations are summarised at the end of the chapter.

Comparison of R-IR-MSP data to other infrared spectroscopy techniques allows for observation of any spectral differences that arise as a result of the measurement geometry rather than the chemical composition of the sample. Comparison to ATR spectra was made as ATR has been used in literature as a technique for classifying vehicle paints by the chemical composition of clearcoat formulations [20, 24] and as ATR is another reflection-based measurement geometry. Comparison to transmission was made to investigate the penetration depth of R-IR-MSP. Comparison to near-IR measurements was made in order to investigate what spectral information might be gained from extended range measurements and because the FieldSpec is another reflection-based instrument (see section 3.3 FieldSpec 4.0 Hi-Res Spectroradiometer for instrument information).

# 4.1. R-IR-MSP of Vehicle Paints

At first glance, the reflection spectra obtained on the Nicolet Continuµm FT-IR Imaging Microscope appear to show the major expected peaks in approximately the expected wavenumber locations. In particular, the carbonyl peak at approximately 1730 cm<sup>-1</sup> is present in most spectra. However, the reflection spectra obtained via R-IR-MSP are vastly different in appearance from usual infrared spectral patterns (Figure 20). The distortion of the peak shapes is particularly interesting.



Figure 20 - Reflection spectrum for CPS006 illustrating distorted peak shapes

Some spectra show sharp rises on the high wavenumber side of the peak (e.g. CPS003) with a more gradual fall on the low wavenumber side, whereas other samples are the opposite (e.g. CPS005) where the sharp slope occurs on the low wavenumber side of the peak (Figure 21). Similar peak shape distortions have been documented throughout the literature and sometimes corrected using the Kramers-Kronig transform if due purely to changes in refractive index [33, 60].



Figure 21 - Reflection spectra for CPS003 and CPS005 showing peak shape distortions

Some spectra also display what appear to be thin film interference patterns, characterised by high frequency oscillations in the baseline of the spectrum. These patterns are most obvious in regions of low absorbance and do not appear to distort the peaks themselves. There is no evidence of

shouldering or split peaks as might be expected if the oscillations from interference were constant across the regions of high absorbance.

Along with the high frequency, low amplitude oscillations in areas of low absorbance, many spectra also show a broad baseline oscillation. For example, CPS011 shows one large oscillation and CPS025 shows a peak and trough emphasising the oscillation style appearance of the baseline (Figure 22). The broad baseline oscillation has a similar appearance to an interference pattern, but with a much larger amplitude and lower frequency than thin layer interference effects usually display.



Figure 22 - Reflection spectra for CPS011 and CPS025 showing broad baseline oscillations

Another baseline distortion seen in many samples (generally the ones that do not show the broad oscillations) is what will be referred to as a 'jumping' baseline. CPS004 shows an essentially flat baseline in areas of low absorbance at the high wavenumber end of the spectrum but after the absorbance peak at approximately 1700 cm<sup>-1</sup>, the baseline does not return to the previous baseline absorbance value, shown as 0.75 absorbance units (Figure 23). Instead it stays higher, around 1 absorbance units at the absorbance peaks, then 'jumps' back down to 0.85 absorbance units in the low absorbance region between 3000-2000 cm<sup>-1</sup>. The baseline then 'jumps' up again to 1.2 absorbance units at 1800 cm<sup>-1</sup>. It does appear that regions of high absorbance (3800-2800 cm<sup>-1</sup> and 1800-600 cm<sup>-1</sup>) have a higher baseline than the areas of low absorbance, when considering peak height. There also appears to be a 'jump' in baseline around 4500 cm<sup>-1</sup> where there are some additional or possibly heightened peaks when comparing the reflection spectra to ATR. This same pattern and location of the baseline 'jump', areas of high absorbance, is present across many of the paint samples but there

does not immediately appear to be a correlation between the phenomena and the physical or chemical nature of the paint.



Figure 23 - Reflection spectrum for CPS004 showing the baseline 'jump'

Interestingly, while most samples only show one or the other of the baseline distortions, some samples appear to show both baseline distortions. CPS015, for example (Figure 24), shows a curving rising baseline, which is consistent with the baseline oscillation trends, *and* shows the 'jump' in regions of high absorbance. Close inspection of the spectra shows that many display a number of the different distortions together but often one effect is more pronounced than the others.



Figure 24 - Reflection spectrum for CPS015 displaying multiple baseline distortions

# 4.1.1. R-IR-MSP of the PMMA Standard

Since paints are complex, a more controlled sample was used to explore the effects of reflection. Use of a standard material is also an accepted method to test an instrument or technique. This approach was applied to R-IR-MSP using a poly(methyl methacrylate) (PMMA) standard. PMMA was chosen because vehicle paint compositions are predominantly polymer binders, of which methyl methacrylate is often a component [5]. PMMA is therefore an analogue of typical binders used in paints; importantly, the PMMA standard is also free of silica, plasticisers or other additives. The PMMA used is more than 95% PMMA with less than 5% toluene.

Two versions of the PMMA standard were created, one as a thick cast block and the other a flake of the cast material (see section 3.6.1 Production of the PMMA Standard for production information). The flake of PMMA produced a typical absorbance spectrum when analysed using R-IR-MSP (Figure 25). The spectrum is similar to the ATR and transmission spectra for the same sample.



Figure 25 - Comparison of reflection and ATR spectra for the flake PMMA standard

The flake PMMA spectrum shows a strong oscillating pattern in the baseline, is otherwise undistorted. An interference pattern is not unexpected as the thin flake is essentially a homogenous thin film.

Interestingly, the spectrum block cast PMMA has a very different appearance. It was expected that the thicker block would absorb more, demonstrating higher peak absorbance values than the flake sample, but what was observed was strong peak distortion. The PMMA cast showed the same peak shape distortions as the vehicle paint samples but much stronger than observed in any of the vehicle paint samples (Figure 26). The cast PMMA did not show any other distortions.



Figure 26 - Comparison of reflection and ATR spectra for the cast PMMA standard

The difference in the spectra of the cast and flake PMMA does indicate that the reflection effects in R-IR-MSP measurements are linked to the thickness of the sample and the relative levels of sample reflectance and absorbance.

#### 4.2. Comparison to ATR Spectra

The ATR technique allows direct measurement of the infrared spectrum of the clearcoat of a vehicle paint without dissection of the sample and has been used in literature as a technique for classifying vehicle paints by the chemical composition of clearcoat formulations [20, 24]. In order to assess the R-IR-MSP as a technique for vehicle paint analysis, and to identify what information might be gained from the resultant spectra, a comparison of the two techniques is required. ATR spectra obtained using the Smart Orbit ATR accessory were comparable to literature in terms of appearance, peak profiles and compositional information (when peaks were interpreted) [8, 24].

Unfortunately, as described above, the reflection spectra appear distorted and compositional information is difficult to discern. The distortions are much easier to see when comparing ATR spectra and R-IR-MSP spectra. It is clear from this comparison that practical interpretation of the spectra in the same way is impossible. In particular, the baseline distortions are more obvious, both the broad oscillations and the 'jumping' in high absorbance regions. It is also easier to see that samples with similar ATR spectra do not share similar reflection spectra, indicating that the distortions are related to sample or geometry characteristics, and not necessarily linked to clearcoat composition.

Peak shape distortions are also more obvious upon comparison to ATR spectra. Comparison makes it apparent that, along with peak shape distortion, the peak maxima appear to have shifted. CPS006, for

example, is heavily affected by peak shape distortions (Figure 27). The carbonyl peak is particularly affected and, in comparison to the ATR spectra, the peak maximum appears to have shifted to the high wavenumber end of the spectrum. Considering that the same sample has been analysed by both infrared spectroscopy techniques and therefore should be displaying the same compositional information, the peak shift must be a direct result of some reflection effect not related to composition.



Figure 27 - Comparison of reflection and ATR spectra for CPS006

Something else that becomes apparent upon comparison is that the relative peak heights are often different. CPS007 shows entirely different peak height ratios in the 4000-2500 cm<sup>-1</sup> region when comparing the peak heights in the ATR spectra with those in the reflection spectra (Figure 28). This could partially be the result of the 'jumping' baseline, but even if the baseline was corrected and flattened to match areas of low absorbance, the peak height ratios would remain dissimilar. The chemical explanation for different peak height ratios is differences in the ratios of the paint formula components. Since the compared spectra come from the same sample the distortions are changing the spectrum enough that the peaks and peak ratios are no longer representative of true chemical composition in the traditional way infrared spectra have been interpreted.



Figure 28 - Comparison of reflection and ATR spectra for CPS007

Many R-IR-MSP spectra also seem to show a new cluster of peaks (or at least a 'bump' in the spectrum) centred at approximately 4200 cm<sup>-1</sup> (Figure 29). It is possible that this is a feature of the basecoat or effect pigment layer, which would explain why the absorbance is not seen in the ATR spectra where light does not penetrate through to these layers (for information on ATR depth penetration see section 1.4.3 Attenuated Total Reflectance).



Figure 29 - Comparison of reflection and ATR spectra for CPS001

Comparison of reflection and ATR spectra might also shed some light on the 'jumping' baseline. The figure below (Figure 30) compares the reflection and ATR spectra for one paint sample where the ATR spectrum also appears to show some signs of a similar 'jumping' baseline to the reflection spectra. in

the ATR spectrum it appears that the higher baseline in regions of high absorbance could more likely be explained by poor resolution of the absorbance peaks from each other. Poor resolution of absorbance peaks could be exacerbated in reflection, and in combination with other reflection effects, result in a more extreme 'jumping' baseline appearance.



Figure 30 - Comparison of reflection and ATR spectra for CPS015

It is clear upon comparison of ATR and R-IR-MSP spectra that reflection spectra are simply not comparable to ATR spectra of the same vehicle paint samples. Instead, the comparison between techniques highlights distortions that are present in R-IR-MSP. While comparison between these techniques is not necessarily required in forensic analysis, comparison of the spectral data acquired using each technique allows for comparison of the techniques themselves.

Interestingly, ATR spectra must be corrected to adjust peak height ratios for the penetration ability of each incident wavelength. The evanescent wave in ATR has different penetration depths depending on incident wavelength and therefore, correspondingly, absorbance values need to be adjusted for the relative level of absorption possible. In spectral terms, peak heights are adjusted and therefore peak ratios are adjusted to be more accurate with regards to molecular composition. As a by-product, using the ATR correction makes ATR spectra much more comparable to transmission in terms of peak ratios. Therefore, there is a premise that incident wavelength and optical properties of the sample will interfere with interpretation of spectra and the ability to define spectra as a direct result of chemical composition and absorbance by molecular vibrations. This creates an interesting precedence for mathematical correction of spectra for optical effects, and has informed the research efforts reported here to interpret and correct R-IR-MSP spectra for reflection effects.

### 4.3. Comparison to Transmission IR-MSP

Reflection spectra, obtained on the Nicolet Continuµm FT-IR Imaging Microscope, and ATR spectra, obtained using the Smart Orbit ATR accessory, were also compared to transmission spectra, also obtained on the Nicolet Continuµm FT-IR Imaging Microscope, for the clear- and basecoats of the same paint samples. Since ATR only penetrates 1-2 µm into the sample, it was expected that the ATR spectra would be essentially the same as the transmission spectra for the clearcoats only. This expectation was met and can be clearly observed in direct comparisons of the ATR and clearcoat spectra (Figure 31).



Figure 31 - Comparison of ATR and transmission (clearcoat) spectra for CPS001

Reflection spectra were also compared to transmission spectra in order to further probe the reflection technique and possibly indicate the penetration depth of the incident IR light in R-IR-MSP geometry. If reflection spectra showed additional peaks, this would provide a further advantage to the reflection mode – the ability to gain information from two paint layers within a single IR spectrum. This is one possible advantage of R-IR-MSP over ATR. To determine if this does occur, direct comparison of the spectra measured by each technique is necessary.

Because the ATR and transmission spectra appear essentially the same, the distortions described above (in section 4.2 Comparison to ATR Spectra) hold true for a comparison of reflection and transmission micro-spectroscopy data. However, comparisons of the acrylic fingerprint region (1300-1000 cm<sup>-1</sup>) showed some additional complex results. Some paint samples, such as CPS010, show very similar spectra for both the clear- and basecoats, indicating that both layers have very similar binder formulations (Figure 32). But, some samples showed more distinct differences in formulation between the different paint layers. CPS006 shows different acrylic fingerprint patterns for the clear- and

basecoat in transmission (Figure 32). However, significant distortion, particularly distortions of the peak shapes, in the corresponding reflection spectrum make it impossible to tell if the reflection spectrum shows either pattern, or indeed, a resemblance to a complex sum of the two spectra.



Figure 32 - Comparison of clearcoat and basecoat transmission spectra for CPS010 (top) and comparison of clearcoat transmission, basecoat transmission and reflection spectra for CPS006 (below), with acrylic fingerprint regions shown on the right (spectra are scaled for comparison)

In comparison, the acrylic fingerprint region of the reflection spectrum for CPS013 is more reminiscent of the basecoat transmission spectrum than the clearcoat transmission spectrum (Figure 33). While there are distortions present in this sample, the distortions are less severe than in others where this was observed, so, it is possible that the incident infrared light could be penetrating both the clear- and basecoats and this could be contributing to the distortions in the resulting spectra. Additionally, this result increases the need to understand and correct for the spectral distortions, because, if a single reflection measurement can obtain information from deeper into the sample than ATR or transmission it could become a much more powerful forensic tool for vehicle paint analysis.



Figure 33 - Comparison of clearcoat transmission, basecoat transmission and reflection spectra for CPS013 (reflection spectrum scaled for comparison)

CPS011 is another interesting sample for reflection-transmission comparison (Figure 34). While the acrylic fingerprint region looks much the same for all spectra (some over-saturation in the basecoat spectrum resulting from sample dissection), there is a distinct peak pattern due to the pigment kaolin in the middle of the spectrum (3700-3600 cm<sup>-1</sup>). Interestingly this peak does not show in the reflection spectrum, which might contradict the hypothesis for deeper IR penetration in reflection. However, it appears that many of the distortions are wavelength (wavenumber) dependent and therefore penetration depth could also be similarly different across the spectrum for reflection.



Figure 34 - Comparison of clearcoat transmission, basecoat transmission and reflection spectra for CPS011 (reflection spectrum scaled for comparison)

In any case, the distortions must be understood and removed in order to properly assess the information present in the reflection spectra and to subsequently compare the reflection spectra to transmission spectra for the different paint layers.

The main difference between the transmission and reflection measurements is that transmission is a much less complex optical system than the reflection system in IR-MSP. All other factors are the same, as the same instrument, objectives and detectors are used for both measurements (for instrument information see section 3.1 3.1Thermo Nicolet FT-IR Spectrometer). Thus, the conclusion must be that the reflection system is contributing to the spectral distortions, rather than instrumentation or similar method discrepancies.

#### 4.4. Comparison to Near-IR Spectra

All IR-MSP and ATR measurements were conducted across the full spectral range from 7000-525 cm<sup>-1</sup>. In transmission and ATR spectra the extended range region (7000-4000 cm<sup>-1</sup>) showed no peaks and an essentially flat baseline. However, in R-IR-MSP additional peaks were observed around 4200 cm<sup>-1</sup>. These peaks have a distinct profile shared by all reflection spectra where these peaks are visible; the peaks present as a broad, low doublet, sometimes with additional smaller peaks between the two major peaks (Figure 35).



