The Forensic Analysis of Counterfeit Pharmaceutical Packaging

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NEVILLE W BROAD

A Thesis submitted in partial fulfilment of the requirements for the Degree of Master of Chemistry of the University of Kent

The School of Physical Sciences
University of Kent
Canterbury CT2 7NZ

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This thesis describes research conducted by Neville W Broad at Authenticate Ltd., Sittingbourne, under the supervision of Michael Went and Stuart Gibson of the School of Physical Sciences, University of Kent. I certify that the research described is original and that any parts of the work that have been conducted by collaboration are clearly indicated. I also certify that I have written all the text herein and have clearly indicated by suitable citation any part of this dissertation that has already appeared in publication.

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Neville Broad

ABSTRACT

Pharmaceutical packaging is the coordinated system that encloses and protects a dosage form. Counterfeit drugs have caused deaths, and lead to the failure of public trust in the healthcare system and the pharmaceutical manufacturers. The authentication of packaging materials requires a trained forensic approach. Advanced instrumentation has become expensive, for example with hyper- and multi-spectral techniques, and multivariate data interpretation can be non-standard. There is always a need for rapid screening of suspect materials, particularly across market surveys where rapid, non-destructive determination counterfeits is required to segregate and allow further downstream forensic analysis.

The development of Fourier transfer infra-red (FT-IR) spectroscopy in the 1970's facilitated the rapid data capture and analysis of solids and liquids. Since then thousands of spectra are commercially available for identification purposes based on transmission and, more recently, attenuated total reflectance (ATR) analysis modes. ATR is a rapid technique requiring pressure exerted from a crystal onto a sample to create a spectrum. Specular reflectance is a third analysis mode that does not require such force to obtain a spectrum.

It was found that the ExoScan FT-IR in specular reflectance mode combined with a *similarity* identification algorithm was most successful for confirming the presence of counterfeit Reductil cartons. Results were in less than a minute with no damage inflicted on the suspect with this non-destructive technique. Results can be shown overlaid or stacked, together with a similarity (hit) value. The repeatability for a single control carton was 0.16% for six replicates.

The use of external reflectance FT-IR has been shown to be able to rapidly uncover counterfeit packaging materials, with the application of bespoke, easy to create libraries. The technique is non-destructive and especially suited to carbon based solids.

DEDICATION

I dedicate this thesis to my wife Karen and my beautiful daughters Hannah Xiuni and Lila Fu Yuan.

ACKNOWLEDGEMENT

I would like to thank Professor Michael Went and Doctor Stuart Gibson for academic supervision and direction. I would also like to thank Authenticate Limited for the funding of this MSc.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
API	Active Pharmaceutical Ingredient
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
CI	Confidence Interval
CV	Coefficient of Variation
DTGS	Deuterated Triglycine Sulfate
ED	Euclidean Distance
EMEA	European Agency for the Evaluation of Medicinal Products
EP	European Pharmacopoeia
FDA	Food and Drugs Administration
FFT	Fast Fourier transform
FIR	Far Infra-red
FT	Fourier transform
FT-IR	Fourier transform Infra-red
HeNe	Helium Neon
IR	Infra-red
KBr	Potassium Bromide
MCT	Mercury Cadmium Telluride
MHRA	Medicines and Healthcare Products Regulatory Agency
N/A	Not applicable
NIR	Near-infrared
RFID	Radio Frequency Identification
SNR	Signal to Noise Ratio
SSFFC	substandard/spurious/falsely-labelled/falsified/counterfeit
USP	United States Pharmacopeia
WHO	World Health Organisation
ZnSe	Zinc Selenide

CHAPTER 1 - INTRODUCTION

1.1 Background

The World Health Organisation (WHO) defines *a counterfeit medicine is one which is deliberately and fraudulently miss-labelled with respect to identity and/or source. Counterfeiting can apply to both branded and generic products and counterfeit products may include products with the correct ingredients or with wrong ingredients, without active ingredients, with insufficient active ingredients or with fake packaging.*[1]

Pharmaceutical companies currently spend one-third of all sales revenue on marketing their products - roughly twice what they spend on research and development. Counterfeiters do not need to invest in research, rapidly bringing their dangerous copies to the unregulated internet market place. As a result of some pharmaceuticals being expensive, or not readily available, an uneducated portion of the human population are tempted to avoid the legal prescription route and instead purchase drugs via the unlicensed routes, most notably the internet.

Packaging materials provide a protective barrier and instructive purpose for the pharmaceutical product. There is much thought devoted to the design complexity of the pharmaceutical pack and the marketing of the product by the brand owner. Since the pack is the most recognised and first encountered feature of a pharmaceutical product, it is therefore the most counterfeited part of the entire product. Counterfeiters invest most effort and investment in mimicking the pack to try to fool the customer (including the doctor and patient).

The decentralization of the pharmaceutical industry in terms of manufacturing and the emergence of the small-scale personal care industry reduces the manufacturer's control on the supply chain and increases the probabilities of counterfeiting. However, the advancement in track-and-trace technologies and increasing practices of multi-layered authentication technologies have brought revolutionary changes in securing original products. Companies with a premium range of products are opting for radio frequency infrared detection (RFID) and electronic (e) Pedigree authentication technologies. Luxury product categories can be better secured with conventional authentication technologies such as holograms, inks and dyes. However, the significant cost structure of track and trace technologies, and complex operations involved in tracking the products are the major challenges for the growth of the anti-counterfeit and related security markets always pave the way for cheaper anti-counterfeiting solutions.

This thesis focusses on the rapid authentication of cartons as a first point of analysis for the brand owner. It is postulated that the portable technology involved could be used both in the testing forensic laboratory and in the field.

1.2 Counterfeit Pharmaceuticals

Counterfeit medicines represent a global public health problem, with solutions requiring a co-ordinated security approach, both within and across pharmaceutical companies and health authorities. According to the Health Research Fund, an estimated 10% to 30% of medicines sold in developing countries are counterfeit. In addition, the value of the counterfeit drug market annually is estimated at $200 billion.[2] However, other statistics report counterfeits are present in up to 10% of the world market and up to 50% in developing countries.[3] Therefore, there is no agreed, nor definitive study and resulting statistics to support absolute conclusions.

In 2013, the World Health Organisation launched a global surveillance and monitoring system to encourage Member States to report *Substandard, Spurious, Falsely labelled, Falsified and Counterfeit* (SSFFC) Medical Products incidents in a structured and systematic format, to help develop a more accurate and validated assessment of the scope, scale and harm caused by this issue. Over nine hundred and twenty medical products have so far been reported representing all main therapeutic categories and representing both innovator and generic medicines.[4] Counterfeit medicines can unscrupulously enter the legal supply chain via a number of routes. Figure 1.1 shows such examples, including the entry via an illegal distributer.

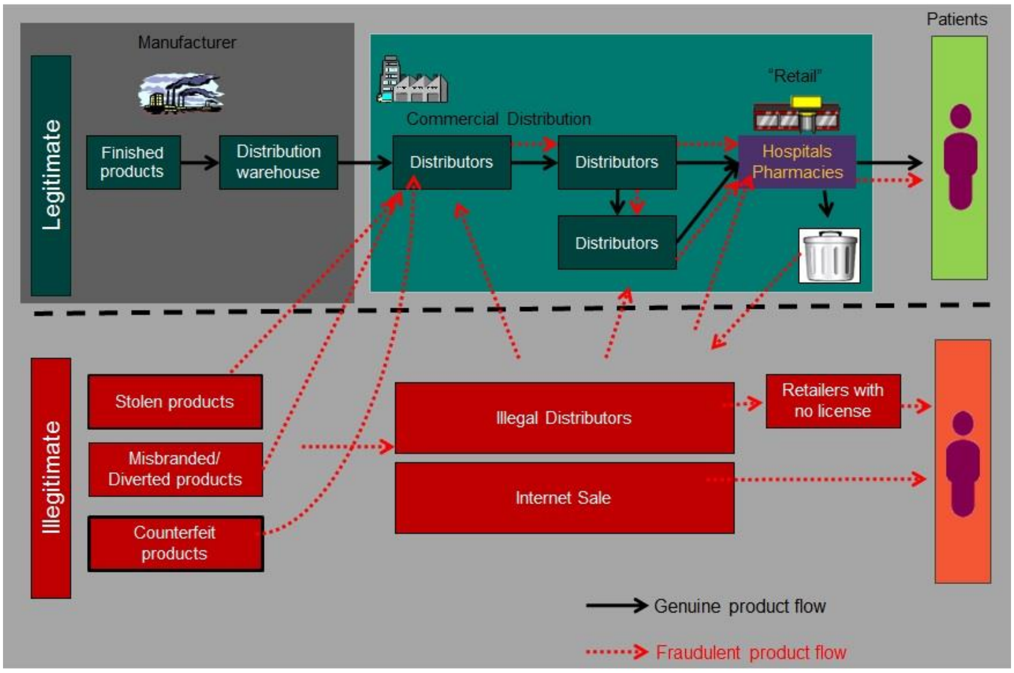


Figure 1.1 - How Counterfeit Drugs can get to Patient via Illegal Routes (*Courtesy of Merck, Sharp and Dohme***)**

Defects in counterfeit pharmaceuticals can be attributed to the wrong coating, active pharmaceutical ingredient (API), excipients, and/or packaging.[5-7] A WHO study published in June of 2012 examined samples of malaria medicines from several countries in South-East Asia and sub-Saharan Africa. In both regions, 35% of the samples failed chemical analysis. In South-East Asia, 46% failed packaging analysis and 36% were classified as falsified. In sub-Saharan Africa, 35% failed packaging analysis and 20% were classified as falsified.[8]

Though this has been more of an issue in the developing/ third World, instances of counterfeiting have occurred in the United Kingdom – see Table 1.1. In some instances this has been due to unapproved wholesalers. One additionally counterfeited product that breached the UK legal supply chain in 2004 was Reductil® (Table 1.1), manufactured by Abbott used for obesity control.[9] As a result, all of Reductil 15 mg Capsules having batch number 65542 were recalled from the UK market. Such drastic measures were to protect the public from the dangers of counterfeit drugs. However, this also tarnished the reputation of Abbott and the Reductil franchise/ brand image.