Figure 35 - Reflection spectrum for CPS015 (left) and close-up of the additional peaks (right)

In order to investigate these additional peaks, visible/NIR reflection spectra were obtained using a FieldSpec 4.0 Hi-Res Spectrophotometer and the extended range region compared across all measurement methods. The additional peaks were also observed in the NIR regions in the spectra taken on the FieldSpec spectrophotometer. Comparing the same region for both spectrometers indicates that the peak positions and profiles are very similar even without application of the correction sequence to R-IR-MSP data (Figure 36).



Figure 36 - Raw spectrum obtained on the ASD FieldSpec spectrophotometer (left) and a comparison of the additional peaks (right) for CPS015 (R-IR-MSP data scaled and offset for visual comparison)

The comparison indicates that these peaks are real and present in reflection spectra but not visible in transmission spectra, indicating that this region might present an interesting option for analysis and may not be as affected by the other distortions seen in R-IR-MSP. It is not clear why these peaks are observed in reflection measurements but not in ATR or transmission measurements (one reason could be optical path length differences), however, it does appear that R-IR-MSP might be able to provide more spectral data in the extended range.

#### **4.5.Comparison to Correction Models**

There are some simple and well-known corrections that can account for and remove undesired spectroscopic behaviours. Thin film interference is well modelled and can present with high frequency oscillations as observed in the reflection spectra of vehicle paints. The Kramers-Kronig transform is also well documented and accounts for anomalous line shapes in reflection spectra. Both of these models were applied to the vehicle paint R-IR-MSP data.

## 4.5.1. Thin Film Interference Modelling

In many cases, in the analysis of sample by IR spectroscopy, high frequency oscillations in the baseline of spectra are the result of thin film interference. In such cases, a constant frequency sine wave can be fitted to the oscillations and subsequently subtracted from the spectrum (for example [20, 47]). Subtraction removes the oscillations and corrects the spectrum for the effects of interference. However, in the case of the vehicle paint samples, high frequency oscillations in the R-IR-MSP spectra did not fit a sine wave and therefore subtraction was not an option. CPS003 is a prime example, where the low absorbance regions in the reflection spectrum show clear high frequency oscillations (Figure 37). Regions of low absorbance towards the low wavenumber end of the spectrum have higher amplitude oscillations than similar regions towards the high wavenumber end. The whole spectrum also showed a strong sloping baseline. Therefore, in order to fit a sine wave function of some description to the full spectrum, the function had to include a factor to adjust the slope of the wave

function, and a factor to adjust the amplitude of the oscillations across the spectrum. Several different wavenumber dependent functions were tried to see which best fit the amplitude decay and an inverse square function showed the best fit.



Figure 37 - Reflection spectrum for CPS003 showing high frequency oscillations in regions of low absorbance

Unfortunately, the modelling showed that the high frequency oscillations did not have a constant frequency across the spectrum. It is clear to see that the modelled sine function is in phase with the oscillations in one area and then completely out of phase in another. This is clearly illustrated in Figure 38, where the sine function and spectrum are in phase around 4900-4850 cm<sup>-1</sup> but out almost completely out of phase around 4700-4650 cm<sup>-1</sup>. The modelled sine function has a constant frequency across the spectrum, therefore, it can be concluded that the observed oscillations do not. It is possible that the oscillations are actually the addition of multiple interferences, although they also do not show distinct 'beat' patterns that would be observed as a result of the addition of sine waves of different frequency, so it is unlikely.



Figure 38 - Region of interest in the reflection spectrum for CPS003, highlighting the change in frequency of the high frequency oscillations in the baseline by comparison to a modelled sine function

Attempts to improve the fit of the sine function included trying sine-squared functions and adding in different additional constants and factors, but no changes to the function could be made which would model a fit where the frequency of the function changed as a function of wavenumber. Without adjusting for the changing frequency, subtraction of the sine function does not even approximate correction. Areas where the sine function is out of phase with the oscillations created addition rather than subtraction of the oscillations resulting in further spectral distortion (Figure 39). Absorbance peaks were also distorted by the subtraction rather than becoming clearer.



Figure 39 - Reflection spectrum for CPS003 fitted with a modelled sine function and the resultant spectrum when the function is subtracted from the spectrum

The same observations were made for the oscillations observed in the spectrum of the PMMA flake: the oscillations are not a constant frequency in wavenumber space (Figure 40).



Figure 40 - Reflection spectrum for a PMMA flake standard fitted with a modelled sine function

The key observation to come from the attempted modelling is that the oscillations do not match expected thin film interference pattern presentation, hence, an explanation for the frequency change across the spectrum needs to be made. If the reason behind the change in frequency of the oscillations with incident infrared wavelength can be uncovered perhaps the same explanation could yield further information on the other distortions in the reflection spectra.

The changing frequency of the oscillations is not representative of a thin film interference pattern as interference patterns create a constant frequency sine wave through a spectrum. Literature has shown this for as long as interference has been investigated, and the underlying reason for constant frequency interference patterns relates back to the refractive index of the material.

'Assuming the index of refraction, *n*, to be constant over a reasonably large region ... these fringes represent a constant frequency sinusoid in wavenumber space, and thus a single spike or "signature" in the interferogram space of a Fourier transform infrared (FTIR) system.' [47]

The high frequency oscillations in R-IR-MSP spectra of vehicle paints do not show a constant frequency sinusoid in wavenumber space so perhaps the underlying assumption is incorrect and the refractive index of the paints is not constant across the spectrum. Additionally, observations of the interferogram (including Fourier transforms and attempted subtraction with band-stop filters) do not

show a spike representative of the oscillations, supporting the supposition that the oscillations do not have a constant frequency and therefore the refractive index is changing across the spectrum.

Refractive index is also an important quantity in the relationship between sample thickness and the peak wavenumbers of the interference fringes. If the thickness of a layer is known then the appearance of interference fringes can be predicted using the mathematical relationship;

$$v_m = \frac{m}{2nd}$$

Where  $v_m$  represents the peak wavenumbers, m is an integer value, n is the sample refractive index and d is the layer thickness [47]. If the refractive index changes across the spectrum, prediction of the position of interference fringes, or indeed determination of the layer thickness from the position of the fringes is nearly impossible. At the very least, each end of the spectrum will deliver a different result.

Conclusively, the high frequency oscillations were found not to have a fixed periodicity or amplitude, therefore, simply subtracting a fitted sine wave to remove these oscillations, as has been done in literature [20, 24], is not an applicable solution. Such results indicate that perhaps the complications are due to the sample refractive index changing as a function of wavelength. Throughout the attempted modelling, it was also clear that the other reflection effects and distortions, particularly the peak shape distortions, were also affecting the fit of the sine function and altering the appearance of the spectrum beyond what is expected for thin film interference effects.

#### 4.5.2. Applying the Kramers-Kronig Transform

As mentioned above (see section 2.7.5 The Kramers-Kronig Transform for additional information), the Kramers-Kronig transform can be used to adjust the peak shapes of reflection spectra when peaks present with anomalous line shapes, including spectra obtained using R-IR-MSP instrumentation. Such methods have been used and documented throughout literature and the transform can be performed by spectral acquisition software without the need for external or post-processing. Therefore, the Kramers-Kronig transform was applied to all the distorted reflection spectra including the PMMA standard (Figure 41).



Figure 41 - Comparison of the reflection spectrum, ATR spectrum and Kramers-Kronig transformed spectrum for the cast PMMA standard

The correction almost completely addresses the distorted peak shapes in the PMMA reflection spectrum. However, it is interesting to note that the absorption index, one output of the transform, actually bares more resemblance to the spectrum than the corrected spectrum calculated by the transform (Figure 42). What is most interesting here is that the spectrum for the cast PMMA standard is fairly well corrected by the KK transform, indicating that the majority of the distortions here are reflection-based and therefore likely come from the surface of the sample. This observation indicates that the Kramers-Kronig transform might not be taking into account the full extent of the distortions in the reflection spectrum for the vehicle paint samples due to some additional effect and indicates the sample has both an absorptive and reflective nature.



Figure 42 - Outputs of the Kramers-Kronig transform for the reflection spectrum of the PMMA standard

If reflection and absorption are occurring at the same wavelength, then the transform performs as it has with the PMMA standard, that is, partially correcting but partially distorting the calculated spectrum. Thus, the Kramers-Kronig transform does not allow for the correction of the spectra of the vehicle paints or the PMMA standard as obtained by R-IR-MSP. This is further illustrated when looking at examples of the calculated spectrum for vehicle paint samples (Figure 43).





It has been reported and cited repeatedly throughout literature on R-IR-MSP (as well as discussions of transflection measurements) that samples with strong absorbance peaks in the infrared region are also subject to complex reflection effects whereby line shape distortions in the spectra result from

anomalous dispersion. As such, the absorptive and reflective line shapes are mixed and cannot be accurately converted into separate reflective and absorptive components as is necessary and described by the mathematics of the KK transform. Instead, there are residual dispersive shapes in the 'corrected' data [45]. Observations of the result of applying the KK transform the vehicle paint spectra indicate that vehicle paints are subject to the complex reflection effects that distort absorption peaks and show a changing refractive index relative to wavelength.

#### 4.6. Summary of Observations

A summary of the different effects and their presence in different samples can be seen below (Table 3). The table also gives comparisons to ATR and transmission spectra, with reference to the peak height ratios, the acrylic fingerprint region and, the presence of peaks at approximately 4200 cm<sup>-1</sup> that do not appear distinctly in the corresponding ATR or transmission spectra. Additionally, compositional information (usually easily visible in IR spectroscopy) might be hidden or distorted as well, because clearly resolved peaks in the defined locations for molecular vibrations are essential in order to correctly identify chemical composition using IR spectroscopy.

Importantly, the distortions in the spectra are reproducible across a sample and across different days. Initial investigations into spectral mapping using R-IR-MSP highlighted this reproducibility. The observation of such similar spectra across a sample does indicate that the effects observed are due to real phenomena and that the phenomena are linked to sample-specific characteristics. The literature seems to indicate that a simple correction of a number of well-described reflection phenomena should remove the distortions and allow useful analysis of spectral absorbance.

On the other hand, the reproducibility of the distortions indicates that reflection spectra might be comparable in terms of the extent or type of distortion, rather than the typical comparison of absorbance peaks. Thus, a greater understanding of the cause of the distortions might still allow R-IR-MSP to be used as a screening technique for the comparison of two samples but based on other sample characteristics, not just IR absorbance.

Sample ID	Peak Shape Distortion?	High Frequency Interference?	Broad Baseline Oscillation?	'Jumping' Baseline?	Additional Peaks at 4200 cm <sup>-1</sup> ?	Peak Ratios Different?	Acrylic Fingerprint Region Different? (1300-1000 cm <sup>-1</sup> )
CPS001	Minor	No	No	Yes	Yes	Yes	Yes
CPS002	Moderate	No	Sloping upwards	Yes	Yes	Yes	Yes - minor pattern changes
CPS003	Moderate	Yes - areas of low absorbance	Sloping upwards	Mild	Yes	Yes	Yes - minor pattern changes
CPS004	Moderate (asymmetry)	No	No	Yes	Yes	Yes	Yes - minor pattern changes
CPS005	Moderate (asymmetry)	Maybe - low absorbance region 2100 cm <sup>-1</sup>	No	Yes	Yes	Yes	Yes - minor pattern changes
CPS006	Major	No	No	No	Yes	Yes	Yes
CPS007	Moderate	No	No	Yes	Yes	Yes	Yes
CPS008	Moderate- Major	No	Single, broad spectrum curve	Yes	Yes	Yes	Yes - peak shapes also different
CPS009	Minor-nil	Maybe - low absorbance region 2100 cm <sup>-1</sup>	No	Yes	Yes	Yes	Yes
CPS010	Minor-nil	Yes - areas of low absorbance	Sloping upwards	Yes	Yes	Yes	Yes
CPS011	Moderate - Major	Maybe - areas of low absorbance	Single, broad spectrum curve	Yes	Yes	Yes	Yes - peak shapes also different
CPS012	Moderate	No	Possible	No	Yes	Yes	Yes
CPS013	Major	Yes - areas of low absorbance Possibly also affecting peaks lower than 1000 cm <sup>-1</sup>	No	Yes - 3000-4000 cm <sup>-1</sup> Peaks	Yes	Yes	Yes - peak shapes also different

#### Table 3 - Summary of the distortions observed in the analysed vehicle paint samples

CPS014	Moderate (asymmetry)	Maybe - areas of low absorbance	Single, broad spectrum curve	Yes	Yes	Yes	Yes
CPS015	Low-nil	No	Low value slope upwards	Yes	Yes	Yes	Yes
CPS016	Moderate -Major	No	Undulation	Yes	Maybe	Yes	Yes - peak shapes also different
CPS017	Moderate	No	No	Yes	Yes	Yes	Yes
CPS018	Moderate -Major	Yes - areas of low absorbance	Yes - sharp undulation	Maybe	Yes	Yes - fewer distinct peaks	Yes - peak shapes also different
CPS019	Minor-nil	Maybe - low absorbance region 2100 cm <sup>-1</sup>	No	Yes	Yes	Yes	Yes
CPS020	Major	No	Low value slope upwards	No	Maybe	Yes	Yes - peak shapes also different
CPS021	Moderate	No	No	Yes	Yes	Yes	Yes
CPS022	Nil	Yes - mid frequency interference	No - maybe slight downwards slope	Maybe – 1200 cm <sup>-1</sup> peaks	No	Minor differences	Yes - pattern changes
CPS023	Nil	Yes - areas of low absorbance	No	Mild	Yes	Yes	Yes
CPS024	Minor-nil	No	No	No	Yes	Yes	Yes - different patterning
CPS025	Major	Yes - areas of low absorbance	Maybe two undulations	Maybe	Yes	Yes	Yes - peak shapes also different
ΡΜΜΑ	Nil	Yes - mid frequency interference	No	No	No	Minor differences	No
PMMA Cast	Major	No	No	No	No	N/A	No - although peak shapes different

# 5. Reflection in Vehicle Paints

While the effects of reflection infrared spectral measurements have been investigated in other research disciplines (such as cell/tissue investigations [36]), these effects have not been documented in the literature for forensic analysis of vehicle paints. The second aim of this dissertation is to describe how vehicle paints act spectroscopically in R-IR-MSP measurements. To address this aim, this chapter will present a model for the reflection system of vehicle paints. The description of the reflection system begins with describing the physical and chemical characteristics of the sample, then using these characteristics to indicate the sample's internal reflection geometry and the possible beam paths once IR light Is incident on the sample surface.

Considering the distortions present in R-IR-MSP spectra of vehicle paints (see chapter 4 Spectral Comparison) it is important to investigate the reflection system of vehicle paints in order to understand and describe possible photo-physical phenomena responsible for these distortions. Some of the results indicate that the effects are wavelength dependent which could relate to a changing refractive index across the infrared spectrum. Other observations indicate that the thickness of the sample, or a similar characteristic, could be altering the relative proportions of reflectance and absorbance by the sample. Additionally, there are some samples which might have peaks corresponding to the basecoat beneath the clearcoat, indicating that penetration of the incident beam is much greater than that of ATR.

Documenting the reflection system will also allow proper assessment of the technique as a potential screening tool for the forensic industry. In order to assess the reflection system, it is important to revise what is known about vehicle paint samples; their physical and chemical characteristics and how these characteristics dictate the interaction of light and matter for vehicle paint samples. The properties of the samples will form the basis of the investigation into the spectroscopic behaviour of vehicle paints. A description of the reflection system for vehicle paint samples will by necessity be essentially qualitative. While a quantitative description with full mathematical modelling would ultimately be more desirable for these real-world samples, it is not necessarily helpful, or possible, at this stage to have a complete mathematical model for the reflection system as the qualitative description will allow for the application of existing models to vehicle paints. The scope of this dissertation focuses on a qualitative description to indicate what models are appropriate and applicable when considering the appearance of the raw reflection spectra in conjunction with the known characteristics of the sample and instrumentation.

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Additionally, quantification of the model is especially difficult for vehicle paints because not all the characteristics can be known or directly measured. For instance, the precise chemical composition of each paint sample is not known and the refractive index, possibly the most important characteristic of the paint samples considering the observations, cannot be directly measured. However, the refractive index can be approximated by considering the refractive index values of analogous pure materials (such as PMMA), or, by applying the Kramers-Kronig transform.

Scanning electron microscopy was used for initial measurements of paint layers and identification of the elemental composition of the lower layers and effect pigments. Unfortunately, samples on plastic substrates were not measured because the paint coating could not be easily separated from the plastic without being stretched and warped resulting in disfigurement of the layers. This was not an issue for reflection or ATR spectroscopy measurements as the samples could be used intact (i.e. with the substrate still present), however the sections of car were too large to be placed in the SEM. Attempts to remove parts of the sample resulted in distortions of the paint which meant any measurements taken through SEM imaging would not be representative of the layer structure. The samples with metal substrates were mounted as described (3.2 FEI Inspect<sup>TM</sup> F50 Field Emission Microscope (Scanning Electron Microscope)) and information on the layers and pigments was recorded as part of a sample catalogue. Layer thickness measurements were particularly useful for further modelling of the reflection system. The PMMA standard was not analysed using SEM as its composition, structure and morphology were known.

## **5.1. Sample Physical Characteristics (Morphology)**

Vehicle paints, as discussed above (see section 1.2 Vehicle Paint Layer Systems for more information), are usually several paint formulations layered on top of each other. The top layer is usually a thick clearcoat (all samples in this dissertation have clearcoats) without any pigments. The surface of the clearcoat is smooth, which gives the paint a glossy finish because scattering is reduced and visibility of the coloured basecoat is increased. The smooth finish also reduces scattering effects in spectrometry, indicating that a reflection or transmission spectrum should have negligible losses due to scattering.

Additionally, the surface of the sample is flat, not curved or undulating, indicating that it is not acting as a lens or similar. This is confirmed by looking through the eyepiece of the microscope before taking reflection spectra; the whole surface of the sample is in focus. Using the eyepiece, it can also be confirmed that the flakes of paint used to take reflection spectra are much larger than the spot size of the incident infrared light meaning that there are no edge effects to consider.

# **5.1.1. Layer Identification**

It was important to record the layer structure of each of the paint samples. The thickness of each layer was also measured so each sample could be compared. It was important to know the thickness of the clearcoat in particular to investigate the penetration depth of the incident IR light because, if peaks from the basecoat are seen in some reflection spectra but not others, this could be related back to the thickness of the clearcoat.

Layer identification via SEM imaging also allowed effect pigments to be visualised in the cross-section. Observations showed the effect pigments appear as flat flakes and are not homogeneously dispersed through the coating layer; some areas have more flakes than others, and the flakes are not all present at the same depth into the coating. However, most paints did show a distinct layer where the effect pigment was present, between the basecoat and clearcoat.

For several samples, the thickness of some layers was difficult to measure. It is possible that these samples were manufactured using the 'wet on wet' spray method where the basecoat is still wet when the next paint layer is applied. This would prevent a clearly visible interface of the layers from forming (Figure 44).



Figure 44 - SEM image of CPS002 indicating the indistinct layer interface between the basecoat and effect pigment layer which could be the result of 'wet on wet' application of the paint layers

As previously mentioned, paints on plastic substrates were difficult to measure using SEM, as the coating could not be separated from the plastic substrate. The exception was CPS013. In this sample, a flake of the coating was able to be removed as it appeared the bumper had been repaired multiple times. The repairs meant that the top coating system could be removed from the top of the sample with full layer system intact. The coatings below (possibly original coatings from factory) were not analysed as they could not be removed from the plastic substrate.

Imaging results also showed that the resin pulls away from the surface of the paint sample as it cures, leaving a 'bubble' around the paint sample. In some cases, this made the identification and measurement of layers easier as the start of the clearcoat was more easily observed.

The table below summarises the data retrieved form the SEM investigation of the paint layers (Table 4).

Sample ID	Layer System	Clearcoat Thickness (approx.)	Effect Layer Thickness (approx.)	Basecoat Thickness	Primer Thickness	
CPS001	Tricoat	49 µm	15 μm	36 µm	13.5 μm	
CPS002	Tricoat	53 μm	13 µm	28 μm (variable across the sample, basecoat + effect layer roughly constant at 40 μm)	26 μm	
CPS003	Tricoat	50 μm	10μm (variable across sample 4- 16 μm)	27 μm (variable across the sample, basecoat + effect layer roughly constant at 40 μm)	25 μm	
CPS004	Tricoat	32 μm	23 µm	30.5 μm	21 µm	
CPS005	Tricoat	29 µm	12 μm	36 µm	18 µm	
CPS006	Tricoat	50.5 μm	18 µm	57 μm	22 μm	
CPS007	Tricoat	55 μm	19 µm	75 μm	19 µm	
CPS008	Tricoat	62 μm	20 µm	47 μm	26 µm	
CPS009	Tricoat	52 μm	14 μm	38 µm	21 µm	
CPS010	Tricoat	37 μm	14 μm	14 μm (11-18 μm variable)	none	
CPS011	Tricoat	56 μm	14 μm	45 μm	none	
CPS012	Plastic substrate	Not measured				

#### Table 4 - Coating system identification and layer thickness measurements by sample

CPS013	Tricoat	163 μm	12.5 μm	72 μm, 83 μm, 5 μm, 60 μm and 59 μm (repaired sample)	none in analysed layer - multiple layers of basecoat and primer in bulk sample	
CPS014	Tricoat	52 µm	16 µm	33 μm	20 µm	
CPS015	Tricoat	39 µm	16 μm	46 μm	22 μm and 15 μm (two layers)	
CPS016	Tricoat	54 µm	13 µm	35 μm	25µm	
CPS017	Tricoat	65 μm	12 μm	43 μm	31 μm and 11 μm (two layers)	
CPS018	Tricoat	55 μm	13 µm	39 µm	30 μm and 7 μm (two layers)	
CPS019	Tricoat	38 µm	13 µm	28 µm	28 µm	
CPS020	Plastic substrate	Not measured				
CPS021	Plastic substrate	Not measured				
CPS022	Tricoat	30 µm	9 µm	14 μm	19 μm and 13 μm (two layers)	
CPS023	Tricoat? (triple clear coat?)	21 μm, 4 μm, 49 μm (70 μm)	11 μm	22.5 μm	none	
CPS024	Clearcoat/Basecoat?	30 µm	incorporated in clearcoat?	4 μm	28 µm	
CPS025	Tricoat (multiple clearcoat?)	10 μm, 21 μm, 44 μm (75 μm)	15 μm	35.5 μm	25.5 μm and 7.5 μm (two layers)	

# 5.2. Sample Chemical Characteristics (Composition)

While the exact chemical composition of each of the paint formulations is not known, vehicle paint formulations contain similar components that are reasonably well documented throughout literature (see section 1.1 Paint Composition for information on vehicle paint composition). The formulations are predominantly polymer binders, with some inorganic and organic pigments or additives present in particular layers. When considering a 'top-down' analysis of a paint sample (as in the R-IR-MSP measurements taken throughout this dissertation) each layer is essentially homogeneous and isotropic (at least on the domain of the infrared beam interrogating the spectrum), that is, there are no patches of higher concentrations of certain components compared to other areas (see section 2.3 Polarisation and Isotropy for more information on isotropy and homogeneity of vehicle paints). This indicates that the compositional spectrum should be the same across a sample and there should be no orientation effects.

There are two types of pigment that should be specially considered when looking at the composition of paint formulations from the point of view of their reflective characteristics in the infrared region: effect pigments and infrared reflective pigments. Effect pigments, predominantly coated mica or aluminium flakes, are designed to be reflective and will reflect infrared wavelengths as well as visible wavelengths. Additionally, the coatings on mica particles are very thin and could be a possible source of thin film interference (or similar) effects [7]. Some paint formulations also contain specially designed pigments that reflect infrared wavelengths as a mechanism for keeping the vehicle cool. Both of these pigment types could complicate the reflection system for vehicle paint formulations by introducing regions of high infrared reflection and altering the absorptive nature of the formulations.

Additionally, the densities of the different paint layers are important. At the interface of two media of different densities, incident waves are both reflected and refracted. If the incident wave is in the less dense medium and therefore the second medium is the denser medium, the reflected light undergoes a phase change of  $\pi$  radians (180°, or, half a wavelength). Therefore, there are two things to consider for vehicle paints. The first is that at every interface, refraction and reflection must be accounted for. The second, is that the relative densities of the different media at the interfaces must be known and a possible phase shift accounted for.

#### **5.2.1. Linescan EDX Results**

The compositions of the different paint layers were determined via a linescan across the sample crosssection. Some inorganic components of the pigments in the basecoat were identified. It is likely that the titanium is due to high levels of titanium dioxide used as both a coloured pigment and to make the paint formulations appear more opaque, covering the primers [5, 12]. In the table below (Table 5), elemental compositions are reported as measured on the SEM: elements reported in brackets showed low intensity peaks in the spectrum. In some cases. Two primer layers were present in the flake sample. For vehicle paints the first is usually a primer surfacer and the second is the electrocoat primer and therefore mostly zinc. The two layers are reported in the same column, with '1' representing the primer surfacer and '2' representing the electrocoat primer. In most cases the electrocoat primer did not flake off from the metallic substrate with the rest of the sample, probably due to its properties as a metal pre-treatment.

No copper pigments were observed in the EDX results; however, it is possible that the signal from the copper pigments was very low in comparison to the titanium signals. Carbon is not reported in the table as organic binders are prevalent throughout all paint layers and this information does not add to the understanding of the system. However, it can be seen in the linescan results that the carbon

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content is high in the clearcoats and lower in comparison to the metallic elements in the basecoats, indicating the high pigment loading.

Linescans were also used to determine the type of effect pigment in the coatings by looking at the elemental composition of the effect pigment flakes (Table 5). Most samples showed only aluminium peaks across effect pigment regions which indicates aluminium flake was used as a reflective pigment, offering a metallic finish. The presence of silicon and aluminium peaks indicates mica was used to create a pearlescent finish. Additional metallic elements present alongside the silicon indicate that the mica was coated with a metal oxide, which may introduce another layer to investigate in the reflection system.

Sample ID	Effect Pigment Composition	Effect Pigment Type	Basecoat Composition	Primer Composition	
CPS001	Al	Al Flake	Ba, Ti (Si)	Ba, Ti, Si, Al,	
CPS002	Al, Ba, Si, Ti (Fe)	Coated Mica	Ba, Ti	Fe, Zn, P,	
CPS003	Ti, Al, Si	Coated Mica	Ba, Ti	Si, Al, Ti	
CPS004	Al	Al Flake	S, Ba, Ti	Al, Ba, Ti, Si	
CPS005	Si, Al	Coated Mica	S, Ba, Ti	Si, Ba, Al, Ti	
CPS006	Si (Al, Ti)	Mica	Ba, Ti, S	Ba, Ti	
CPS007	Al, Fe	Al Flake	Ba, Ti	Al, Si, Ba, Ti	
CPS008	Si	Mica	Ba, Ti, (S)	Ba, Ti, S, (Si, Al)	
CPS009	Al	Al Flake	Ba, Ti, A, Si	Si, Al	
CPS010	Ti, Ba, Si, Al	Coated Mica	Ba, Ti, S	None sampled	
CPS011	Al, Si, Ti, Mg	Coated Mica	Ba, Ti, S, Si, Al	None sampled	
CPS012	Plastic substrate	Unknown			
CPS013	not scanned because too thick	Unknown			
CPS014	AI	Al Flake	Ba, Ti, (S, Si, Al)	Si, Al	
CPS015	Al	Al Flake	Ba, Ti, (Si, S, Al)	1 - Ti, Ba, Si, Al, Fe; 2 - Na, Zn, Fe	
CPS016	Al, Ba, Si, Ti	Coated Mica	Ba, Ti, (S)	Si, Al	
CPS017	Al, Ti, Ba	Al Flake	Ba, Ti	1 - Ba, Ti; 2 - Fe, Zn	

 Table 5 - Compositional information on each sample analysed using SEM, brackets indicate low intensity peaks in EDX spectra

CPS018	Ti, Ba, Si, Al	Coated Mica	Ba, Ti, (S, Si)	1 - Ba, Ti; 2 - Fe, Zn		
CPS019	Al	Al Flake	Ba, Ti, S	Ba, Ti, Si		
CPS020	Plastic substrate	Unknown				
CPS021	Plastic substrate	Unknown				
CPS022	Al	Al Flake	Ba, Ti, (Fe, S)	1 - Ba, Ti, (Si); 2 - Fe, Zn		
CPS023	Al	Al Flake	Ba, Ti, Cl (Si)	None sampled		
CPS024	Al (in clearcoat layer)	Al Flake	Ba, Ti	Ba, Ti, S, Si, Al		
CPS025	Al	Al Flake	Ba, Ti (S, Si, Al, Fe)	1 - Ba, Ti (S, Si, Al); 2 - Fe, Zn		

### 5.3. Simple Reflection Model

Considering what is known about vehicle paint sample characteristics, the reflection and spectroscopic behaviour of the samples could be quite simple. This is especially pertinent when considering thicknesses of samples where complex photo-physical phenomena have been observed and reported in literature (see section 2.9 Sample Thickness for more information). Since the clearcoat of the vehicle paint is very thick relative to the wavelength of the incident infrared light it is not unreasonable to expect that the incident infrared light would not be able to penetrate very far into the sample. If this were the case, the majority of the detected light would be reflected light from the sample surface with attenuation due to absorption. Optically thick samples may also produce spectra where the reflection signal is quite low, depending on the amount of light that was not reflected and instead lost to the spectrum, decreasing the amplitude of peaks and causing poor signal-to-noise ratios. It would not be unreasonable to expect some scattering losses although these losses would be negligible given the smooth surface of clearcoats. Such a reflection system is illustrated below in Figure 45.