Table 1.1 - Examples of SFFC Medicines

SFFC medicine	Country/Year	Report
1. Avastin (for cancer treatment)	United States of America, 2012	Affected 19 medical practices in the USA. The drug lacked active ingredient
2. Viagra and Cialis (for erectile dysfunction)	United Kingdom, 2012	Smuggled into the UK. Contained undeclared active ingredients with possible serious health risks to the consumer
3.Truvada and Viread (for HIV/AIDS)	United Kingdom, 2011	Seized before reaching patients. Diverted authentic product in falsified packaging
4. Zidolam-N (for HIV/AIDS)	Kenya, 2011	Nearly 3 000 patients affected by falsified batch of their antiretroviral therapy
5. Alli (weight-loss medicines)	United States of America, 2010	Smuggled into the USA. Contained undeclared active ingredients with possible serious health risks to the consumer
6. Anti-diabetic traditional medicine (used to lower blood sugar)	China, 2009	Contained six times the normal dose of glibenclamide. Two people died, nine people were hospitalized
7. Metakelfin (antimalarial)	United Republic of Tanzania, 2009	Discovered in 40 pharmacies. The drug lacked sufficient active ingredient

Source: WHO

The United States Food and Drugs Administration (FDA) declare that *Counterfeit medicine is fake medicine. It may be contaminated or contain the wrong or no active ingredient. They could have the right active ingredient but at the wrong dose. Counterfeit drugs are illegal and may be harmful to your health.*[10] The FDA regulates both finished dietary supplement products and dietary ingredients, one of which on the watch-list is Subutramine – the active pharmaceutical ingredient in Reductil.

1.3 Packaging Materials for the Pharmaceutical Industry

Packaging materials for the pharmaceutical industry come in a variety of types, in some cases with a specific function. Packaging materials, which include cartons, blisters, and bottles, help to protect the drug product from sunlight, moisture and tampering. There are three sub-categories of packaging:

- Primary – Packaging materials, including blisters, syringes, and bottles, that come directly into contact with the drug product
- Secondary – The outer pack that contains the primary pack (a carton for example)
- Tertiary – These are typically large cartons or plastic packaging which contains the secondary and primary packs.

Figure 1.2 shows an example commercial pharmaceutical pack (Alli® – a GlaxoSmithKline product for anti-obesity):

Figure 1.2 - Alli® (Orlistat 60mg) Pharmaceutical Packaging Commodities *(Courtesy of GSK)*

Modern digital scanning and printing techniques mean that packaging can be easily and cheaply duplicated. A counterfeiter will spend most of their production costs in such replication, primarily to fool the potential patient. The pharmaceutical industry tries to keep one step ahead of the counterfeiter, employing such inclusions on the pack as codes (e.g. 2 dimensional bar codes), taggants, markings and holograms.

Many of these 'solutions' are costly and may remain within the company intellectual property.

1.3.1 Cartons for the Pharmaceutical Industry

The carton is the most popular choice as secondary packaging for the pharmaceutical industry. It typically houses a blister of the drug products (e.g. tablets) as well as a patient information leaflet. The carton box is usually flat, with a surface area available for printing. Their visibility to the pharmacist and consumer makes them the most popular commodity for the positioning of anti-counterfeiting features.

The anatomy of a printed, disassembled Reductil® carton is shown in in Figure 1.3, with lacquered white areas. The region of variable data can be non-lacquered to aid printing.

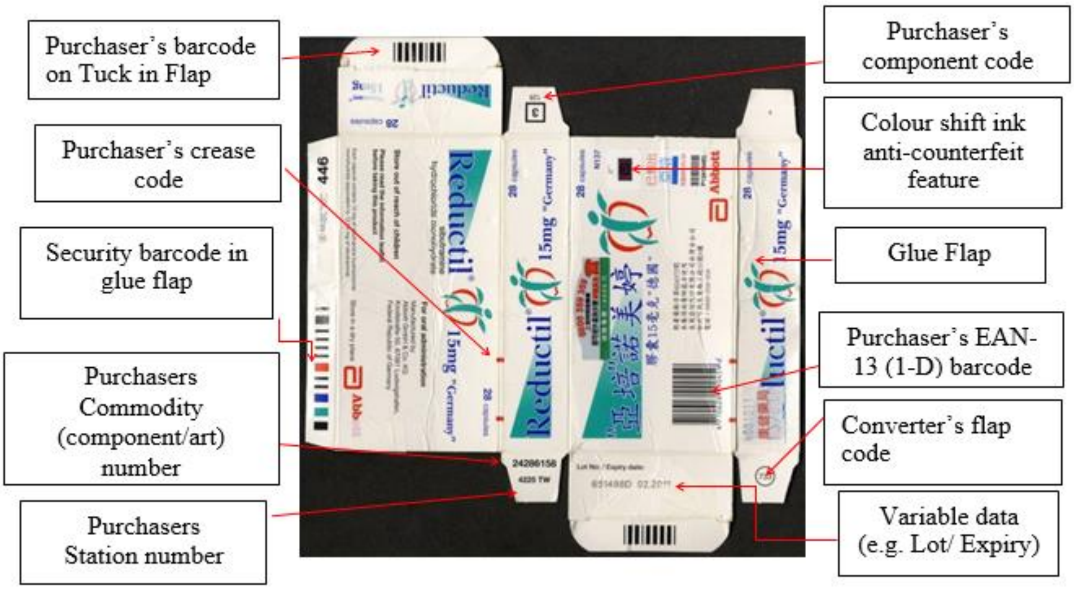


Figure 1.3 - Anatomy of a Printed Carton

The thesis will explore the potential of infra-red spectroscopy to identify counterfeit packaging.

1.4 Fundamentals of infra-red spectroscopy

The electromagnetic spectrum is the common name given to the broad band of radiations from gamma rays to radio waves. A portion of the electromagnetic spectrum including IR is shown in Figure 1.4:

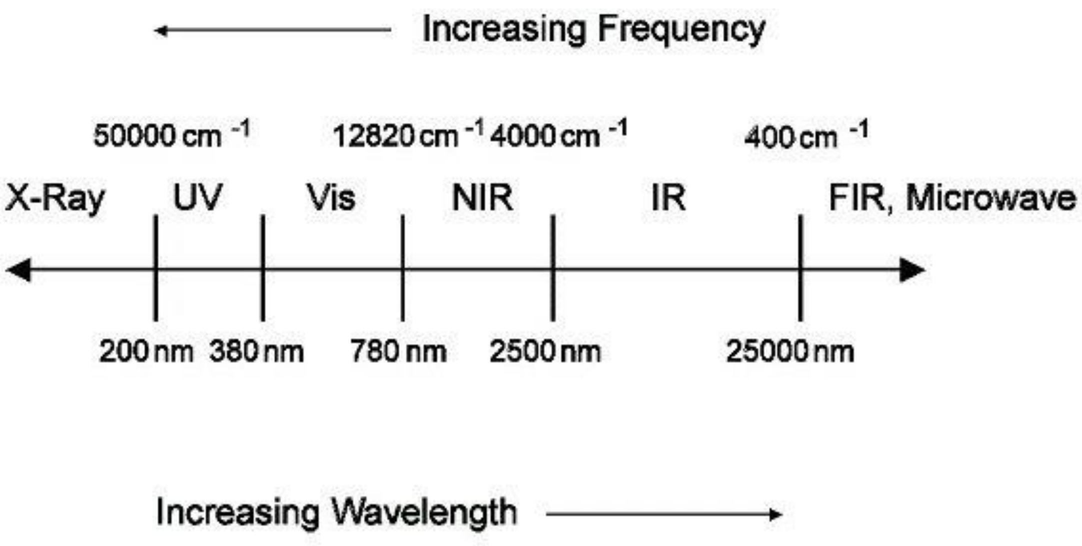


Figure 1.4 - The electromagnetic spectrum ***(Courtesy of Foss NIRSystems Inc.)***

The IR region was the first part of the electromagnetic spectrum discovered beyond the visible region. In 1800 Herschel observed that the red portion of a spectrum (generated by a prism) caused a thermometer to register a temperature rise.[11] However, on passing the thermometer beyond the red region of the spectrum the temperature dramatically increased and Herschel assumed that an invisible band existed, which became known as the IR region.

The IR region of the spectrum is, by convention, further sub-divided into three different regions based on wavelength:

- Far-infrared, usually defined as the spectral range below 400 cm^{-1} to 20 cm^{-1}

- Mid-infrared, usually defined as the spectral range 4000 cm^{-1} to 400 cm^{-1}

- Near-infrared, usually defined as the spectral range 12820 cm^{-1} to 4000 cm^{-1} (780 to 2500 nm)

The far-infrared region is primarily used for measuring heavier atoms and inorganic materials, so is not relevant to these types of samples. Mid-infrared spectroscopy is used for observing fundamental vibrations within molecules and will generate spectra that can be used as a fingerprint for different types of materials. Absorption of IR radiation is associated with the bonds between atoms within a molecule. This gives rise to vibrational and rotational motions that are specific to the type of covalent bond present. The energy absorbed by the bond is specific to the atoms themselves, as well as the number and type of atoms attached to the atoms in question. As a result, the mid-IR range has been used for structural elucidation of pure organic compounds for many years.

The American Society for Testing and Materials (ASTM)[12] defines the Mid-IR region as having a wavelength range from approximately 2500 to 25000 nm (wavenumber range 4000 to 400 cm^{-1}). For IR radiation to be absorbed it must be of the correct frequency to produce vibrational transitions in the molecules concerned, i.e. the radiation frequency should be the same as the fundamental vibration frequency for the specific molecule. The molecule should also undergo a change in its dipole moment by virtue of its fundamental vibration.

The vibrational frequency, *f*, for a diatomic molecule is given by equation 1.1 (equation for a harmonic oscillator) in which it is assumed that an atom shifts from its equilibrium position with strength proportional to the shift (Hooke's Law):

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.1}$$

Where, *k* is the bonding force constant (in units of dyne/cm, a measure of the strength or rigidity of a chemical bond in its normal equilibrium position) and μ is the reduced molecular mass (in amu, or atomic mass units).

In this case the variation in potential energy as a result of stretching or compressing the bond is a parabola centred about the equilibrium distance. The application of the Schrödinger wave equation gives evenly spaced vibrational energy levels. The energy E_V of each energy level will be given by:

$$E_v = f(\mathrm{v} + \frac{1}{2}) \tag{1.2}$$

Where, v is the vibrational quantum number.

As the selection rule for a harmonic oscillator is Δv ±1, and the energy levels are evenly spaced, then the energy difference between two consecutive levels will then always be:

$$E_{(v+1)} - E_{v} = f \qquad (1.3)$$

Where, *f* is known as the 'fundamental frequency' of the bond.

Other transitions, for example from $v_{2\leftarrow 0}$ and higher, are forbidden.

Vibrations in polyatomic molecules involve complex movements of their constituent atoms. These movements can be resolved into individual vibrations called 'normal vibrations'. The energy of each normal frequency is independent of the others, so the total vibrational energy of the molecule is the sum of the individual energies (equation 1.4).

$$E_{Tv} = \sum_{i=0} f(v_i + \frac{1}{2}) \qquad (1.4)$$

In practice, molecular vibrations tend to be non-harmonic. The potential energy curve for real bonds is only approximately parabolic, with small deviations at the lower energy levels that become more marked at the upper energy levels (Figure 1.5). Also, the spacing between energy levels are not identical but decrease (subsequent levels become closer) with increasing energy.

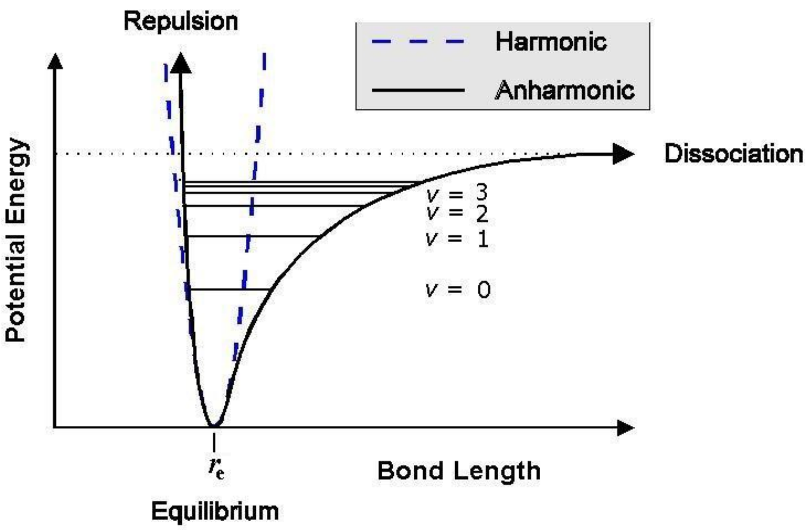


Figure 1.5 - Harmonic and anharmonic potential functions for a diatomic oscillator

The energy E_V of the vibrational levels will be given by:

$$E_v = f_e(v + \frac{1}{2}) - f_e\chi_e(v + \frac{1}{2})^2 + \text{higher order terms} \quad (1.5)$$

Where, χ_e is the anharmonicity constant for a molecule (which measures the deviation of the potential function from the parabola), and f_e is the frequency spacing between levels corresponding to a parabola with its centre at the equilibrium distance (r_e).

One further consequence of introducing the quadratic term into Hooke's law is that the selection rule becomes $\Delta v = \pm 1, \pm 2$, etc.. Hence, in addition to the fundamental transition, $v_{1 \leftarrow 0}$, other, higher transitions called overtones appear at frequencies at approximately two, three, etc., times higher than the fundamental frequency. The intensity of these bands decay abruptly, since the transition probability decreases markedly with increase in the vibrational quantum number and, in practice, only the first two or three overtones are observed. For the vast majority of organic molecules and complex ions the fundamental vibration occurs in the mid-IR and the overtones appear in the NIR albeit one to three orders of magnitude smaller. The transition probabilities for overtones and combination bands are 10 to 1000 times smaller than those for the fundamental frequency and, consequently, such absorbances are weak.

Polyatomic molecules possess several fundamental frequencies so they may exhibit simultaneous changes in the energies of two or more vibrational modes: the frequency observed will be the sum of ($f_1 + f_2, 2f_1 + f_2,$ etc.). This results in very weak absorptions that are called combination bands. Anharmonicity results in combination bands that are smaller than the combined fundamental frequencies involved.

With polyatomic molecules there is a significantly higher number of modes of vibration possible (3N – 6, where N is the number of atoms, or 3N – 5, for linear molecules), those typically encountered are shown in shown in Figure 1.6.

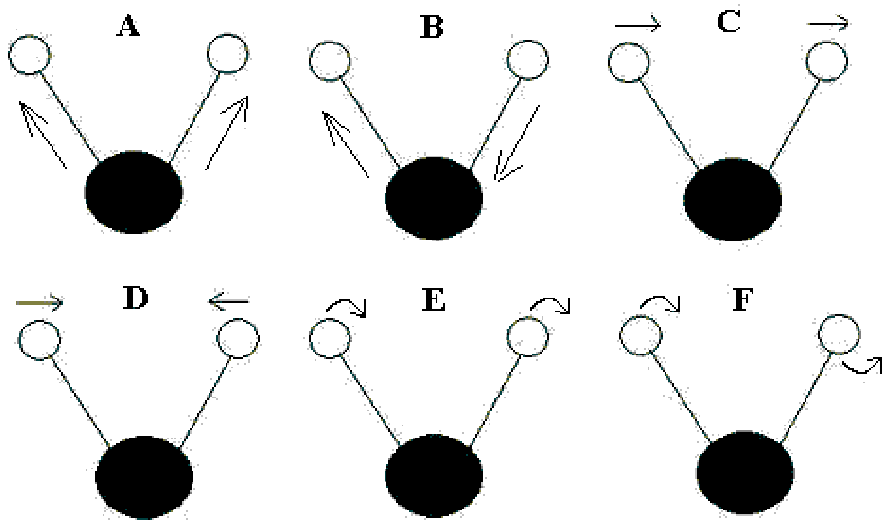


Figure 1.6 - Vibrational modes for a molecule of the type XH_2 : A - symmetric stretching, B - asymmetric stretching, C - rocking (in-plane deformation), D - scissoring (in-plane deformation), E - wagging (symmetric out-of plane deformation), and F - twisting (asymmetric out-of-plane deformation)

Key: white circle = Hydrogen, Black Circle = Oxygen, Nitogen or Carbon

(Courtesy of Thermo Fisher Scientific)

Many IR absorptions are fundamentals arising from bonds in which one of the atoms is hydrogen (e.g. C–H, N–H, O–H and S–H), Figure 1.7.

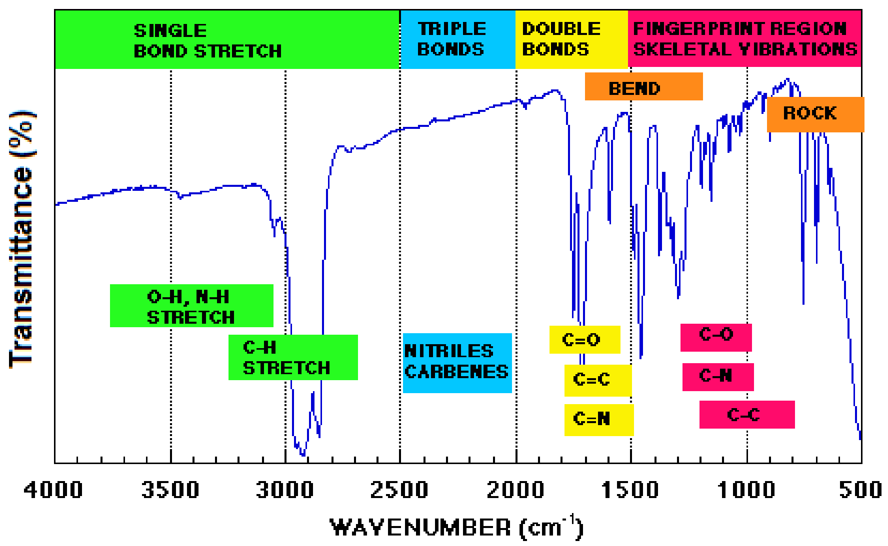


Figure 1.7 - Example Fundamental IR Frequencies (*Courtesy of Perkin Elmer*)

The small mass of the hydrogen atom coupled with the large force constants for C–H bonds form the origin of high fundamental frequencies and hence the appearance of the first few overtones in the NIR region. X–H bonds also have significantly higher anharmonicity constants than other groups. C=C, C–C, C–F, and C–Cl groups fundamental vibrations occur at low frequencies in the IR region, where their first few overtones also appear as a result. Carbon tetrachloride has no absorptions in the IR region as it is a symmetrical molecule (though it has weak asymmetric vibrations).

In IR spectroscopy, the frequency (or wavelength) where absorptions occur allows for identification, the amplitude or intensity of the absorption can allow quantification. Figure 1.8 shows an example IR absorbance spectrum, and the previous Figure 1.7 explains some of those frequencies (for a transmission spectrum).