Figure 45 – Simple reflection model indicating low penetration of the incident infrared beam into the clearcoat

If such a simple model were the case, it would then follow that the spectral peaks would be the result of absorbance due to vibrational modes present in the clearcoats and reflection spectra would be most similar to ATR spectra. From the observations above (documented in chapter 4 Spectral Comparison) it is clear that there are reflection effects distorting the reflection spectra which indicates that the appearance of the spectra do not support the model described above. Transmission measurements of the same samples (on the same instrument) do not show the same spectral characteristics of the reflection spectra, which indicates that the bulk sample properties are contributing. ATR spectra of the same samples also do not show the same spectral characteristics which indicates that light penetration into the sample of further than 2  $\mu$ m is contributing in some way.

Additionally, there is some support from the observations of the reflection spectrum for the cast PMMA standard (see section 4.1.1 R-IR-MSP of the PMMA Standard for further discussion). The peak shape distortions in this spectrum were easily corrected into a typical absorbance spectrum using the Kramers-Kronig transform. The cast PMMA standard is, in optical terms for infrared light, infinitely thick and therefore the signal contributing to the spectrum is almost exclusively due to reflection from the surface of the sample. Thus, the Kramers-Kronig transform works well because the spectral distortions are entirely due to reflection and therefore are well described by the Kramers-Kronig model. This does not appear to be the case for the vehicle paints, as their spectra are not well corrected using the Kramers-Kronig transform (see section 4.5.2 Applying the Kramers-Kronig Transform). Thus, the observations indicate that layers of intermediate thickness, not as thick as the

PMMA standard but much thicker than the nanofilms reported in literature (see section 2.9 Sample Thickness) appear to present anomalous behaviour and complex reflection systems.

# 5.4. Description of the Reflection System for Vehicle Paints

Observations and theory show that the reflection system of vehicle paints is complex. Rather than a simple case of reflection from the surface (with some attenuation due to absorption) there is evidence of a complex convergence of absorption and reflection. Additionally, the resultant reflection spectra and comparison to ATR and transmission spectra indicate there is likely to be additional reflection from areas of the sample other than the surface.

The reality of the way in which paints absorb and reflect light in the infrared region is highly complex and the beginnings of explanations and models are emerging in modern literature. The phenomena associated with such complex systems can be described through investigations into the physics of reflection and refraction, with special consideration to the wave nature of light (see chapter 2 Introduction Part II – Photo-physical Phenomena in R-IR-MSP for more information and a full discussion of photo-physical phenomena). For vehicle paints, it is important to first acknowledge the nature of the sample and the possible interactions of light with the sample before investigating which physical (or indeed photo-physical) phenomena might need to be considered.

Returning to what is known about the sample, if all expectations are removed, it is possible to follow a number of potential beam paths in order to visualise and represent the reflection system for vehicle paints. Once described, each path can then be rated on its merits – the evidence of the beam path in the spectrum and the likelihood of the path with reference to spectroscopic and wave theory. The various paths considered here are shown in the figure below (In order to reduce the complexity of the diagram, not all the possible beam paths are shown) (Figure 46). Much of the following discussion relies on theory which has been introduced in previous chapters (chapters 1 Introduction Part I – Vehicle Paint Analysis, 2 Introduction Part II – Photo-physical Phenomena in R-IR-MSP and 4 Spectral Comparison).



Figure 46 - Diagram representation of possible reflection beam paths overlayed on a SEM image of a typical vehicle paint sample

Initially, some light will be reflected from the surface, to travel directly to the detector (Path 0), while some light will be refracted into the clearcoat. The refracted light will experience some attenuation due to absorption when it meets a vibrational mode of the same energy and electric field orientation. Light not absorbed in the clearcoat could continue through the clearcoat to be reflected from the surface of an effect pigment. After reflection from the effect pigment, the light will travel back through the clearcoat, continuing to experience attenuation due to absorbance, before reaching the surface of the surface again. At the surface interface, refraction and reflection will occur again with refracted light exiting the sample to travel to the detector; this could be described as 'Path 1'. Reflected light will once again enter the sample and move through the clearcoat.

In some samples Path 1 might be slightly altered as the effect pigments are contained within their own clearcoat formulation. At the interface of the clearcoat and the effect pigment medium, reflection and refraction of the beam can occur again, resulting in refracted light travelling to reach the effect pigment and reflected light moving back through the clearcoat. This will be described as 'Path 1A'.

Considering again the path of the incident light, some light might move through the clearcoat and not meet with any effect pigment. This beam path will then encounter the interface of the clearcoat and the basecoat. At this interface some light will be refracted into the basecoat and some light will be reflected from this interface, to be transmitted through the clearcoat again before reaching the surface of the clearcoat again. At the surface, the beam will once again undergo reflection and refraction, with the refracted light leaving the sample to travel to the detector; 'Path 2'.
It is possible that the incident light could travel further through the sample after refracting into the basecoat to then meet the interface of basecoat and primer (Path 3), but at this point is it much more likely that any light penetrating this far will not have sufficient energy to reach the surface again; or, that the received signal from that deep in the sample will be very weak due to absorbance attenuation, scattering losses and reflection at the interfaces on the path back to the surface.

It is important to remember reflection and refraction will occur at each interface whether the light is travelling into or out of the sample. It is therefore possible to have a single beam path that shows multiple reflections within one layer ('Path 4' is one example of this). Successive orders of reflection and refraction will contribute complexity to the signal received at the detector by introducing multiple regions of interference and strong attenuation of the signal due to both absorption and energy loss. Additionally, it must be remembered that at each interface where light is incident on a denser medium than the one through which it travels, reflected light will undergo a phase shift of  $\pi(180^\circ)$ .

It is important when considering any of the above beam paths to take into consideration that each pass through a paint layer will result in further attenuation due to absorbance, meaning that any absorbance measured will be proportional to the thickness of the clearcoat multiplied by the number of passes (with some consideration for the angle of incidence and Snell's law of refraction). In addition to the possible paths of the incident light, there will be some losses due to scattering at the surface and points of reflection. Scattering at the surface is minimal as the clearcoat surface is smooth and has been polished at manufacturing but also wiped clean with ethanol prior to measurements. The layer interfaces are less smooth than the surface of the sample, especially in the cases of wet-on-wet application where the distortion of the lower layer is clear (Figure 47), so it is likely that there will be more signal loss due to scattering deeper into the sample. Losses from deeper in the sample will reduce the signal from these layers that can reach the detector and will also increase noise in the spectrum.



Figure 47 - SEM image of CPS002 indicating the indistinct layer interface between the basecoat and effect pigment layer which could be the result of 'wet on wet' application of the paint layers

The reality of the reflection system in vehicle paints is quite complex and there are a number of the described paths being travelled all at once which makes isolation and neutralisation of any of these factors just as difficult as interpretation of the resultant spectra. Consideration of the different possibilities is necessary and reporting of these possibilities is the only way to begin interpretation and understanding of the spectra with reference to known phenomena.

Considering the above possible beam paths, Path 1 is the most likely scenario. Path 1 is the path most similar to transflection as the effect pigments are designed to act like reflective mirrors. Path 2 is another likely scenario as the interface between the clearcoat and basecoat is a good candidate for a reflective interface as the basecoat is significantly denser than the clearcoat due to the increased pigment loading creating a dramatic change in the refractive index of the medium.

## 5.4.1. Transflection in Reflection

From the above considerations, it is clear that vehicle paints, investigated in a reflection geometry do not result in a detected signal that is purely reflection. It is also clear that the detected absorbance is likely to be the result of more than one 'transmission' pass through the sample. Such a signal is much more reminiscent of 'transflection' measurements, where thin samples are mounted on reflective substrates to deliberately cause the incident light to pass through the sample, reflect from the substrate and then pass through the sample again before reaching the detector.

The reflection measurements made for the vehicle paints in this dissertation appear quite similar to some transflection measurements and artefacts reported in literature (see chapter 2 Introduction Part II – Photo-physical Phenomena in R-IR-MSP for a full discussion of photo-physical phenomena). Considering the different beam paths described above (Figure 46) it is clear that many of them, particularly Paths 1 and 2, which are also the most likely, include a first pass through the clearcoat, followed by a reflection followed by a second pass through the clearcoat – highly reminiscent of the transflection measurement. For metallic paints, effect pigments are also likely to contribute to reflection complexities as these pigments have highly reflective surfaces.

The reflection system for vehicle paints only mimics a transflection measurement, because the sample itself is responsible for the reflection. In this way, the transflection artefacts are less 'contamination' and more a true representation of the sample. However, the spectra are not a traditional representation of the sample composition with respect to vibrational modes and are influenced by the sample structure and the photo-physical phenomena that occur with the complexities of the reflection system.

## 6. Photo-physical Phenomena and Vehicle Paints

It is clear that the reflection system for R-IR-MSP measurements of vehicle paints is complex due to both the composition and morphology of the samples. Additionally, each of the potential beam paths through the sample shows several regions where complex interactions between reflection and refracting beams are possible. Many such interactions are the result of photo-physical phenomena that are also present in transflection mode measurements. Now that R-IR-MSP spectra have been observed and the reflection possibilities documented it is possible to address the third aim of this dissertation and identify photo-physical phenomena by comparing the presentation of such phenomena in literature and vehicle paint reflection spectra. Identification of such phenomenon can allow modelling and removal of the distortions resulting in clear absorbance spectra the development and subsequent application of a correction sequence is reported in the second portion of this chapter.

#### **6.1. Considered Phenomena**

Modelling of reflection effects is based heavily on optical theory and mathematical principles. The modelling approach is a long-term solution and will take far more research and precision to develop a widely applicable solution, particularly for samples of forensic interest. Determining a model from the mathematical principles requires a different approach than interpretations applied by the forensic scientist. Instead, the impact on the spectrum of the various phenomena known to occur in R-IR-MSP measurements is compared to the observed distortions in the spectra of vehicle paints.

#### **6.1.1. Thin Film Interference**

Thin film interference was previously discussed extensively with reference to the high frequency oscillations observed in the baseline of the reflection spectra of vehicle paints (see section 4.5.1 Thin Film Interference Modelling). Attempts to fit and subtract a sine wave, the presentation of thin film interference, were unsuccessful as the oscillations in the spectra do not have a constant frequency in wavenumber space [47]. Additionally, displaying the spectrum in wavelength (microns or nanometres) does not change the oscillations to a constant frequency. This observation does however, confirm the inference that the refractive index changes across the spectrum, i.e. with incident wavelength.

While the high frequency oscillations cannot be removed,  $v_m = \frac{m}{2nd}$  might still be applied to the oscillations in the region of best fit for a fitted sine function. For CPS003 the region of best fit is approximately 4900-4800 cm<sup>-1</sup> with two maxima at 4890 cm<sup>-1</sup> and 4809 cm<sup>-1</sup> (refer back to Figure 38). Using the average refractive index over this region (using the data from the applied Kramers-Kronig transform) indicates a thin film of thickness 27 µm is responsible for the oscillations. This thickness does not correspond to any of the measured layer thicknesses for this sample (refer back to Table 4) which belies the application of the thin film interference model to the data and indicates that either

thin film interference is not responsible for the high frequency oscillations or it is being compounded by additional factors.

Since thin film interference does not explain the presentation of the high frequency oscillations nor does it clearly correlate to a known film thickness in the samples, it appears that thin film interference is a poor explanation for the oscillations in R-IR-MSP of vehicle paints. Although many samples in the focus group for this dissertation display the high frequency oscillations in areas of low absorbance, it does not appear that these oscillations affect peak shapes or ratios in a significant way. For this reason, combined with the poor model correlation, the high frequency oscillations were considered of low importance compared to the distortions that prevent accurate identification of the chemical composition of the sample from the infrared spectrum.

#### **6.1.2. The Christiansen Effect**

Since pigments in vehicle paints are essentially suspended in the binder matrix, it is not unreasonable to consider the Christiansen effect might occur in vehicle paint spectra. However, initial observations show that the peak distortions in R-IR-MSP of vehicle paints do not manifest in the same way as the Christiansen effect. The Christiansen effect only alters absorption bands present across Christensen wavelengths, whereas the paint spectra show the majority, if not all, absorption bands present with distorted peak shapes. Additionally, it is difficult to identify the part of the paint sample that could be described as a crystalline powder. Potentially there could be crystalline pigments in the basecoats, or the mica effect pigments could be described as crystalline in some sense. However, paints with aluminium flake exhibit the same peak shape distortion and it is hard to identify a truly crystalline pigment from the IR or SEM-EDX spectra obtained.

#### 6.1.3. Mie Scattering

Spherical dielectric particles, of an appropriate dimension to scatter IR light, have not been observed in the vehicle paint samples investigated here. Therefore, although Mie scattering describes similar spectral artefacts, a discussion of Mie scattering has limitation in its practical application in this dissertation. One positive is the explanation for both 'positive' and negative' line shape distortions, but, this is can be corrected for by the same mathematical processes which correct for peak distortions due to anomalous dispersion (see below). Additionally, the characteristic baseline oscillations have not been observed in transmission spectra for individual paint layers. It is therefore unlikely that Mie scattering is the cause of the spectral distortions observed in R-IR-MSP data for vehicle paints.

## 6.1.4. Anomalous Dispersion

The distortion of the peak shapes in reflection spectrum is arguably the most important distortion to remove in order to accurately interpret the spectral information. Accurate peak shapes allow for

accurate identification of the wavelength of maximum absorbance for each peak which allows for accurate identification of the vibrational mode responsible for the absorbance peak. Additionally, accurate peak shapes, with symmetrical profiles reduce confusion in the spectral profile.

Anomalous dispersion presents in reflection spectra as an asymmetrical peak with a sharp change in slope around the wavelength of maximum absorbance. Most of the vehicle paint spectra show asymmetrical peak shapes and distortions that present with the same appearance as anomalous dispersion. It is highly likely that anomalous dispersion is the cause of the peak shapes as the vehicle paint samples experience changes in refractive index across regions of absorbance.

Mijkovic [45] reports that these effects have been observed in diffuse and specular reflection infrared spectroscopy, surface enhanced infrared absorption, infrared reflection-absorption spectroscopy from surfaces, ATR and transflection infrared measurements. It was also reported that dispersive peak shapes can also be due to sample morphology, as spherical and near-spherical particles can mix the reflective and absorptive peak shapes due to Mie scattering [64]. Such particles are not present in the morphology and composition of vehicle paint samples but, the correction for the mixed line shapes remains the same as the effect on the spectrum is still the mixing of reflective and absorptive line shapes regardless of cause.

## 6.1.5. The Electric Field Standing Wave Effect

Second to the peak shapes, the next most important distortion to correct is the relative peak heights. Relative peak heights can give indications of the quantity of each component in the sample formulation and observable patterns of peaks, or relative peak profiles, can provide conformation of the presence of certain chemical components.

With the effect pigment layer creating a metallic surface for reflection, and the paint layer interfaces offering additional surfaces for reflection, there is an opportunity for an electric-field standing wave to present and alter the appearance of vehicle paint spectra. The spectra also show differing peak height ratios when compared to the transmission spectra for the same samples. The electric field standing wave accounts for this as it is wavelength dependent based on the interference of the wave with thickness.

## **6.2.The Proposed Correction Sequence**

It is clear that there are a number of complex interactions and phenomena that can occur in reflection systems and complicate spectral measurements. The reproducibility of the reflection effects indicates that none of the major distortions described can be superficially subtracted and ignored in further interpretation; accurate modelling and understanding of the cause of the distortions is crucial for accurate analysis. In short, a 'cosmetic' approach is inadequate.