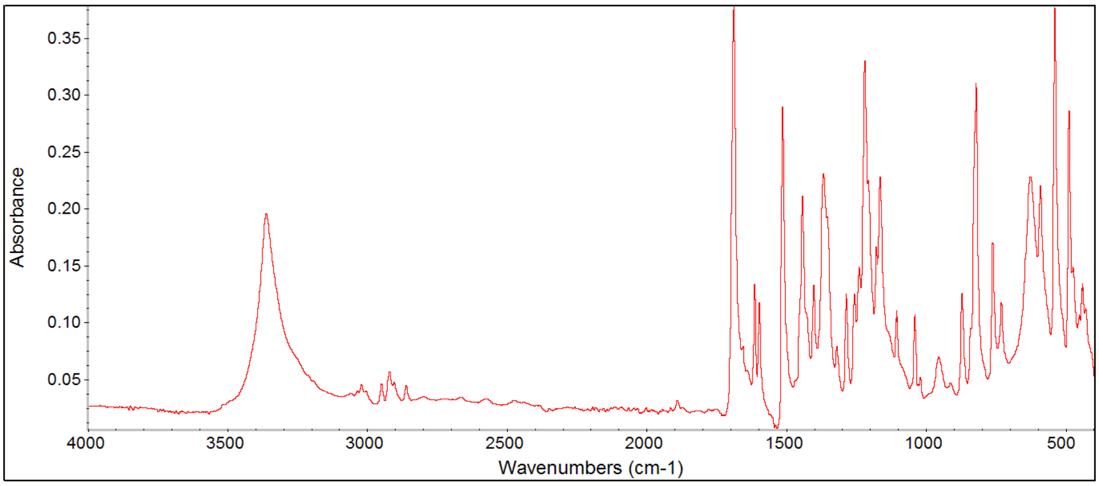


Figure 1.8 - An Example Absorbance IR Spectrum of Paracetamol

The region from 1500 to 500 cm^{-1} is known as the identification region, and is frequently utilised for identification purposes due to the finer, detailed structure. It is typical to show data from solids in absorbance or reflectance, unless the spectra results from transmission, for example through a media such as a potassium bromide disk.

Equation 1.6 shows the relationship between transmittance and absorbance:

$$\text{Absorbance (A)} = 2 - \log(\text{\% Transmittance (T)}) \qquad (1.6)$$

Although the positions of IR absorptions can be estimated from the principles of the anharmonic oscillator, in practice these may vary. This could be related to the degree of hydrogen bonding in the molecule, interaction with other molecules and the temperatures at which the spectrum is measured. The presence of hydrogen bonding typically broadens absorptions in higher frequencies of IR spectra. Also, deformation from a crystalline to an amorphous solid state results in peak broadening. There is also the added complication that may arise when transitions are of similar frequencies, however, this is more likely in the NIR region, formed by the combinations and overtones of fundamental IR absorbances.

1.5 IR analysis of pharmaceutical packaging

IR spectroscopy has been extensively used in the forensic laboratory for the identification of unknown, as well as the authentication of known chemicals. A significant advantage IR spectroscopy has compared with other complementary techniques, such as Near Infra-red (NIR) and Raman spectroscopy, is its maturity, and because of this, many diverse libraries are commercially available for the identification of unknown chemicals.

FT-IR spectroscopy offers the infrared spectroscopist throughput and sensitivity advantages that make it possible to accommodate a wide range of sampling accessories. This in turn makes possible the routine collection of spectra from various solids, including cartons.

Though there is much written in the literature about the use of IR for the analysis of counterfeit drugs, surprisingly little has been published on the use of IR for the analysis of counterfeit cartons.[13] In 2012 Andria *et al* described the use of IR for the analysis of counterfeit blisters, where attenuated total reflectance mode was used to identify the plastics within them.[14] Rodomonte *et al* described the use of colorimetry to discriminate counterfeit secondary packaging and Broad *et al* used multispectral visible - near-infrared to successfully identify counterfeit Reductil cartons.[15, 16]

The body of work described in this thesis utilises two interface technologies coupled with FT-IR. Both external specular reflectance and attenuated total reflectance (ATR) were used, compared and evaluated.

1.6 FT-IR instrumentation and producing a spectrum

Fourier transform (FT) instruments are commonly used within the laboratory.[17-23] Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. Early IR instruments were dispersive, with many moving internal parts and slow scanning speeds, many time lacking good reproducibility. A solution, Fourier transform infra-red (FT-IR), was developed which employed a very simple optical device called an interferometer. An example of the instrumentation optical arrangement is shown in Figure 1.9 below.

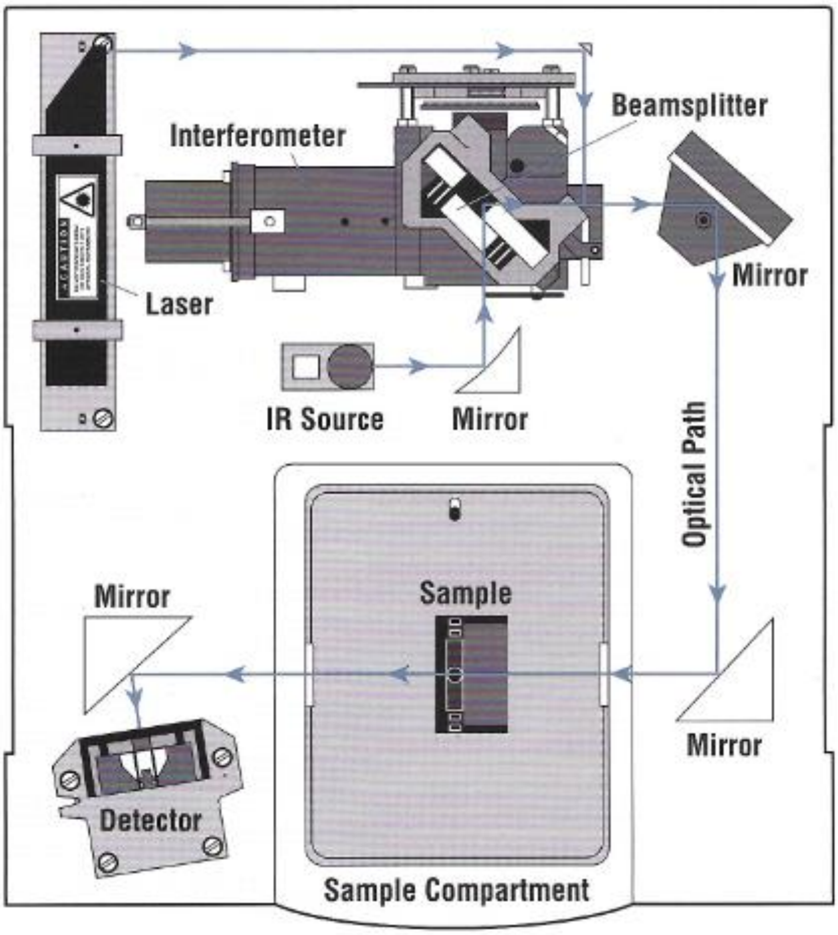


Figure 1.9 - Example FT-IR Instrument Optics (*Courtesy of Thermo Fisher Scientific*)

The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded". The signal can be measured very quickly, usually in approximately one second. Thus, the analysis time per sample is reduced to a matter of a few seconds rather than several minutes. The essential component of an interferometer is a system for splitting a source radiation beam and then recombining the two beams after introducing a path difference. This combined beam passes through the sample to the detector. Division of the beam is achieved with a beamsplitter that transmits about 50 % and reflects about 50 % of the radiation. One part of the beam goes to a fixed mirror, and the other to a mirror that can be moved to introduce a varying path difference (Figure 1.10).

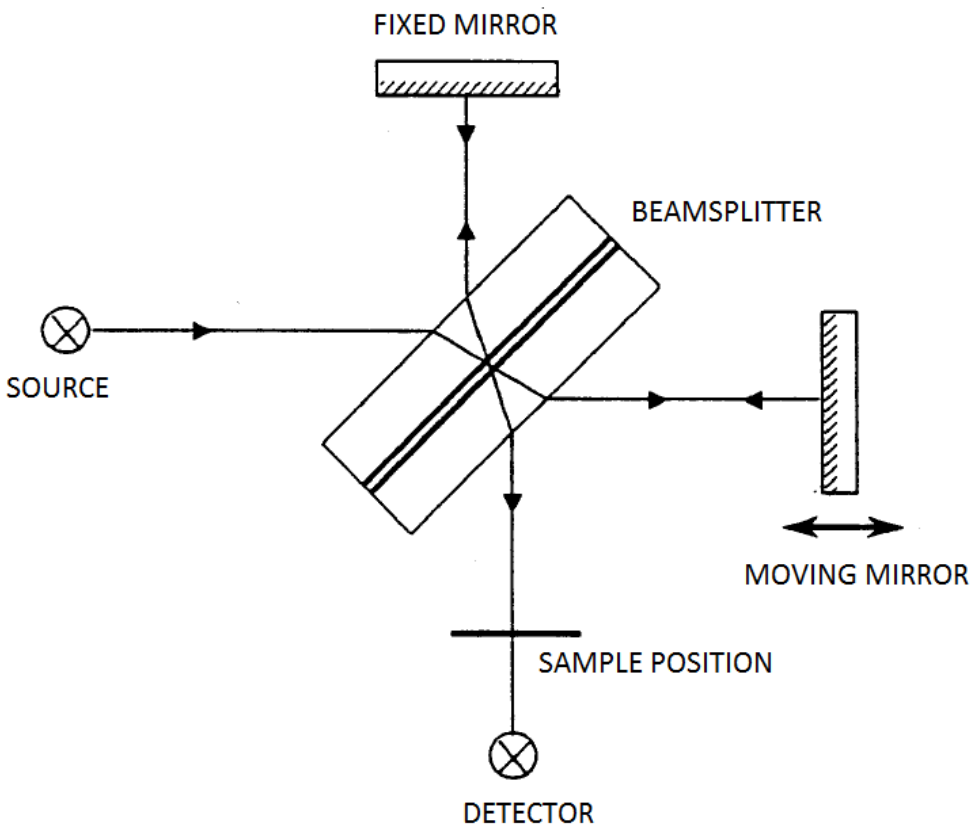


Figure 1.10 - The Michelson Interferometer (*Courtesy of Perkin Elmer*)

One beam reflects off a flat mirror which is fixed in place. The other beam reflects off a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimetres) away from the beamsplitter. The two beams reflect off their respective mirrors and are recombined when they meet back at the beamsplitter. The distance the mirror can move determines the maximum possible resolution. The most commonly used beamsplitter is a plate of KBr with a germanium coating. The instrumentation used for this work uses ZnSe beamsplitters.

Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements.

When the beams are recombined, an interference pattern is obtained as the path difference is varied. For a single frequency, the interference pattern is a sine wave with maxima when the two beams are exactly in phase and minima when the two are 180 degrees out of phase. The spacing between the maxima corresponds to a change in path difference equal to the wavelength (Figure 1.11):

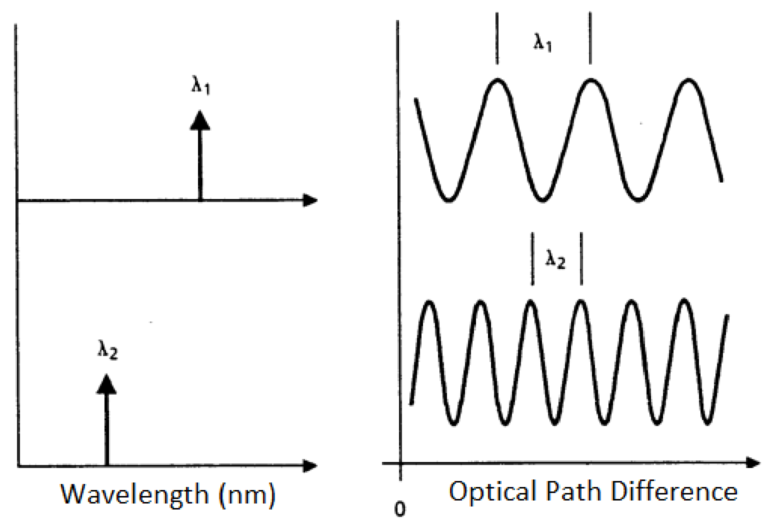


Figure 1.11 - Relationship between optical path difference and wavelength

For a broadband source the interference pattern is the sum of the sine waves for all the frequencies present. This interferogram consists of a strong signal at the point where the path difference is zero, falling away rapidly on either side. As the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal cannot be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a mathematical technique called the Fourier transformation.[18, 20] This transformation is performed by the computer which then presents the user with the desired spectral information for analysis. The customary spectrum, showing energy as a function of frequency, can be obtained from the interferogram by the mathematical process of Fourier Transformation (Figure 1.12).

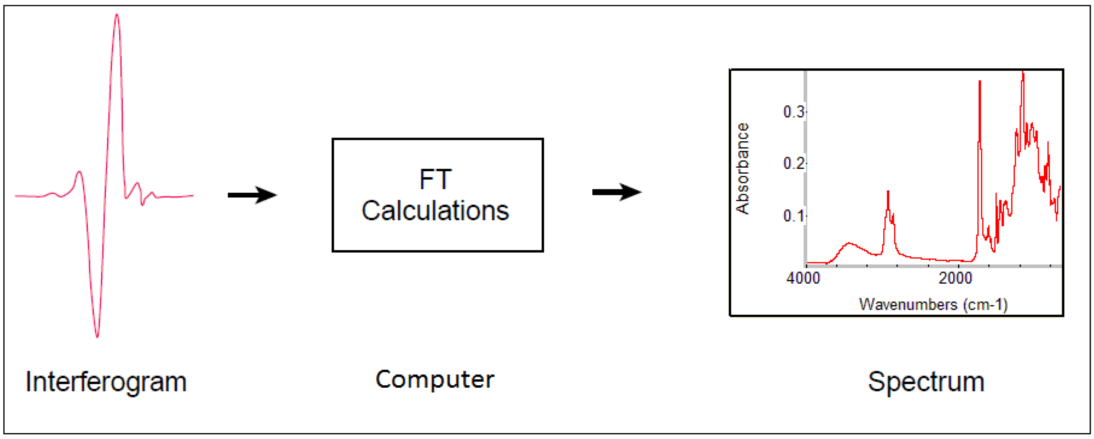
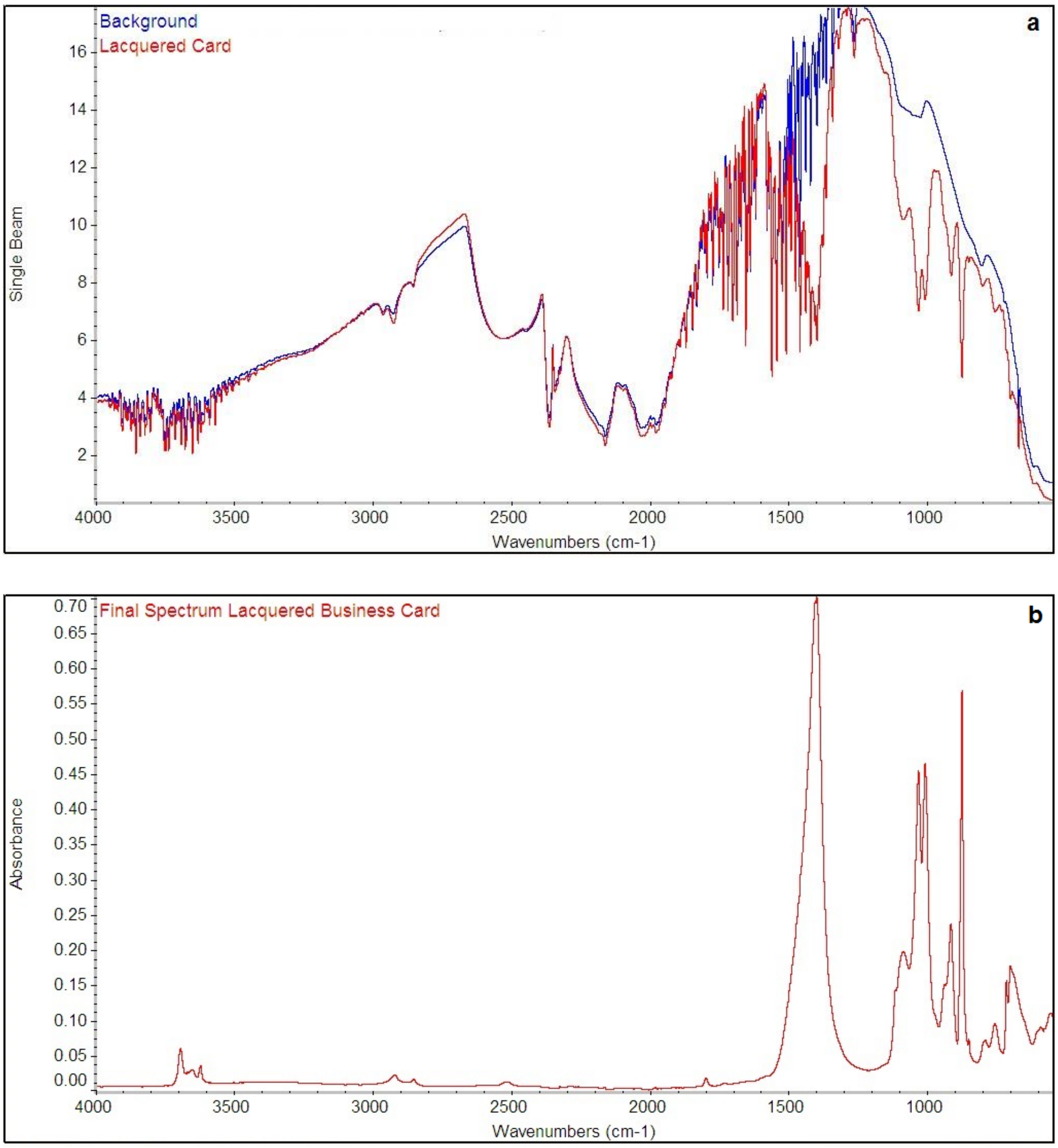


Figure 1.12 - Fourier Transformation

Fourier transformation is the mathematical process by which the interferogram is analysed into its component frequencies with their corresponding amplitudes. To achieve this rapidly and efficiently, the Cooley-Tukey algorithm (also known as a Fast Fourier Transform (FFT)), is used.[21]

When no sample is present this gives a single beam spectrum, the overall shape of - which is largely determined by the characteristics of the beamsplitter. Normally, interferometers operate by first recording this background and then ratioing the spectrum recorded with a sample against it (Figures 1.13a and b):



Figures 1.13a and b – a) Background (blue) and Sample (red) Records, and b) Final Spectra of Lacquered Card

The five important components required for IR spectral collection are:

1. The Source: Infrared energy is emitted from a glowing black-body source such as tungsten filament. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. The Interferometer: The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. The Sample: The beam enters the sample compartment where it is transmitted through, or reflected off, the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

4. The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal. IR detectors include PbS and PbSe photoconductive detectors, InAs and InSb photovoltaic detectors, and, HgCdTe and InSb photoconductive detectors.

5. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation. Modern FT-IR instruments are computer controlled; enabling spectra to be measured and saved as a data file typically within seconds. The fast Fourier transform (FFT) is done on-

board, with the computer being an advanced chart recorder and meta data handler. Extreme wavenumber accuracy enables signal averaging and it is common to measure many scans to enhance signal (greater signal to noise).

1.6.1 The Advantages of FT-IR Spectroscopy

In principle, a well-designed interferometer has eight basic advantages over a classical dispersive instrument:

1. Multiplex Advantage (Fellgett Advantage)[21]

All frequencies are measured simultaneously in an interferometer, whereas in a dispersive spectrometer they are measured successively. A complete spectrum can be obtained very rapidly and many scans can be averaged in the time taken for a single scan of a dispersive spectrometer.

2. Throughput Advantage (Jacquinot Advantage)[22]

For the same resolution, the energy throughput in an interferometer can be higher than in a dispersive spectrometer where it is restricted by the slit size. In combination with the *Multiplex Advantage*, this leads to one of the most important features of an FT-IR spectrometer; the ability to achieve the same signal-to-noise ratio as a dispersive instrument in a much shorter time.

3. Connes Advantage[22]

The frequency scale of an interferometer is derived from a helium neon laser that acts as an internal reference for each scan. The frequency of this laser is known very accurately and is very stable. As a result, the frequency calibration of interferometers is much more accurate and has much better long term stability than the calibration of dispersive instruments. FT-IR instrument typically employ a HeNe laser as an internal wavelength calibration standard, however portable instruments can use solid state lasers.

4. Negligible Stray Light

Because of the way in which the interferometer modulates each frequency, there is no direct equivalent of the stray light found in dispersive spectrometers.

5. Constant Resolution

Resolution is the same at all wavelengths. In a dispersive instrument the resolution varies because of the slit program.

6. No Discontinuities

As there is no grating or filter changes, there are no discontinuities in the spectrum.

7. Sensitivity

Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the *Jacquinot Advantage*) which results in much lower noise levels, and the fast scans enable the co-addition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

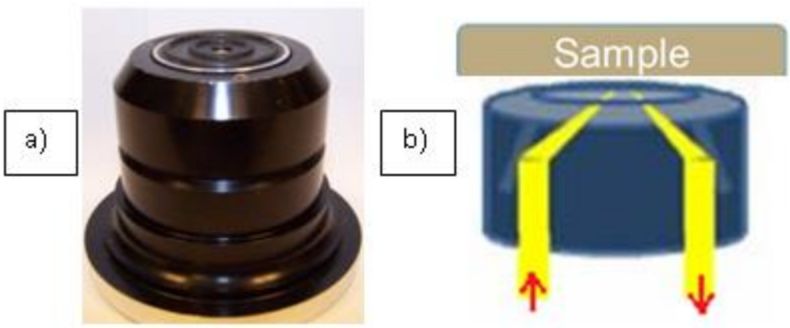
8. Mechanical Simplicity

The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

In summary, FT-IR is much simpler optically than dispersive technology, harnessing computer power to enable all frequencies to be collected at once during data acquisition. The analyst can collect a spectrum within a second compared to minutes.

1.7 Specular reflectance FT-IR analysis of solids

Agilent Technology's ExoScan 4100 Fourier transform infrared (FT-IR) spectrometer is based on a Michelson interferometer coupled with ZnSe beamsplitter technology. On an axis angle of 45°, the collimated beam is reflected by a parabola and the cone of IR light travels through a ZnSe window, reflects off the sample / background cap, penetrates approximately 350 microns into a laminated carton in reflectance mode, with spot size of 1.55 mm diameter (1.76 cm^2 area) acquired (see Figures 1.14a and b). The cone angles are from 35-55° with a beam spot size of 1.5 mm.



Figures 1.14a and b - Spectral Path and Active Area Dimensions 'Spot Size' Diameter using a 45º Specular Reflectance Head *(Courtesy of Agilent)*

Specular reflectance sampling in FT-IR represents a very important technique useful for the measurement of thin films on reflective substrates, analysis of bulk materials and measurement of monomolecular layers on a substrate material. Specular reflectance Fourier transform infrared measurements allow thin coatings layers on reflective surfaces to be analysed with little or no sample preparation.[22-27]

In specular reflectance the infrared beam strikes the sample at an angle of incidence, for example of 45 degrees, but the variable-angle accessories commercially available can provide different sensitivity. The smaller the angle of incidence, the more sample the IR beam must pass through. Note that the nature of the solid sample itself will determine the ultimate depth of penetration. The primary difficulties associated with specular reflectance measurements involve spectral distortions caused by the mixing of the absorption information and refractive index variation in the measured radiation. A second difficulty is low signal:noise ratio (SNR) of highly absorbing solids. This can be overcome by collecting more spectra, and/or using more advanced detectors (for example, cooled Mercury Cadmium Telluride (MCT) technology).

The basics of the sampling technique involves measurement of the reflected energy from a sample surface at a given angle of incidence. The electromagnetic and physical phenomena which occur at, and near, the surface are dependent upon the angle of incidence of the illuminating beam, refractive index and thickness of the sample and other sample and experimental conditions.

In the case of a relatively thin film on a reflective substrate, the specular reflectance experiment may be thought of as similar to a “double-pass transmission” measurement and can be represented as shown in Figure 1.15:

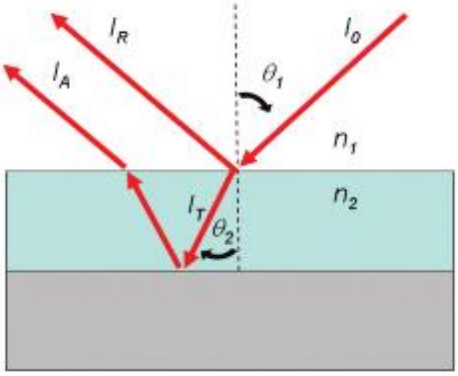


Figure 1.15 - Representation of specular reflectance Beam path for Reflection-Absorption of a relatively thin film measured by Specular Reflectance (*Courtesy Pike Technologies Inc.)*

The incident FT-IR beam, represented by I_0, illuminates the thin film of a given refractive index, n_2 and at an angle of incidence, θ_1. Some of the incident beam is reflected from the sample surface, represented by I_R at the incident angle, θ_1

and is also known as the specular component. Some of the incident beam is transmitted into the sample represented by I_T at an angle of θ_2 – calculated by

$$n_1 \sin\theta_1 = n_2 \sin\theta_2 \qquad (1.7)$$

At the reflective substrate, the beam reflects back to the surface of the thin film. When the beam exits the thin film it has geometrically passed through the film twice and is now represented as I_A. Infrared energy is absorbed at characteristic wavelengths as this beam passes through the thin film and its spectrum is recorded.

The specular reflectance spectra produced from relatively thin films on reflective substrates measured at near-normal angle of incidence are typically of high quality and very similar to spectra obtained from a transmission measurement. This result is expected as the intensity of I_A is high relative to the specular component, I_R.

For relatively thick samples, specular reflectance produces results which require additional considerations, as the specular component of the total reflected radiation is relatively high. As per Figure 1.16, the incident FT-IR beam represented by I_0 illuminates the sample of a given refractive index, n_2 and at an angle of incidence, θ_1. Some of the incident beam is reflected from the sample surface, represented by I_R at the incident angle, θ_1. Some of the incident beam is transmitted into the sample represented by I_T at an angle of θ_2. The percent of reflected versus transmitted light increases with higher angles of incidence of the illuminating beam. Furthermore, the refractive index of the sample, surface roughness and sample absorption coefficient at a given wavelength all contribute to the intensity of the reflected beam.

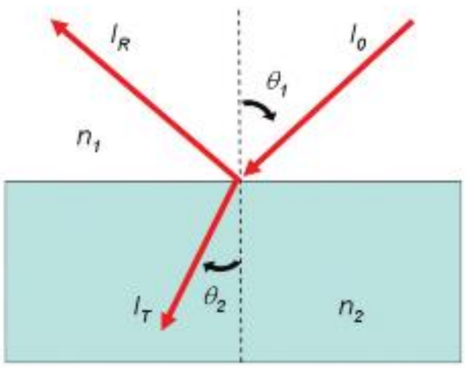


Figure 1.16 - Beam path for a relatively thick sample measured by Specular Reflection (*Courtesy Pike Technologies Inc.*)

By increasing the incident angle of infra-red radiation, the effective pathlength through the sample can be increased (Figure 1.17). Grazing Angle Specular reflectance is the measurement of relatively thin films and mono-molecular layers using a shallow grazing angle of incidence. At high angles of incidence, between 60 and 85 degrees, the electromagnetic field in the plane of the incident and reflected radiation is greatly increased relative to a near normal angle of incidence. The perpendicular component of the electromagnetic field of the reflecting radiation is not enhanced.

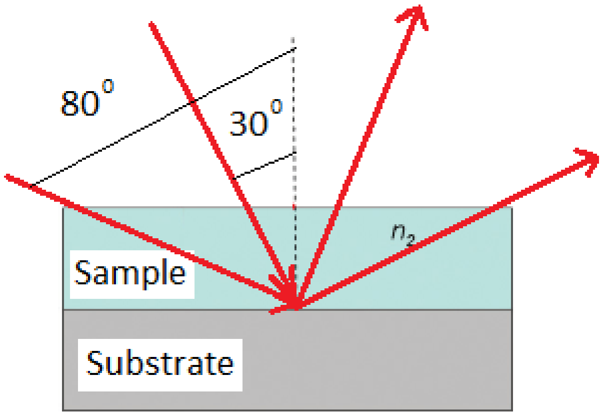


Figure 1.17 - The effective pathlength variation as a function of the angle of incident radiation

1.8 Attenuated Total Reflectance (ATR) analysis of solids

Attenuated Total Reflectance (ATR) spectroscopy enables FT-IR analysis of solids and liquids without the need for sample preparation. In ATR, a liquid or solid is placed on top of a suitable crystal material. An infrared beam passes through the crystal and is internally reflected from the top crystal surface. The ATR used for this thesis is ZnSe supported with diamond. A small evanescent wave then penetrates a small distance from the crystal surface into the sample itself before it is reflected back into the crystal and the infrared detector.[25-27] The penetration of the infrared beam into the sample is sufficient to generate an infrared spectrum of the various suspect samples.