Since the reflection system of absorbing samples alters the measured spectra in ways that cannot be easily corrected by traditional methods, such as the KK transform, the literature has begun to document theoretical models and corrections based on the mathematics and optics of reflection. The most common approach is an algorithm that applies models of phenomena and then removes their influence from the measured spectra.

Correction approaches are good but often require knowledge of many sample parameters, such as layer thicknesses and refractive indices, that cannot be measured prior to the infrared spectra for forensically relevant samples. Vehicle paint samples taken directly from the bulk vehicle (such as in a forensic context) are, prior to dissection and measurement, almost completely unknown. Therefore, any type of correction or compensation must be done to the spectra post-collection and must be iterative or similarly manipulated by the user to model a closer representation of clearly resolved spectral data.

The application of a correction sequence allows application of the models for phenomena to investigate the suitability of the models as a compensation for observed phenomena. It also allows for clearer identification of phenomena based on the appropriateness of the transform.

The proposed correction sequence uses models of the known phenomena to approximate and remove the distortions in the spectra. The chosen corrections were applied as a result of comparing the known presentation of the photo-physical phenomena to the distortions in the reflections spectra of vehicle paints. There are three major steps in the sequence that correct the three major distortions, the oscillating baseline, the EFSW effects on peak ratios, and the anomalous line shape distortions. The baseline correction is applied before the line shape corrections in order to prevent the peak shape corrections from enhancing baseline features and overwhelming peak features. Performing the peak shape corrections (such as the rotation described in 6.2.3 Step 3 – Line Shape Corrections) on spectra prior to baseline corrections enhances distortions such as the 'negative peak' (which will be discussed below in 6.3.6 Rotation Distortions and the 'Negative Peak'). For similar reasons, the baseline correction follows the sequence reported in the referenced literature [51].

The proposed correction sequence is a manual and iterative process that is applied to individual spectra one at a time. As each sample has a unique composition and morphology, and therefore unique refractive index values and layer thicknesses, it is important to consider each sample

individually when applying any corrections. The correction values used for one sample will not be valid to use on a different sample. The observed distortions corrected by observing the visual match of each correction and adjusting the free parameters and scaling factors to obtain the closest fit and/or best adjustment. In particular, the characteristics of the carbonyl peak (approx. 1730 cm<sup>-1</sup>) were used as a guide for the necessary level of correction, similar to the method applied by Bassan, where the amide peaks were used to indicate suitability of correction [61, 64]. Sample thickness (as a parameter) was also adjusted to improve the fit of baseline and EFSW corrections. The applied MATLAB code can be found with annotations in 9.4 Appendix 4 – MATLAB Code for the Proposed Correction Sequence.

#### 6.2.1. Step 1 – Oscillating Baseline

Filik [51] mathematically describes an interference effect between upward reflected light from the top surface of the sample and from reflective surfaces in the sample (or the mirror surface in transflection measurements). The equation bases the effect on the spectrum as following the standing wave intensity on the surface and includes a scaling factor,  $b_0$ .

Baseline 
$$(\lambda) = b_0 \sin^2\left(\frac{2\pi nl}{g\lambda}\right)$$

The equation also takes into account the thickness of the absorbing layer l (the layer through which the light passes twice), the refractive index of the sample n, and the numerical aperture of the focusing optics g. Interestingly, it is also reported that the oscillation in the baseline of EFSW-affected spectra could be caused by scattering instead of interference, but the equation to describe that situation would be the same [51].

The correction sequence uses this baseline equation to model the broad baseline oscillations in the reflection spectrum and then subtracts the resultant curve to obtain a baseline corrected spectrum. Filik [51] indicates that the baseline is the result of the electric field standing wave intensity at the surface of the sample but concedes that similar interference effects would produce a baseline of similar appearance that could be modelled by the same equation. It is unclear if the broad baseline oscillations observed in the vehicle paint spectra are the result of the electric field standing wave, but it is clear through observation that these oscillations are not a standard sine curve and are dependent on the factors accounted for in the baseline equation.

The refractive index is approximated from the application and resultant outputs of the Kramers-Kronig transform. While the transform does not remove the distortions in the spectra, it does offer a wavelength dependent refractive index function. The baseline function using this refractive index is similar to the baseline function obtained using n = 1.5 (which is the approximate refractive index of

poly-methyl methacrylate, a viable model and a high composition component of the binders in vehicle paint formulations) but the fit obtained with the refractive index from the KK transform is actually a closer model for the oscillations in the baseline (Figure 48).



Figure 48 – Reflection spectrum for CPS011 with oscillating baseline function using the refractive index obtained from the KK transform (left) and reflection spectrum for CPS011 with oscillating baseline function obtained using refractive index of 1.5 as for PMMA (right)

#### 6.2.2. Step 2 – EFSW Contributions

Filik [51] recommends an equation for the EFSW contributions to the spectrum which is as follows:

$$A(\lambda) = a_0(\lambda) \left(\frac{l}{2} - \frac{\lambda}{8\pi n} \sin\left(\frac{4\pi n l}{g\lambda}\right)\right) \times [1 + R(\lambda)] \sin^2\left(\frac{2\pi n l}{g\lambda}\right)$$

The equation includes a parameter for optical geometry (the numerical aperture of the focusing optics) g, the thickness of the layer responsible for the EFSW, l, and an interference coefficient  $R(\lambda)$ . The equation can be applied to the data with  $a_0$ , a series of scaling coefficients, and n, the refractive index, as free parameters but wavelength dependent.

The correction sequence applies the EFSW equation with the refractive index obtained from applying the Kramers-Kronig transform. Since the EFSW effect is multiplicative, the baseline corrected reflection spectrum (from step 1) is then scalar divided by the EFSW equation, taking into account the wavelength dependence of the effect.

#### 6.2.3. Step 3 – Line Shape Corrections

Anomalous line shapes are corrected using a phase correction approach similar to that reported by Miljkovic [45]. The reported approach performs a Fourier transform on the spectral data to separate out real and imaginary components in interferogram space, then takes these components, zero-fills them separately, then performs a phase shift according to the following equation using a phase angle of  $\phi$ :

$$\binom{RE'}{IM'} = \begin{pmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{pmatrix} \binom{RE}{IM}$$

The correction sequence performs an inverse Fourier transform on the baseline and EFSW-corrected reflectance spectrum (as step 1 and 2) returning the spectrum to the interferogram space. Each component is then zero-filled by a factor of two (that is, the number of data points in the interferogram is doubled and the extra points are filled as zeros) before a forward Fourier transform back to the spectral domain. The real and imaginary components of the zero-filled spectrum are then separated out and the rotation performed as per the above equation. The correction rotates the spectrum through steps of  $\frac{\pi}{32}$ . The phase angle for each spectral correction is based on the appearance of the spectrum with special consideration to the symmetry of peaks, flatness of the baseline through the absorption regions and the appearance of the carbonyl peak. The angle is selected manually through visual comparison and then selected in the final iteration of the correction sequence. Both the resultant absorbance component and reflective component are observed. The new components are then recombined into the final 'corrected' spectrum.

#### **6.3.Results of the Proposed Correction Sequence**

Generally, the applied models for the photo-physical phenomena visually match the R-IR-MSP data well (particularly the baseline fit such as in Figure 48) and begin to remove distortions and reveal more familiar absorbance spectra. But some spectra display different distortions as a result of the sequence's adjustments. Visually, there are a number of differences that are easily categorised. Some of these differences are easily described and could be explained by reflection effects, but others are likely the direct results of the correction sequence steps. A summary of the changes and observed effects of applying the correction sequence to the R-IR-MSP data of the vehicle paint samples is provided below (Table 6) along with several described examples. Descriptions such as 'negative peak' and 'jumping baseline' are discussed in sections below. Peak shapes correction was assessed as observation of the shapes of individual peaks with special attention to the symmetry of peaks. Peak profiles were assessed as the overall relative peak appearances, observable patterns of peaks within the spectrum and the way the shapes of the peaks look relative to each other across the spectrum. All spectra are presented in appendices (Chapter 9 Appendices).

Sample ID	Ref	lection Spectrun	n	Correction Sequence Result							
	Peak Shape Distortion?	Broad Baseline Oscillation?	'Jumping' Baseline?	Peak Shapes Corrected?	Peak Profiles Corrected?	Rotation 'Negative Peak' Introduced?	Rising Baseline Present?	Comments			
CPS001	Minor	No	Yes	Yes	No	Yes	Yes	Acrylic fingerprint region profile very different before and after correction Rising baseline observed although no mica detected in effect pigment layer			
CPS002	Moderate	Sloping upwards	Yes	Yes	Yes	Yes	No	Peak profile much closer to ATR profile after correction The edges of the spectrum are particularly affected by rotation appear to curve upwards rather than flatten			
CPS003	Moderate	Sloping upwards	Mild	Yes	No	Yes	Yes	Symmetry of the carbonyl peak improved but peak profiles possibly more distorted			
CPS004	Moderate (asymmetry)	No	Yes	Yes	No	Yes	No	Peak height ratios better after EFSW correction but correction diminished after rotation Peak profiles remain broad but not dissimilar to ATR spectrum			
CPS005	Moderate (asymmetry)	No	Yes	Yes	No	Yes	No	Peak profiles remain broad which makes it appear that peaks have 'shoulders' after applying rotation in the correction sequence even though the symmetry of the peaks is much better			
CPS006	Major	No	No	Yes	Yes	No	Yes	Sloping baseline could be representative of mica absorbance Peak profile comparable to ATR spectrum			
CPS007	Moderate	No	Yes	Yes	No	Yes	Yes	Peak ratios (middle absorbance regions vs. acrylic/carbonyl absorbance region) are much better after EFSW correction but then distorted again by the rotation Peak profiles for 2000-1500 cm- <sup>1</sup> region is comparable but acrylic fingerprint region is not			
CPS008	Moderate- Major	Single, broad spectrum curve	Yes	Yes	Yes	Yes	No	Peak profiles are much better (see below for discussion) although peaks aren't fully corrected in terms of the peak shift, $\lambda_{max}$ is still high frequency side of the ATR peaks, and the acrylic fingerprint region is shifted Baseline noise enhanced above 6000 cm <sup>-1</sup>			

Table 6 - Summary of the effects of the proposed correction sequence on reflection spectra, compared to the distortions observed before application of the correction sequence

CPS009	Minor-nil	No	Yes	Yes	No	No	No	Peak shapes more symmetrical but the profiles are not much improved		
CPS010	Minor-nil	Sloping upwards	Yes	Yes	No	Yes	No	Curve in the baseline introduced by rotation but peak shapes are well adjusted and symmetrical after rotation Some improvement in the peak profile, some peaks have become clearer, however still very different to ATR spectrum		
CPS011	Moderate - Major	Single, broad spectrum curve	Yes	Yes	Yes	Yes	No	Very well corrected and looking much more like the ATR spectrum although peak ratios are still different and $\lambda_{max}$ is still just high frequency side of the ATR peaks Baseline undulation removed		
CPS012	Moderate	Possible	No	Yes	No	Yes	No	Lots of noise throughout the spectrum makes identifying the peaks for correction very difficult and also affects the capabilities of the rotation. The noise throughout is likely an artefact of the sample morphology, the sample was cut from plastic substrate and it is likely that this process has deformed the paint coating. Baseline undulation reduced		
CPS013	Major	No	Yes - 3000- 4000 cm <sup>-1</sup> Peaks	No	No	Yes	Yes	Carbonyl peak symmetrical after rotation although other peaks not so well adjusted Profile changed but not clearer High frequency interference pattern likely causing additional distortions through the absorbance regions		
CPS014	Moderate (asymmetry)	Single, broad spectrum curve	Yes	No	Yes	Yes	Yes	Carbonyl peak symmetrical after rotation although other peaks not so well adjusted Peak profiles clearer and more comparable to ATR spectrum		
CPS015	Low-nil	Low value slope upwards	Yes	Yes	No	Yes	Yes	Peak profiles remain broad but not dissimilar to ATR spectrum		
CPS016	Moderate - Major	Undulation	Yes	Yes	Yes	Yes	No	Baseline undulation removed Peak shapes and profiles comparable to ATR Noise at the edges of the spectrum enhanced after applying the correction sequence		
CPS017	Moderate	No	Yes	Yes	No	Yes	No	Peak profile clearer and closer to ATR spectrum profile after applying the correction sequence but not well comparable		

CPS018	Moderate - Major	Yes - sharp undulation	Maybe	Yes	Yes	Yes	No	Sharp undulation in the baseline adjusted Peak shapes and profiles corrected although $\lambda_{max}$ is still just			
CPS019	Minor-nil	No	Yes	Yes	No	Yes	No	Carbonyl peak symmetry corrected however other peaks remain broad and therefore difficult to directly compare to ATF spectrum			
CPS020	Major	Low value slope upwards	No	Yes	Yes	Yes	Yes	Baseline slope mostly corrected although rising baseline introduced Peak shapes and profiles adjusted and similar to ATR after applying the correction sequence			
CPS021	Moderate	No	Yes	Yes	No	Yes	No	Carbonyl peak symmetrical after application of the correction sequence but other peaks remain broad and $\lambda_{max}$ values are to the high frequency side of the ATR peaks Acrylic fingerprint region profiles remain different			
CPS022	Nil	No - maybe slight downwards slope	Maybe – 1200 cm <sup>-1</sup> peaks	No correction applied	No correction applied	N/A	N/A	The correction sequence was not applied to this sample as distortions were minor if present Peak profiles not too dissimilar to ATR spectrum			
CPS023	Nil	No	Mild	Yes	Yes	Yes	No	Peak profiles similar to ATR spectrum after application of the correction sequence although peak height ratios remain different Only minor rotation applied			
CPS024	Minor-nil	No	No	Yes	No	No	Yes	Baseline smoothed by fitting multiple oscillations in the baseline correction step Possible interference pattern more prominent after application of the correction sequence Peak profiles closer to ATR profile after application of the correction sequence although peak ratios still different			
CPS025	Major	Maybe two undulations	Maybe	Yes	Yes	Yes	Yes	Baseline partially adjusted, spectrum appeared well corrected after EFSW and baseline correction but heavily distorted again during rotation Peak shapes more symmetrical and peak profile clearer and similar to ATR			

# 6.3.1. Proposed Correction Sequence Results Comparable to ATR Spectra

Despite some difficulties there are some very good correction sequence results. Of the twenty-five vehicle paint samples in the focus group, there are six samples that, after the correction sequence was applied, displayed peak shapes and profiles very similar to their corresponding ATR and transmission spectra. All six samples, CPS006, CPS008, CPS011, CPS016, CPS018 and CPS020, displayed major or moderate-major peak shape distortions prior to correction (Figure 49 through Figure 54).



Figure 49 - Correction sequence result and raw reflection spectrum (right), and ATR comparison to the correction sequence result (left) for CPS006 (spectra scaled and offset for visual comparison)



Figure 50 - Correction sequence result and raw reflection spectrum (right), and ATR comparison to the correction sequence result (left) for CPS008 (spectra scaled and offset for visual comparison)



Figure 51 - Correction sequence result and raw reflection spectrum (right), and ATR comparison to the correction sequence result (left) for CPS011 (spectra scaled and offset for visual comparison)



Figure 52 - Correction sequence result and raw reflection spectrum (right), and ATR comparison to the correction sequence result (left) for CPS016 (spectra scaled and offset for visual comparison)



Figure 53 - Correction sequence result and raw reflection spectrum (right), and ATR comparison to the correction sequence result (left) for CPS018 (spectra scaled and offset for visual comparison)



Figure 54 - Correction sequence result and raw reflection spectrum (right), and ATR comparison to the correction sequence result (left) for CPS020 (spectra scaled and offset for visual comparison)

The baselines of the reflection spectra, prior to application of the correction sequence, for these samples are quite different, CPS011 and CPS016 display a single broad baseline oscillation (Figure 51 and Figure 52), CPS018 displayed sharp undulations (Figure 53), and still others show no baseline undulations at all (Figure 50 and Figure 54). It does not appear that there is any correlation that indicates why these six samples have well corrected peak shapes and profiles when the other samples were instead further distorted by application of the correction sequence. Additionally, despite well corrected peak shapes and profiles, there are other distortions in these spectra that are also present in poorly corrected spectra, such as a rising baseline (Figure 49) and peak shifts (Figure 50 and Figure 51).

#### 6.3.2. Absorbance Peak Profiles and Peak Ratios

None of the correction sequence results display absorbance peak ratios that are the same as in the corresponding ATR spectra. Generally, after adjustment for EFSW contributions, the peak ratios are much closer to the ATR and transmission spectra but rotation to correct the peak shapes alters these ratios again. This observation is not wholly unexpected as the peak ratios in the original reflection spectra were also different to ATR and transmission spectra. Importantly, peak ratios in ATR spectra are adjusted in post-processing to account for the penetration depth of the evanescent wave. It is possible that reflection spectra are similarly affected by a phenomenon separate to the EFSW and more akin to such penetration depth issues. Although the peak ratios are not fully corrected after applying the correction sequence, the absorbance peak profiles, the way the shapes of the peaks look relative to each other across the spectrum, are often much improved.

Although the same instrument is used for transmission and reflection IR-MSP, it is perhaps a simplification of spectroscopy to expect the two types of spectra to display the same appearance. While it is routine to apply a correction to ATR spectra to account for relative intensity differences compared to transmission spectra, there are still some observable differences between transmission

and ATR spectra, so it is not, perhaps, all that much of a leap to suggest that, due to differences in measurement, reflection spectra will not be exactly the same as ATR or transmission spectra. However, since spectroscopy is the interaction of light of known characteristics with a sample of interest and governed by the vibrational modes of the sample, the absorbance peaks should be qualitatively the same no matter the mode of measurement. Interestingly, Davis [34] has some insight into these spectral differences, concluding that 'since the instrument uses different optical paths for the transmission and transflection measurements, these two source spectra cannot be expected to be equal or proportional'. However, Davis makes it clear that spectral profiles should be qualitatively consistent after reflection effects are considered [34]. Despite this, a number of the samples in the focus group do not display corrected peak profiles after application of the correction sequence. This could be the result of unmodeled elements or variations in measurements, or a combination of the below discussed observations. Generally, the samples which do not display corrected peak profiles were the samples with broad and indistinct peaks in the acrylic fingerprint region combined with the 'jumping' baseline.

#### 6.3.3. Rising Baseline

After applying the correction sequence, ten samples display a rising baseline (Figure 55). The rising baseline displays as a flat baseline profile but with a linear increase in absorbance towards the high wavenumber end of the spectrum.



Figure 55 – Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for CPS024 (spectra scaled and offset for visual comparison)

This rising baseline could be due to mica effect pigments, which have been shown to produce a rising absorbance across the infrared region due to scattering losses [16]. However, only two of the ten samples displaying this rising baseline were also shown to contain mica when analysed using SEM-EDX. It is possible that there might be fumed silica in the paints that would also have scattering effects on the spectrum, and SEM results show this cannot be ruled out (see section 5.2.1 Linescan EDX Results for discussion of SEM results). It is therefore not clear what is causing this rising baseline.

Generally, the samples with the rising baseline did not have this clear rise after the baseline correction step of the correction sequence. The rising baseline is most pronounced after applying the rotation for anomalous dispersion correction, the correction which adjusts the asymmetry of the absorbance peaks.

## 6.3.4. Peak Shifts

While peak shapes are easily corrected by application of the correction sequence, the shifts in  $\lambda_{max}$  values are not so readily adjusted. When the peaks are rotated to correct for anomalous dispersion, which distorts peak shapes, the  $\lambda_{max}$  values are shifted in the direction of the sharp decline on the distorted peaks. For example, if the anomalous line shape displayed by an absorbance peak is characterised by a sharp rise on the high wavenumber side and a more gradual decline on the low wavenumber side, rotation will shift the  $\lambda_{max}$  of the peak towards the high wavenumber side of the peak. However, even excellent correction of peak shapes doesn't guarantee the  $\lambda_{max}$  will be shifted enough to match that of ATR or transmission spectra (Figure 56).



Figure 56 - Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for CPS010 (spectra scaled and offset for visual comparison)

The figure above shows the vehicle paint reflection spectra after application of the correction sequence for CPS010. It is clear that although the peak shapes are symmetrical, and the peak profiles are not dissimilar to the corresponding ATR spectra, the  $\lambda_{max}$  values for the peaks are still quite different. In particular, the carbonyl peak at approximately 1730 cm<sup>-1</sup> for the reflection spectra is somewhat to the high frequency side of the  $\lambda_{max}$  for the same peak in the ATR spectra.

## 6.3.5. 'Jumping Baseline' Revisited

Observations of the initial results (see section 4.1 R-IR-MSP of Vehicle Paints for initial discussion of results) showed a 'jumping' baseline in many of the vehicle paint reflection spectra. The 'jumping' baseline is characterised by an apparent rise in the baseline, where the peak heights do not come back down to the spectral baseline, in areas of high absorbance and numerous absorbance peaks. In the raw reflection spectra, the 'jumping' baseline is often accompanied by a higher baseline in the region where there are no absorbance peaks (3000-2000 cm<sup>-1</sup>), in comparison to the low absorbance region beyond 4500 cm<sup>-1</sup>. Comparison of the correction sequence results and ATR spectra indicate that the 'jumping' baseline is also often accompanied by broad and indistinct absorbance peak profiles (Figure 57).



Figure 57 - Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for CPS019 (spectra scaled and offset for visual comparison)

After application of the correction sequence, the 'jumping' baseline remains largely unchanged despite adjusted peak shapes. It is possible that the indistinct peak profiles point to the cause of the 'jumping' baseline; simple poor peak resolution in regions of high absorbance. Considering this hypothesis, it can be observed that the peak heights in corresponding ATR spectra also do not return to the baseline each time. Additionally, of relevance is that the peak intensity ratios in all reflection spectra are different from those observed in either ATR or transmission of the same vehicle paints.

## 6.3.6. Rotation Distortions and the 'Negative Peak'

The rotation which allows for the correction of peak shapes distorted by anomalous dispersion was perhaps the most obvious and necessary correction to be applied to the reflection spectra. It is therefore surprising that the rotation is also the source of two new distortions, one to the edges of the spectra and the other in the middle. Both of these distortions are direct results of the rotation and occur even if the other correction sequence corrections are not applied. Not all samples are distorted after rotation, and not all show both distortions, but the distortions are frequent enough and significant enough to be a strong limitation on the applicability of the rotation for anomalous dispersion correction. Additionally, the EFSW correction often adjusts peak ratios and profiles to be much closer to the ATR spectra; however, the distortions introduced by rotation then overwhelm the previous correction.

The first distortion is curving of the baseline at the edges of the spectrum and the second is the introduction of a 'negative peak', a large dip, in the middle of the spectrum, approximately 3700 cm<sup>-1</sup>. The 'negative peak' appears like a minimum in the spectrum that is then emphasised by rotation in the same way as the absorbance peaks. CPS007 is strongly affected by both of these distortions and this has limited visual comparison of the result of the correction sequence and the corresponding ATR spectrum (Figure 58).



Figure 58 – Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for CPS007 (spectra scaled and offset for visual comparison)

In comparison, CPS024 does not display the rotation distortions, although it does show the previously discussed rising baseline (Figure 59). Comparing the two samples shows that the reflection spectrum for CPS024 displays an upward curving baseline before rotation, particularly at the high wavenumber end, and the peaks in CPS007 are more asymmetrical than the peaks in CPS024. However, the angle of rotation required to adjust the asymmetry for both samples is actually the same. It seems that some samples are more prone to dramatic rotation effects than others, and neither the level of peak shape distortion nor the required angle of rotation are determining factors for the extent of these rotation effects.



Figure 59 – Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for CPS024 (spectra scaled and offset for visual comparison)

#### 6.3.7. PMMA Spectrum Correction

The reflection spectrum for the cast PMMA standard does not display any of the baseline distortions present in many of the vehicle paint reflection spectra. It does, however, show the peak shape distortions characteristic of anomalous dispersion (Figure 60). Because of these observations, the PMMA spectrum only underwent rotation to adjust the peak shapes rather than the whole correction sequence.



Figure 60 - Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for the cast PMMA standard (spectra scaled and offset for visual comparison)

After rotation, the resultant spectrum appears very similar to the ATR spectrum for the cast PMMA standard; the peak ratios are very similar as are the peak profiles. There are none of the additional distortions that were observed in the vehicle paint samples after rotation, but it is clear that the peak maxima ( $\lambda_{max}$ ) are not at the same wavelengths. It appears that the rotation corrects the peak shapes but does not ensure that the reflection spectra are then comparable to ATR or transmission spectra. It seems likely that, although the reflection spectra appear very similar to transflection spectra affected by the described photo-physical phenomena, there are additional considerations in reflection

that alter the spectra further and make comparison difficult even after adjustment for known phenomena.

## 6.3.8. Unique Case 1 – CPS022

CPS022 is a unique case among the vehicle paints investigated because the reflection spectrum for this sample is almost completely free of any distortion. When the reflection spectrum is compared to the corresponding ATR spectrum, one immediately obvious difference is the oscillations in the baseline that are characteristic of thin film interference (Figure 61). The oscillations are lower in frequency than those observed in regions of low absorbance for other samples but certainly significantly higher in frequency than the broad baseline oscillations also seen in other samples.





Upon closer inspection, it can be observed that the peak ratios are different, for example, the peak at approximately 3000 cm<sup>-1</sup> is much closer in height to the carbonyl peak (1740 cm<sup>-1</sup>) in the reflection spectrum than in the ATR spectrum. Additionally, the profile of the acrylic fingerprint region is quite different, although closer in profile than for many other samples.

Reviewing the sample characteristics does not reveal a significant difference between this sample and many others; the clearcoat is 30  $\mu$ m thick which is similar to measurements made on a number of other samples and the effect layer is 9  $\mu$ m thick, containing aluminium flake. Considering the EFSW theory, it is possible that the thickness of the reflective layer in this sample allows the surface to fall at a node in the EFSW and therefore enhances reflection rather than absorption leading to a clearer absorption spectrum after collection of the interferograms.

## 6.3.9. Unique Case 2 – CPS012

CPS012 is also a unique case as the reflection spectrum is heavily contaminated with noise (Figure 62). It is likely that the noise is an artefact of the sample morphology. Interestingly, CPS012 is a section cut from the plastic panel of a car bumper, so it is likely that difficulties in obtaining the required sample for microscopy have made a significant contribution to the appearance of the reflection spectrum. In order to place a sample of the paint flat under the microscope, a flake must be removed from the curved plastic. The nature of the plastic and adherence of the paint makes this quite difficult without distorting the paint. It is likely that this distortion has contributed to the difficulty in obtaining a clear reflection spectrum. Obtaining an ATR spectrum is somewhat easier, as the bulk sample can be placed on the instrument, and the key to a clear spectrum is contact of the sample surface with the ATR crystal.



Figure 62 – Correction sequence result and raw reflection spectrum (right) and ATR comparison (left) for CPS012 (spectra scaled and offset for visual comparison)

The low signal-to-noise ratio in the reflection spectrum makes it very difficult to easily identify absorbance peaks and to observe changes in the symmetry or profile of those peaks during correction. However, the rise and fall in the baseline is still very clear and this is revealed by the smoother, flatter baseline obtained after applying the correction sequence.

## 6.4.Sample Thickness

The baseline and EFSW corrections used in the correction sequence visually fit the R-IR-MSP data very well, and easily correct some of the distortions and spectral profile issues observed. The correction sequence relies on fitting models based on free parameters as well as measurable sample characteristics. The two main sample characteristics are refractive index and the thickness of the reflective layer. The value for sample thickness that produced the best baseline fit was then also used for the EFSW model. Since the thickness of the sample used for R-IR-MSP measurements is not directly measured, and the region of the sample responsible for reflection is not known, the thickness values used in the correction sequence were adjusted to obtain the best fit for correction. The thickness

values used were then compared to the paint layer thicknesses measured using SEM (see section 5.1.1 Layer Identification for SEM results and discussion) and reported below (Table 7). Because the infrared beam is incident at an angle, the path of the incident beam does not directly correspond to the thickness of the paint layers, and therefore Snell's Law has been used to approximate the experienced distance travelled by the incident beam, taking into account the widest and narrowest angles of incidence.