In ATR-IR spectroscopy the infrared beam is coupled into an internal reflection element (IRE). The latter consists of a material of high refractive index (n_1) and is transparent in the mid-IR, such as diamond or Zinc Selenide (the latter is used in this thesis – see Chapter 3). The geometry of the IRE allows the radiation to be totally reflected once, or multiple times before it leaves the IRE. Total internal reflection of an electromagnetic wave occurs at the interface of the IRE and an optically rare medium (the sample, $n_2 < n_1$) when the angle of incidence of the radiation exceeds the critical angle (θ_c) defined by the law of refraction:

$$\theta_c = \sin^{-1}\left(n_2 / n_1 \right) \qquad (1.8)$$

where n_1 is the refractive index of the medium immediately outside the IRE

An indication of the fraction of sample probed by the electromagnetic field is given by the penetration depth (d_p):

$$d_p = \frac{\lambda}{2\pi + n_1 \sqrt{\sin^2\left[\theta - \left[\frac{n_2}{n_1}\right]^2\right]}} \qquad (1.9)$$

Where dp is the distance from the IRE surface where the electric filed vector E drops to a value of 1/e of its amplitude at the interface. The penetration depth depends on the wavelength, λ, the angle of incidence (θ) and the refractive indices of the IRE and the sample (n_1 and n_2).

The reflected radiation sets up a standing wave, known as the evanescent wave. The intensity of the evanescent wave decays exponentially with distance from the surface; the distance at which the intensity of the evanescent wave has decayed to 1/*e* of its original value at the surface is known as the depth of penetration (d_p). At the point of reflection an *evanescent electromagnetic field* is generated into the sample (Figure 1.18):

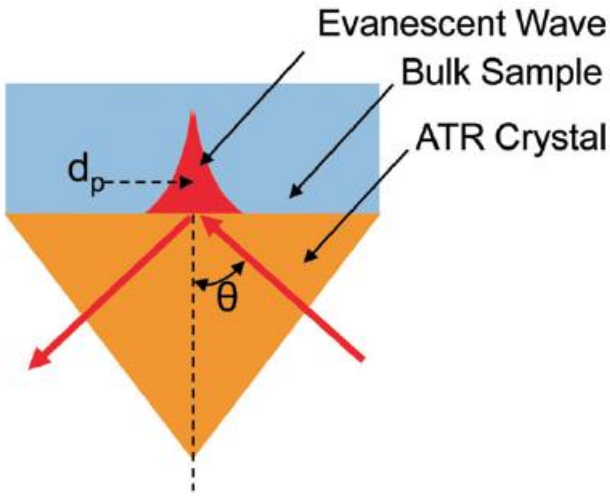


Figure 1.18 - Graphical representation of a single reflection ATR

The amplitude of the evanescent wave field decreases exponentially from the surface of the IRE into the sample.

Upon internal reflection no energy is lost if no absorption occurs in the sample. When absorption occurs at the interface, the evanescent field is attenuated and the infrared spectrum of the sample (the analyte) is generated.

The typical effective pathlength d_p for a sample in an ATR measurement is in the range 0.5 - 20 microns, depending on the crystal type and the number of reflections in the crystal. Generally, a single reflection ATR is ideal for qualitative analysis, however the effective path length (EPL) is increased by increasing the number of reflections (N) within the ATR crystal (effective pathlength is directly proportional to the number of internal reflections). Table 1.2 shows the commercially available crystals and their properties:

Table 1.2 – ATR Crystal Characteristics for FT-IR Sampling

Material	$\boldsymbol{n_1}$	$\boldsymbol{d_p}$**, microns**	**Water Solubility, g/100g**	**pH Range**	**Hardness, Kg,mm**
Diamond/ ZnSe	2.4	2.01	Insoluble	1-14	5,700
Ge	4.0	0.66	Insoluble	1-14	550
KRS-5	2.37	2.13	0.05	5-8	40
Si	3.4	0.85	Insoluble	1-12	1,150
ZnS	3.3	3.86	Insoluble	5-9	240
ZnSe	3.4	2.01	Insoluble	5-9	120

Most organic chemicals have a refractive index, n_1, around 1.5. In this case *dp* is equal to about 0.2λ for ZnSe and 0.066λ for Ge when the angle of incidence at the surface is 45º. Since the depth of penetration is directly proportional to the wavelength of the infrared radiation, the bands in the ATR spectrum are weaker at the short-wavelength (high-wavenumber) end of the spectrum than the long-wavelength end.

1.9 Algorithms used for Identification

Arguably the most common single spectroscopic technique used for algorithmic library searching is FT-IR. This is mostly due to the selective and sensitive nature of FT-IR spectra to the material being examined. This enables even small differences to be discriminated, however judicious use of the correct algorithm requires testing and examination of the results.

There are many algorithms to enable the user to accentuate particular spectral differences over others to suit the data, since these are purely mathematical algorithms they do not consider the condition, or chemistry, or contamination issues therefore a variety of algorithms were developed to suit different types of data and differences. All software quotes either an index, quality index, hit quality, hit quality index, etc.. The hit percentage or more correctly the hit quality index is an indication of how well a test spectrum matches the library (based on the algorithm). The value is algorithmic and spectrally dependent. Most software report a value of "Hit Quality" value between 0-100, this quality value in essence has no units whatsoever, they are literally an indicator. Correlation values are typically between 0 and 1, again these a purely a measure of how well two spectra match (e.g. a library spectrum and a test sample spectrum).

Agilent FT-IR software has several algorithms available for identification purposes – *correlation*, *derivative correlation*, *Euclidean*, *Similarity* and *Derivative Similarity*. These are detailed in the following sub-sections 1.9.1 to 1.9.5.

1.9.1 Correlation

The correlation search algorithm facilitates a linear regression of the query spectrum intensities versus the library spectrum intensities. The correlation coefficient of the resulting linear function is very characteristic through deviations from linearity. The closer the correlation coefficient is to 1, the better is the accordance and match of both spectra. Correlation can cope with mild negative bands such as present in reflectance spectra.

$$correlation = \frac{(L_m \bullet Q_m)^2}{(L_m \bullet L_m) \bullet (Q_m \bullet Q_m)} \qquad (1.10)$$

where $L_m = L - \frac{\sum_{i=1}^{n} L_i}{n}$ and where $Q_m = Q - \frac{\sum_{i=1}^{n} Q_i}{n}$

and,

Q = query spectrum intensity vector

L = Library spectrum intensity vector

● = Dot product, scalar product or inner product. Euclidean maths definition takes two equal length sequence of numbers and returns a single value

1.9.2 Derivative Correlation

Derivatisation of an untreated (zero order) spectrum can be a useful technique for enhancing the fine structure within the IR spectrum (i.e. resolution is enhanced).[27] The presence of overlapping peaks in spectroscopy are resolved by taking the derivative of the raw data, where the derivative describes the rate of change of the original signal.

The first derivative spectrum is the slope of the spectral curve at each point of the original spectrum. It has peaks where the original spectrum has maximum slope and crosses zero where peaks occurred in the original. Taking the first derivative of a spectrum largely removes the effects of baseline offsets and slopes to improve resolution for analysis.

The second derivative is the slope of the first derivative and utilised to remove both baseline offset and slope from the spectrum (i.e. the physical information is almost completely removed to leave only chemical information).[28]

The visual advantage of derivatives is the separation of overlapping peaks, as in Figure 1.19. The peaks corresponding to the two components overlap, with the peak for component **b** appearing as a shoulder on the peak corresponding to component **a**. Thus visual separation of components pre-derivatisation is difficult. The second derivative spectrum resolves the over-lapping peaks into their individual component peaks, with the relevant position and size of the original peaks maintained.

The common derivative algorithms include the gap and Savitsky-Golay methods.[28-36] In the former algorithm, typical parameters required for this calculation are the segment and gap size. The principle of this approach is to calculate the difference between the mean values of segments (blocks) of data points either side of the point at which the derivative is required. The segment size represents the number of data points to average (for smoothing purposes) and the gap is the number of data points between these segments.

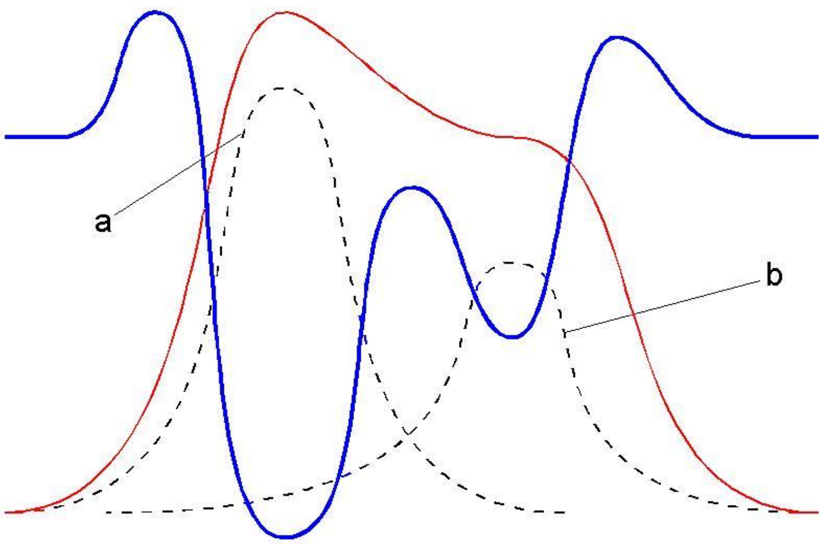


Figure 1.19 - Effect of derivatisation for resolution of individual components a and b: (—) raw spectrum, and (—) second derivative of raw spectrum

For example, Figure 1.20 calculates data using a segment (block) size of 7 data points with a gap size of 3 data points. To calculate the first derivative using the data in Figure 1.19 the mean value of intensity in the second block is subtracted from the mean value in the first to obtain a new value. This is then repeated across the complete spectrum moving one point at a time.