 Table 7 - Measured layer thicknesses (refer to Table 4 for more information) compared to the thickness values used to fit the baseline (highlighted) and EFSW contributions in the spectrum. For comparison, calculated path lengths using the angle of incidence (smallest angle and largest angle) and refractive index for PMMA (1.5). Data ordered by the correction sequence fit thickness

Sample ID	Clearcoat	Effect Layer	Basecoat	Correction	Clearcoat +	Clearcoat +	Snell's Law	Snell's Law	Snell's Law	Snell's Law	
	Thickness	Thickness	Thickness	Sequence Fit	Effect	Effect Layer	(clearcoat +	(clearcoat +	(clearcoat +	(clearcoat +	
				Thickness	Pigment	+ Basecoat	effect)	effect)	effect +	effect +	
							$\theta_i = 16^{\circ}$	θi = 35.5°	base)	base)	
									$\Theta_i = 16^{\circ}$	$\Theta_i = 35.5^\circ$	
CPS013	163 µm	12.5 μm	72 μm	200 µm	176 µm	248 µm	201 µm	424 μm	284 µm	599 µm	
CPS003	50 µm	10 µm	27 µm	210 µm	60 µm	87 µm	69 µm	145 μm	100 µm	210 µm	
CPS019	38 µm	13 µm	28 µm	210 µm	51 µm	79 µm	59 µm	123 µm	91 µm	191 µm	
CPS023	21 μm, 4 μm,	11 µm	22.5 µm	210 µm	85 µm	108 µm	98 µm	206 µm	123 μm	260 µm	
	49 µm (70										
	μm)										
CPS005	29 µm	12 µm	36 µm	220 µm	41 μm	77 μm	47 μm	99 µm	88 µm	186 µm	
CPS014	52 μm	16 µm	33 µm	225 μm	68 μm	101 µm	78 μm	164 μm	116 µm	244 µm	
CPS002	53 μm	13 µm	28 µm	235 µm	66 μm	94 μm	76 μm	160 μm	108 µm	227 μm	
CPS006	50.5 μm	18 µm	57 μm	235 µm	68.5 μm	126 µm	79 μm	166 µm	144 μm	304 µm	
CPS016	54 μm	13 µm	35 µm	235 µm	67 μm	102 µm	77 μm	162 μm	117 μm	247 μm	
CPS010	37 µm	14 µm	14 µm	240 µm	51 µm	65 μm	59 µm	123 µm	75 μm	157 μm	
CPS011	56 µm	14 µm	45 μm	240 µm	70 µm	115 µm	80 µm	169 µm	132 μm	278 µm	
CPS015	39 µm	16 µm	46 µm	240 µm	55 µm	101 µm	63 µm	133 µm	116 µm	244 µm	
CPS024	30 µm	incorporated in clearcoat?	4 µm	240 µm	30 µm	34 µm	34 μm	73 μm	39 µm	82 µm	
CPS001	49 µm	15 µm	36 µm	250 µm	64 µm	100 µm	73 μm	155 μm	115 µm	242 µm	
CPS004	32 µm	23 µm	30.5 µm	270 µm	55 µm	86 µm	63 µm	133 µm	98 µm	207 µm	
CPS007	55 µm	19 µm	75 μm	280 µm	74 µm	149 µm	85 μm	179 µm	171 µm	360 µm	
CPS017	65 μm	12 µm	43 µm	280 µm	77 µm	120 µm	88 µm	186 µm	138 µm	290 µm	
CPS020	Plastic substrate – not measured			280 µm	Unknown						
CPS008	62 μm	20 µm	47 μm	285 µm	82 µm	129 µm	94 µm	198 µm	148 µm	312 µm	
CPS018	55 µm	13 µm	39 µm	310 µm	68 µm	107 µm	78 µm	164 µm	123 µm	259 µm	
CPS009	52 μm	14 µm	38 µm	350 µm	66 µm	104 µm	76 µm	160 µm	119 µm	252 μm	
CPS021	Plastic substrate – not measured			390 µm	Unknown						
CPS025	10 µm, 21	15 µm	35.5 μm	435 µm	90 µm	126 µm	103 µm	218 µm	144 µm	304 µm	
	μm, 44 μm (75 μm)										
CPS012	Plastic substrate – not measured			820 μm		Unknown					
CPS022	30 µm	9 µm	14 µm	nil applied	39 µm	53 µm	45 μm	94 μm	61 µm	128 µm	

Comparing the thickness values used in the correction sequence and the calculated possible distances travelled by the incident infrared beam, it can be observed that the correction sequence values are most similar to the values obtained using Snell's law to calculate the path length experienced by an infrared beam incident at the maximum angle of incidence (35.5°) and penetrating the clearcoat, effect layer and basecoat of the paint sample. Therefore, the numbers suggest that the incident light penetrates into the basecoat and is possibly reflected at the basecoat-primer interface. However, this is not a conclusive deduction (nor is it necessarily logical) as the calculations and correction sequence model are limited.

Firstly, the thickness values calculated using Snell's law can only approximate the refractive index ratios using the refractive index for PMMA, 1.5. The correction sequence is also applied using a similar approximation, as the refractive index functions are obtained using the Kramers-Kronig transform, which is limited when applied to samples with absorbing and reflecting characteristics. Sample thickness measurements are also limited because, although the sample thickness can be measured and characterised by SEM, SEM cannot directly measure the same region as measured by R-IR-MSP. The two refractive index approximations could compound to create a larger discrepancy between the correction sequence values and calculated values, which is further compounded because the thickness values for the paint layers are not measured at the same place as the reflection spectra. It is also possible that these approximations are exacerbated due to the nature of the baseline and EFSW model mathematics applied in the correction. In both models, refractive index and thickness are combined as a single factor, optical path length. Therefore, any shortcoming in the refractive index function and values would necessarily be made up by the thickness value required to fit the models in the correction sequence.

#### **6.5.Discussion**

It is clear from the above observations that the proposed correction sequence and chosen models do have some limitations. While the EFSW model is a reasonably good correction for peak ratios and profiles, the rotation adjustment for anomalous dispersion is the most limited of the models. It is counterintuitive that the rotation, arguably the most obvious and easily confirmed model for correction of the most obvious and easily confirmed artefact of the R-IR-MSP measurement, is the one that causes further distortion. Because of the mathematics in the rotation model, there isn't a way of limiting the effect of the rotation on the rest of the spectrum and just applying it to the absorbance peaks – it is an all or nothing approach.

Measurements and approximations of the refractive index also remain a limitation that cannot be overlooked. It is almost impossible to obtain wavelength dependent refractive index information for vehicle paint samples due to the nature of the samples, and also the restrictions inherent in forensic science investigations. Perhaps the only way to avoid the limitation of these values is to model each known component of vehicle paint formulations and to attempt a calculation for refractive index based on the formulation proportions. Even with extensive research and modelling of the components of vehicle paints, it is likely that these limitations will not be overcome but only reduced. Similarly, the layer structure and morphology of the samples is not known, and can only be estimated.

Davis [34] also highlights the difficulties of unknown sample factors even with comprehensive modelling of IR-MSP instrumentation, indicating that unknown sample geometry complicates the process of 'inverting the developed model in order to estimate optical constraints of the sample directly'. Davis' conclusion is that further developing a model to describe reflection effects and to remove distortions in reflection spectra is made much more difficult as sample geometry must be co-estimated with the optical constraints of the sample, and, complementary to the above observations of refractive index estimations, further estimation compounds the limitations of such models.

Additional to the limitations of applied models, it is likely that there are other elements that have not been modelled, for example, it is known that thin film interference effects have not been corrected for. It is possible that, there are other effects and phenomena that are, as yet, unknown, and will need to be identified with further investigation into the reflection system for vehicle paints and the nature of R-IR-MSP measurements.

Despite limitations, one clear advantage is that some of these models do work well and therefore highlight that the observed distortions in the spectra are the result of real phenomena. ATR corrections set a precedent that different infrared spectroscopy techniques will result in spectra with different appearances, and corrections for well-understood differences can be accepted practise. The correction sequence demonstrates that it is possible to model and remove the effects of photophysical phenomena from reflection spectra. It is clear that the correction sequence is not yet enough to fully remove these effects, but it is a positive step towards developing reflection infrared spectroscopy into a technique for quick, non-destructive analysis of vehicle paints. If the phenomena are real and repeatable (as they appear to be when their spectral data are considered), even if only partially correctable, then the R-IR-MSP approach might still be a feasible first step in examining a questioned sample and comparing it to the control without having to dissect the individual layers and destroy evidence in forensic investigations.

## 7. Conclusions, Implications and Future Work

This dissertation has presented an investigation into the application of R-IR-MSP to vehicle paint analysis, culminating in a proposed correction sequence based on observations of photo-physical phenomena in reflection spectra. While the proposed correction sequence demonstrates that photophysical phenomena are present in R-IR-MSP measurements of vehicle paints, the results of the correction sequence show that the application of correction processes is not yet developed enough to fully remove the effects of these phenomena from the spectra. For the forensic science sector, there is still some work to be done before R-IR-MSP can be routinely used for vehicle paint analysis. Certainly, there are some positives; the baseline correction suggests interference is responsible for the lower frequency, high amplitude oscillations observed in the spectra and can easily be removed with a simple baseline fit and subtraction. Additionally, the thickness values required for the model supports the suggestion that R-IR-MSP measurements could penetrate into the basecoat and provide spectral information for multiple paint layers with a single measurement. The limitations of the correction sequence lie in the number of assumptions and estimations that are required in order to apply the modelled corrections.

## 7.1. Conclusions

The results presented in this dissertation will inform both the forensic science and defence industries of the complexities of R-IR techniques when applied to vehicle paints. This dissertation had three aims that have been achieved:

- 1) R-IR-MSP signatures of vehicle paints have been described and the observed distortions documented
- 2) A reflection system for vehicle paints has been described and is consistent with the morphology and composition of such samples
- 3) Photo-physical phenomena such as anomalous dispersion and electric field standing waves have been identified in R-IR-MSP measurements of vehicle paints based on the presentation of reflection spectra and the reflection system for vehicle paints

While not wholly successful, this dissertation also documents a proposed correction sequence which can be used as a basis for removing the effects of photo-physical phenomena from R-IR-MSP measurements.

In conclusion, this dissertation has opened up the realm of forensic trace evidence analysis to the complexities of photo-physical phenomena and suggested that understanding of the latter could lead to advances in the former. It has been clearly observed that the apparent distortions in reflection spectra obtained on IR-MSP instrumentation are the reproducible result of effects that can be

described and modelled as part of the complex reflection system. The reflection system incorporates the complexities of the instrumentation, the sample structure and the sample composition. Specifically, R-IR-MSP measurements of vehicle paints are complicated by the inclusion of effect pigments and the layered structure of such coatings. Despite this, it is still possible that with further investigation, the advantages of R-IR-MSP, such as its non-destructive nature and potential for basecoat penetration, could be used to the advantage of forensic investigations. Since the phenomena observed in R-IR-MSP have been shown to be real and repeatable, even if the effects on the spectra can only be partially removed, R-IR-MSP might still be a feasible first step in examining vehicle paint evidence without dissection. R-IR-MSP still offers this non-destructive advantage over ATR and transmission techniques.

#### 7.2. Implications for R-IR-MSP of Vehicle Paints

It is clear that approaching the use of R-IR-MSP from a forensic analysis point of view is very difficult. Since determining the chemical composition of a sample is a key part of the use of infrared spectroscopy, if spectral peaks are not in the positions defined by the energies of vibrational modes, the chemical composition cannot be correctly deduced (at least not from first principles using conventional reference to characteristic frequency tables or spectral databases). Similar issues in interpretation can be inferred with regards to peak height ratios, baseline distortions and interference patterns. For vehicle paints, the acrylic fingerprint region (1300-1000 cm<sup>-1</sup>) in particular is an area of high discrimination for clearcoat formulations [19, 24]. Distortions in this area make identification of paint formulations very difficult and lead to further complications when attempting vehicle classification. Furthermore, a desire to keep the paint sample intact limits the ability to measure sample parameters that are, at this stage, necessary for modelling of photo-physical phenomena. It is unlikely that the forensic approach, interrogating the spectrum of an unknown sample, will yield the secret of the complex spectroscopic interactions and thus yield to easy analysis. Therefore, laboratorybased forensic analysis of R-IR-MSP must still be approached with caution and there is further work to be done before this method can be used routinely for vehicle paint evidence, although there is support for the use as a screening and comparison technique to determine suitability for more involved analyses.

From this research, it is unlikely that R-IR-MSP would currently be recommended as a technique for the analysis of bulk vehicle paint samples in a forensic laboratory, especially considering there are viable alternatives currently being used. Currently, the difficulties in interpreting reflection spectra outweigh the advantages, such as the speed and non-destructive nature of analysis. However, in a defence or surveillance capacity, reflection is the only viable method of obtaining field, stand-off or *in situ* infrared spectra. For these applications, it will be necessary to continue investigating reflection

options. In particular, there is a need to investigate whether the phenomena observed in R-IR-MSP would manifest in a stand-off measurement scenario using similar optics. Furthermore, it would be important to investigate if these effects would be observable when considering the need to avoid regions of high atmospheric absorbance.

#### 7.2.1. Remarks on R-IR-MSP

Considering the above implications, the question now becomes, do the problems with interpreting R-IR-MSP spectra outweigh the advantages, or possible advantages, of the reflection mode? For chemical analysis, the answer would seem to be yes, especially if instrument geometry has an influence on the pattern. For any sort of cross-instrument or cross-laboratory comparison, the answer would seem to be yes. There are most certainly some real, practical concerns with continuing, or starting, to use R-IR-MSP for the analysis of bulk vehicle paint samples.

When turning back to the literature, some interpretations might also see this conclusion as the only option and determine that the use of R-IR-MSP is ill-advised. For example, Mayerhofer concludes that 'the use of reflectance absorbance must be strongly discouraged' [52]. However, these conclusions do not hold up to scrutiny from the perspective of vehicle paint analysis where transflection measurements are not the intention but similar photo-physical phenomena are the result of sample morphology (see section 5.4.1 Transflection in Reflection for discussion of vehicle paints mimicking a transflection geometry). Furthermore, such conclusions are mediated by statements requiring further investigation into the spectroscopic interactions and further development of instrumentation [34, 52, 61].

This dissertation argues that the investigation into the use of reflection spectra for forensic analysis of vehicle paints should not be abandoned, but implementation of R-IR-MSP in forensic casework should be approached with caution. While the forensic style approach (starting with the sample and interrogating the spectrum) is unlikely to yield the secrets of the complex spectroscopic interactions, pursuit of further understanding and knowledge is always of benefit. The interactions here are clearly highly complex but if understood could allow analytical chemists and forensic scientists to enhance their use of R-IR-MSP as a tool rather than to discard it, especially where transflection measurements (intentional or not) might be the only option. The reproducibility of the spectra presented in this dissertation indicates that there are genuine, sample-based phenomena responsible for the distorted appearance of reflection spectra. Since, fundamentally, spectroscopy is the study of the interactions of light and matter, it would be a poor reflection on spectroscopy research and the applied sciences to abandon these investigations.

## 7.3. Suggestions for Future Work

The results presented in this dissertation open up several areas of possible further research in the application of R-IR-MSP to vehicle paint investigations, particularly those of relevance to the forensic science sector. An empirical approach could allow for more accurate modelling and is beginning to present in literature, additionally, perseverance with application of correction sequences and photophysical modelling could result in a methodology for obtaining clear absorption spectra from R-IR-MSP measurements. Alternatively, working with the raw reflection spectra and applying chemometric analysis could lead to an alternative style of interpretation for R-IR-MSP where spectral characteristics would be used to differentiate paints, rather than chemical composition. Despite the challenges presented in this dissertation, there are still avenues of pursuit for R-IR-MSP and vehicle paint analysis.

## 7.3.1. Empirical Approach

The approach of the correction sequence is a hybrid of 'cosmetic' correction of reflection spectra in order to achieve a spectral appearance closer to that of ATR and transmission spectra, and the optical modelling approach which takes into account the optical interactions of the reflection system. While this approach is really the only one possible for the forensic sector, it is difficult to apply because there are so many unknown variables and models can only be chosen from the closeness of the fit to sample data. Considering the results of the correction sequence, it appears that there are more factors, or different phenomena, contributing to the appearance of reflection spectrum than have been accounted for thus far. An empirical approach would allow for modelling focused on vehicle paint samples.

An empirical approach would involve constructing samples and carefully controlling variables in order to observe phenomena occurring in reflection spectra. Interrogation of the spectral results as sample characteristics are altered might reveal the origins of spectral distortions and allow the development of corrections based on such empirical evidence. The parameters that an empirical approach might work with could be thickness of a single layer of PMMA, adjustments to the composition of a single coating, multiple layers with varied compositions, multiple layers with varying thicknesses, introduction of an effect pigment layer, thickness of a single coating above an effect pigment layer etc. There are innumerable combinations and parameters to investigate and each change is likely to lead to other investigations based on observations. Changing parameters slowly and carefully would allow for the observation of changes in the reflection spectra in order to directly observe the impact of sample characteristics, and combinations of sample characteristics and therefore used to create models of phenomena that can occur. For example, if increasing thickness results in a measurable change in peak ratios, thickness could be modelled with reference to a peak ratio variable and therefore spectra could be adjusted based on the model.

The empirical approach is likely to be the only approach that can definitively determine the cause and correction for the observed spectral distortions. Such approaches are beginning to emerge in the literature, but there is such a large number of parameters that this approach will take considerable time. Vehicle paints also complicate models with unique characteristics and compositions, most notably (in this dissertation) the effect pigment layer. An empirical approach for vehicle paints would be a unique investigation, particularly if achieved with reference to the needs of the forensic science sector.

## 7.3.2. Revision of the Proposed Correction Sequence

The correction sequence in its current form is not complete enough or widely successful enough to fully remove the distortions in vehicle paint spectra obtained through R-IR-MSP. The results presented in this dissertation are by no means definitive, and further work is necessary in order to ensure R-IR-MSP is a viable technique for the analysis of vehicle paints. There are three areas in particular that should be followed in order to continue working towards this aim. Firstly, it will be necessary to test and develop models for the reflection system using carefully constructed samples. Secondly, the correction sequence itself will need constant improvement in order to keep up with increased understanding of the photo-physical phenomenon contributing to the appearance of reflection spectra. Finally, application of chemometric analysis will be useful for the categorisation of reflection spectra and subsequent identification of vehicle information from paint samples.

The observations of post- correction sequence spectra show that there are limitations in the applied models (see section 6.3 Results of the Proposed Correction Sequence for discussion). Revision of the models applied to remove distortions, particularly the rotation correction for anomalous dispersion, will be a necessary first step in order to prevent further distortions post- correction sequence application. Further application of the correction sequence to a larger number of samples may also help to illuminate trends in both the presentation of distortions and correction requirements. A wider variety of samples could also be used to connect trends using a data mining approach, investigating the connection and grouping of phenomena. Such revision methods could also be used in conjunction with the previously discussed empirical approach.

Since the line shape correction employs a Fourier transform to transpose the spectrum back into interferogram space, use of the original interferograms from the instrument, rather than the resultant spectra, was considered. Using the interferograms in the correction sequence would remove any possibility of interference from the instrument processing procedures and bring the focus of spectral

assessment closer to the direct optical measurements. Use of interferograms was attempted in early iterations of the correction sequence but was abandoned due to the complexities of processing symmetrical interferograms and also a desire to adjust the spectral baseline before correction of peak shapes. However, this approach should not be entirely abandoned and may present a more suitable avenue for correction of the spectra in interferogram space.

Additionally, further development of the correction sequence to reduce user dependence and increase automation would also be a worthy avenue of pursuit. For example, future implementation could automate the determination of the best angle for rotation using analysis of peak position and peak shape.

## 7.3.3. Chemometrics

Situations were several different variables are measured for each sample result in large multivariate data sets [68]. Such large data sets can make it very difficult to easily identify patterns and relationships between samples. It would be possible to compare each variable separately, but that would be laborious, additionally representing the comparisons between variables graphically becomes difficult when it is necessary to look at more than two or three variables [68]. Software driven multivariate techniques, eliminate many of these problems and provide rapid, robust tools for data analysis.

Chemometrics are essentially methods of pattern recognition that use mathematical and statistical methodologies to extract chemical information from spectral data, allowing a statistical measure of how similar or dissimilar spectral data are. Chemometric approaches, such as principal component analysis (PCA), cluster analysis and artificial neural networks, can be used to group and compare spectra based on quantifiable similarities, eliminating subjectivity in spectral interpretation [68]. Principal component analysis has been used in a number of forensic and analytical chemistry applications in order to group samples together and assign categories. There are several notable examples of chemometric applied to vehicle paints in literature including the work by Maric [20], who classified vehicle paint samples according to ATR spectral features and was able to discriminate between different manufacturers using only measurable differences and similarities in the spectra. There is also a wealth of work by Lavine (for example, [29]) on combining chemometric approaches with spectral matching using libraries such as the paint data query database.

Unfortunately, the same spectral distortions that make reflection spectra difficult to interpret visually, also have an impact on statistical classification of the spectra. These distortions must be removed in order to reliably compare spectra based the spectral characteristics that are determined by chemical composition, such as peak shape, peak ratios and spectral positioning. This has been acknowledged

time and again in the literature, particularly for peak shape distortions which 'make an automatic analysis of spectral data sets (by multivariate techniques such as principal component analysis, PCA, or hierarchical cluster analysis, HCA) nearly impossible' [45]. Therefore, while chemometric analysis is vital to the progression of R-IR-MSP as a method for vehicle paint analysis, classification based on the chemical contributions to the spectra can only come after development of methods to remove spectral distortions.

In order to apply a chemometric analysis to corrected R-IR-MSP spectra, inter-sample variance would need to be thoroughly investigated, both in terms of the spectral variance (in samples and effects from the measurements) and the variance from correction. After this, chemometric approaches could be used to classify or group paints together. Chemometric classifications can be used to determine provenance of the sample, identify shared characteristics, or simply to compare samples to known classifications. Comparison to known classifications is particularly useful for surveillance applications where determining 'friend or foe' is often a key aim. Similarly, comparison to known classifications is useful in the forensic task of assigning unknown paints to groups such as make or model, where comparison to a suspect vehicle is not available.

Spectral distortions make chemometric analysis very difficult and would also mean that the differences between spectra are likely not based on composition differences in the paint formulation, but instead on comparison of the distortions. It would be an interesting avenue of investigation to accept this possibility and apply chemometric analysis to the raw reflection spectra. It is possible that this approach could allow for categorisation of the samples based on the extent of distortions rather than chemical compositions. Categorising the distortions might reveal more information on the factors that contribute to the distortions. However, while this type of grouping might be useful, the information could not be understood without a thorough investigation into the causes of the distortions.

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## 9. Appendices

Below are the raw spectra referenced and used in the results chapters of this dissertation. All data reported below was obtained by the author as part of the research conducted for the completion of this dissertation.



## 9.1.Appendix 1 - Transmission IR-MSP Spectra



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## 9.2.Appendix 2 - ATR Spectra

















# 9.3.Appendix 3 – Reflection Spectra (ASD FieldSpec)













### 9.4. Appendix 4 – MATLAB Code for the Proposed Correction Sequence

The following record of the correction sequence shows the final parameters used to analyse the reflection spectrum for CPS001. For details on the application of the sequence refer to section 6.2 The Proposed Correction Sequence. For information on the mathematics and photo-physical phenomena applied refer to chapter 2 Introduction Part II – Photo-physical Phenomena in R-IR-MSP and section 6.1 Considered Phenomena.

#### Step 1 – Importing Data

The correction sequence begins by importing the spectral data from a text file where the first column of data is the measured wavenumber value (in cm<sup>-1</sup>) and the second column is the corresponding absorbance value at that wavenumber. The refractive index (which is an output of applying the Kramers-Kronig transform to the spectrum) is also imported in the same way.

#### **%% import data**

```
% import data
% get file names
sample_file = uigetfile( '*.CSV', 'Select the sample spectrum');
refractive_index = uigetfile( '*.CSV', 'Select the sample refractive index');
% load the data
data{ 1} = xlsread( sample_file);
data{ 2} = xlsread( refractive_index);
% get wavenumber data
WN_SPEC = data{ 1}( :, 1);
% get spectrum intensity data
SPEC = data{ 1}( :, 2);
% get refractive index data
RI = data{ 2}( :, 2);
```

#### Step 2 – Define New Parameters

Once the data is imported, a number of new parameters are defined in order to perform the spectral corrections. Using the wavenumber data, the lambda values are defined by converting wavenumber to wavelength (measured in nm). Parameter 'n' is defined as the refractive index data. Parameter 'g' is the numerical aperture of the instrument (0.58 in the case of the Nicolet Continuµm FT-IR Imaging Microscope). The other correction parameters (intensity scaling factor 'b' and sample thickness 'l') are variables that are manually optimised to give the best spectrum upon review of the outputs of the correction sequence. The optical path length is defined by multiplying 'n' and 'l'. the final new

parameter is a 'zeroed' spectrum where the baseline is adjusted to 0 absorbance units by subtracting a chosen value from the spectrum (in the example 0.85 absorbance units).

```
%% define new parameters
% convert wavenumber data into wavelength (nm)
WL SPEC = (1 ./ WN SPEC) * 10000000;
% lamda is wavelength
lambda = WL SPEC;
% b is the scaling factor (describing the intensity of the oscillation)
b = 0.05;
% g is a parameter for optical geometry (from the numerical apperture)
q = 0.58;
% refractive index
n = RI;
% thickness (micron)
1 = 250;
% optical path length
nl = n * l;
% correct to zero spectrum
SPEC 0 = SPEC - 0.85;
```

### Step 3 – Correction 1 Baseline Subtraction

Once the new parameters are defined the first correction is applied. The baseline subtraction fits an oscillating baseline and subtracts it from the spectrum. The oscillating baseline is defined as 'baseline1' and calculated based on the mathematics defined by Filik et al [51]. If necessary, the calculated baseline ('baseline 1') can be 'zeroed' to align with the spectrum (this was not necessary in the case of CPS001 and therefore 'baseline' is equal to 'baseline1' plus 0). The baseline fit is then plotted for comparison. If adjustments are necessary Steps 2 and 3 of the sequence are repeated with the necessary adjustments to the values of the parameters until the fit and correction are acceptable. Once accepted for the baseline fit, the parameters are not changed again. The baseline corrected spectrum is then defined as 'BCSP'.

```
%% step 1 - baseline subtraction
%% based on Filik et al.
% removes oscillating background
% calculate baseline
baseline1 = b .* sin((2 .* pi .* nl) ./ (g .* lambda)).^2;
baseline = baseline1 + 0;
% subtract baseline from spectral data
BCSP = SPEC_0 - baseline;
% plot comparison and subtraction result
figure(1)
clf;
plot(WN_SPEC, SPEC_0, 'b-', WN_SPEC, baseline, 'r-', WN_SPEC, BCSP, 'g-');
legend( 'Instrument Spectrum', 'Calculated Baseline', 'Baseline Corrected');
```

#### Step 4 – Correction 2 EFSW Contributions

Two new parameters are defined before the EFSW contributions can be calculated ('R' and 'a'). These parameters are variables set by visually observing the changes in the spectrum after applying the EFSW correction. The EFSW contributions are calculated in two steps, separating out the equation into two components before calculating the EFSW contribution (defined as 'EFSW'). If necessary, 'EFSW' can be offset to match the baseline of the baseline corrected spectrum ('BSCP') and redefined as 'EFSW1'. The corrected spectrum is defined as 'CSPEC' and plotted for comparison to the baseline corrected spectrum. If necessary, the EFSW parameters are readjusted until 'CSPEC' is accepted. Accepting the spectrum here relies on adjusting relative peak heights with reference to the transmission and ATR spectra for the sample.

```
%% step 2 - remove EFSW contributions
%% based on Filik et al.
% removes contributions to absorbance from EFSW
% define EFSW components
R = 20;
a = 0.0000002;
a0 = a .* lambda;
% EFSW components
component1 = (1/2) - ((lambda ./ (8 .* pi .* n)) .* sin( (4 .* pi * nl) ./ (g .* lambda)));
component2 = 1 + (R .* (sin( (2 .* pi *nl) ./ (g .* lambda) ) .^2));
EFSW = a0 .* component1 .* component2;
% EFSW offset and divide
EFSW1 = EFSW + 0.8;
CSPEC = BCSP ./ EFSW1;
% plot division
figure(2)
clf;
plot( WN SPEC, BCSP, 'b-', WN SPEC, EFSW1, 'r-', WN SPEC, CSPEC, 'g-');
legend( 'Baseline Corrected', 'EFSW Contribution', 'EFSW Corrected');
```

#### Step 5 – Correction 3 Anomalous Line Shapes

Correcting the anomalous line shapes starts by taking the baseline and EFSW corrected spectrum ('CSPEC') and performing a reverse Fourier transform. The transformed spectrum is then zero filled and forward Fourier transformed back to the spectral domain to create a new spectrum ('NSPEC').

```
%% step 3 - correcting anomalous line shapes
%% based on Diem, Bird and Miljkovic
% line shape correction
% Reverse Fourier transform spectrum to 'IF' in optical path difference domain
SPEC_IF = ifft( CSPEC);
% Zero fill each 'IF' by a factor of two "i.e., zero filling until the
%interferogram is twice it's original length"
SPEC_IF_a = SPEC_IF;
SPEC_IF_a( ( end+1) / 2 + 1):end) = [];
SPEC_IF_Z = padarray(SPEC_IF_a, [6715 0], 0, 'post');
% Forward FT the zero-filled spectra - back to spectral domain
NSPEC = fft(SPEC_IF_Z);
```

The new spectrum is then separated into real and imaginary components before it is passed through an iterative matrix rotation. The rotations are plotted which allowed the best rotation angle to be chosen visually.

```
% Perform phase correction (rotation) to recombine real and imaginary components
 % define vectors
 Re = real(NSPEC);
 Im = imag(NSPEC);
 % define angles and choose range
 angs = 0:( pi / 32):( 2 * pi);
 % set up for display
 figure(10)
 clf;
 % phase rotation loop over all angles
\Box for i = 1:numel( angs)
     % choose the angle for this iteration
     ang = angs( i);
     % rotation the fourier data
     Ren = (Re .* cos(ang)) + (Im .* sin(ang));
     Imn = (-1 .* Re .* sin(ang)) + (Im .* cos(ang));
     % prepare to plot
     index final = linspace( 0, 1000, numel( Ren));
     % plot result
     plot( index final, Ren, 'r-', index final, Imn, 'g-')
     legend( { 'reflectance', 'absorption'});
     title( sprintf( 'Angle = %0.2f', ang));
     pause
 end
```

Once an angle is chosen, the spectrum is corrected and the result ('RES\_SPEC') is plotted for comparison to the EFSW corrected spectrum.

```
% choose spectrum
theta = 2 * (pi/32);
CORR = (Re .* cos(theta)) + (Im .* sin(theta));
% Adjust to plot
RES_SPEC = real(CORR) * 2 + 0.04;
% plot corrected lineshapes
figure (3)
clf;
plot( WN_SPEC, CSPEC, 'b-', WN_SPEC, RES_SPEC, 'g-');
legend('Corrected Spectrum', 'Algorithm Result');
```

#### Step 6 – Plotting the final spectrum

The correction sequence result can then be plotted and compared to the instrument reflection spectrum. The spectra can also be scaled and offset for easy comparison on the same set of axes.

```
%% plot for thesis
RES_SPEC1 = RES_SPEC .* 1;
SPEC_01 = SPEC_0 .* 1.5 + 1.6;
figure1 = figure;
axes1 = axes('Parent',figure1,'XDir','reverse');
xlim(axes1,[525 7000]);
ylim(axes1,[525 7000]);
ylim(axes1,[0 3]);
box(axes1,'on');
hold(axes1,'all');
plot( WN_SPEC, RES_SPEC1, 'r-', WN_SPEC, SPEC_01, 'b-');
xlabel('Wavenumber (cm-1)');
ylabel('Absorbance (log(1/R))');
legend('Algorithm Result', 'Reflection Spectrum');
set(legend,'Location','NorthWest');
```

# 9.5.Appendix 5 – R-IR-MSP Spectra and Proposed Correction Sequence Results