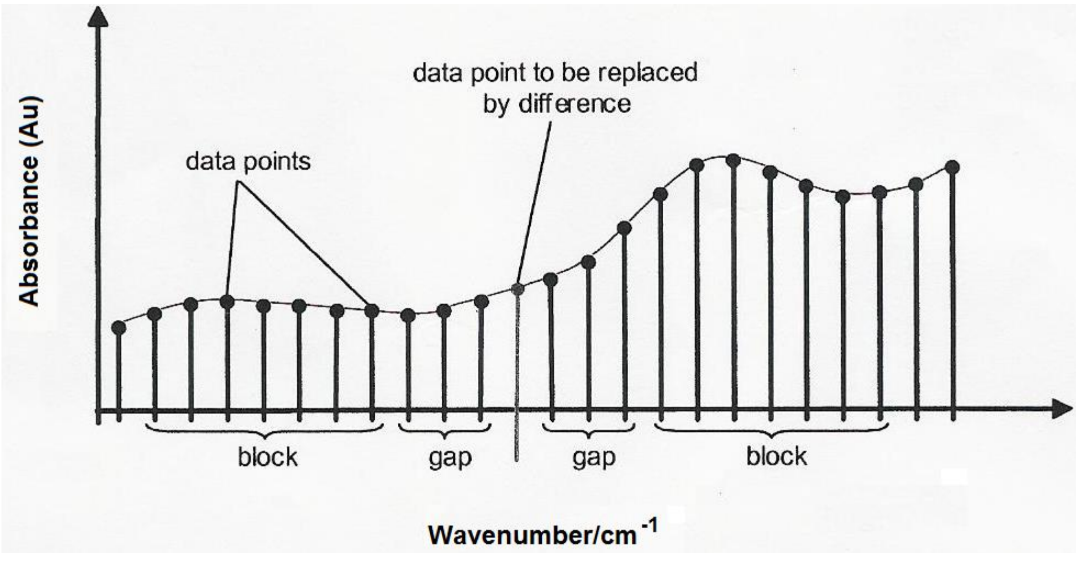


Figure 1.20 - Representation of spectral data points for calculation of a derivative using a gap approach *(Courtesy of FOSS NIRSystems Inc.)*

For each data point, A_i, from the original spectrum the calculation of the first derivative absorbance using this algorithm is,

$$A_i^{1'} = \bar{A}_c - \bar{A}_a \qquad (1.11)$$

Where, $A_i^{1'}$ is the first derivative absorbance at the i^{th} wavelength, $\bar{A}_c$ is the average absorbance of the segment proceeding A_i, and $\bar{A}_a$ is the average absorbance of the segment preceding A_i with a gap of the specified size between segments. The original data point, A_i, is located at the centre of the gap.

For higher order derivatives this procedure is simply repeated on the first derivative data, or, alternatively for each data point, A_i, from the original spectrum the calculation of the second derivative absorbance using this algorithm is,

$$A_i^{2'} = \bar{A}_a - 2\bar{A}_b + \bar{A}_c \qquad (1.12)$$

Where, $A_i^{2'}$ is the second derivative absorbance at the i^{th} wavelength, $\bar{A}_a$ is the average absorbance of the segment preceding A_i, $\bar{A}_b$ is the average absorbance of the segment at which A_i is centrally located (i.e. the mid-point of the gap) and $\bar{A}_c$ is the average absorbance of the segment proceeding A_i with a gap of the specified size between segments.

Figure 1.21 shows the effect of selecting different segment sizes (in data points) on second derivative spectral data, the smaller the segment the more significant the noise. However, more detailed spectral information can appear. Optimisation of segment size is therefore usually a compromise of the signal to noise ratio.

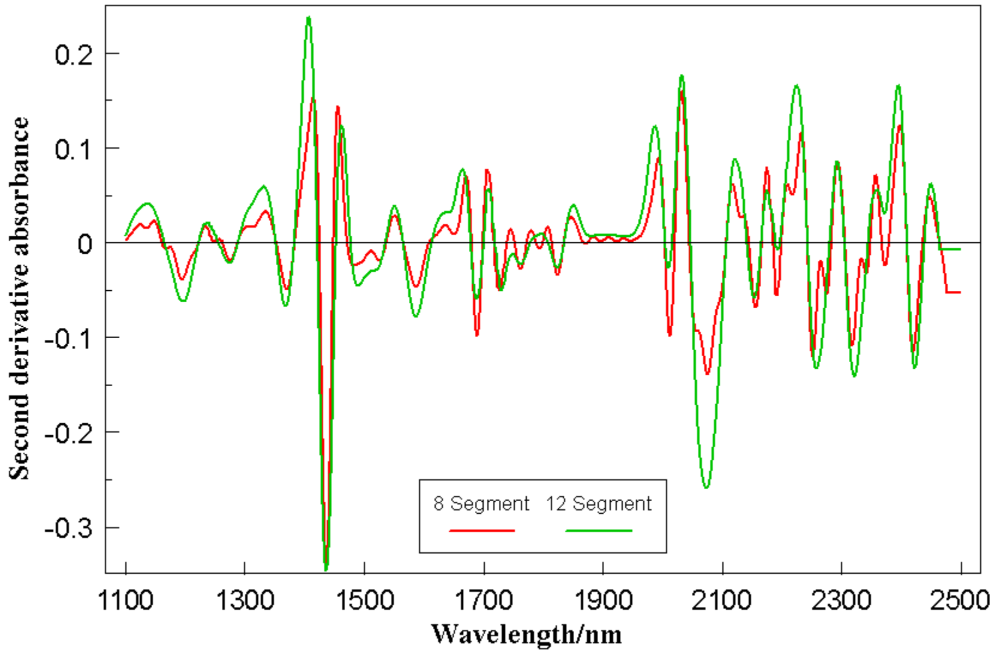


Figure 1.21 - Effect of varying segment size of second derivative spectral data (gap size = 0)

The derivative correlation search algorithm facilitates a linear regression of the derivative of the query spectrum intensities versus the library spectrum intensities. The correlation coefficient of the resulting linear function is very characteristic through deviations from linearity. The closer the correlation coefficient is to 1, the better is the accordance of both spectra.

Derivative Correlation, as the name suggests, applies a first derivative adjustment to the correlation calculation.

1.9.3 Similarity

Similarity is simply the subtracted result of correlation from (the number) 1. Therefore the smaller the numerical outcome, the higher the similarity.

$$Similarity = 1 - \left[\frac{(L_m \bullet Q_m)^2}{(L_m \bullet L_m) \bullet (Q_m \bullet Q_m)} \right] \tag{1.13}$$

1.9.4 Derivative Similarity

Derivative Similarity, as the name suggests, applies a first derivative adjustment to the similarity calculation.

1.9.5 Euclidean Distance

The Euclidean Algorithm is the most commonly used algorithm in commercial library search packages. Mathematically it shares some similarity in its operation with the correlation algorithm. It is better suited to spectra with the following three attributes, a well-behaved baseline, only positive peaks, and good signal to noise. It is a slightly faster algorithm than correlation. If the baseline is not flat then it will require baseline correction prior to invoking the search. Values nearest zero indicate a good match, these values are often converted to 100.00-computed value.

$$Euclidean = \sqrt{2} \times \left[\sqrt{1 - \frac{(L \bullet Q)}{\sqrt{L \bullet L}\sqrt{Q \bullet Q}}} \right] \tag{1.14}$$

1.10 Aims and objectives

This thesis focusses on the rapid authentication of cartons as a first point of analysis for the brand owner. It is postulated that the portable technology involved could be used both in the testing forensic laboratory and also in the field, ensuring a cheaper technology for anti-counterfeiting.

Specular reflectance and attenuated total reflectance are both non-destructive techniques that could potentially be applied to the authentication of intact pharmaceutical packaging in a significantly shorter time than traditional, destructive and time consuming analysis methods. This work will recommend which of the two technologies and identification algorithms is better suited to such work.

CHAPTER 2 – THE ANALYSIS OF COUNTERFEIT SLIMMING PILL CARTONS USING SPECULAR REFLECTANCE FOURIER TRANSFORM INFRA-RED SPECTROSOCPY

2.1 Introduction

This Chapter describes in detail the analysis of counterfeit and authentic Reductil® cartons using specular reflectance FT-IR, and compares and evaluates the results of the identification algorithms available.

2.2 Background

A total of sixteen suspects and nine control cartons were available for ATR and specular reflectance analyses. These were divided into sub-sets according to similarity and time period of manufacture, resulting in three sets of counterfeit strains to study. The aim of this Chapter was to evaluate the effectiveness of specular reflectance combine with various identification algorithms for carton authentication. Should specular reflectance be successful, this would facilitate rapid, non-destructive analysis to be envisaged at-line/ in the field.

2.3 Experimental

2.3.1 Suspect and Control samples

Suspect and Control Samples for Analysis

Table 2.1a - Suspect Reductil Cartons Set 1

ID	Description	Lot and Expiry	Component (Count)	Component #
S1	Reductil 15mg	Lot 583998D Exp 08-2010	Carton (1)	24286161*
S2	Reductil 10mg	Lot 633288D Exp 12.2010	Carton (1)	24181219
S3	Reductil 15mg	Lot 651878D Exp 02-2011	Carton (1)	24286161*
S4	Reductil 15mg	Lot 762618D Exp 01.2012	Carton (3)	24286161*
S5	Reductil 10mg	Lot 720658D Exp 07.2011	Carton (1)	24181219
S6	Reductil 10mg	Lot 220808D Exp 06.2007	Carton (2)	24181154
S7	Reductil 10mg	Lot 282298D Exp 09.2009	Carton (2)	24181154

Note*: Component Number Matches Control C1 Component Number

Cartons Set 1 - Suspects S1 to S7 and control cartons:

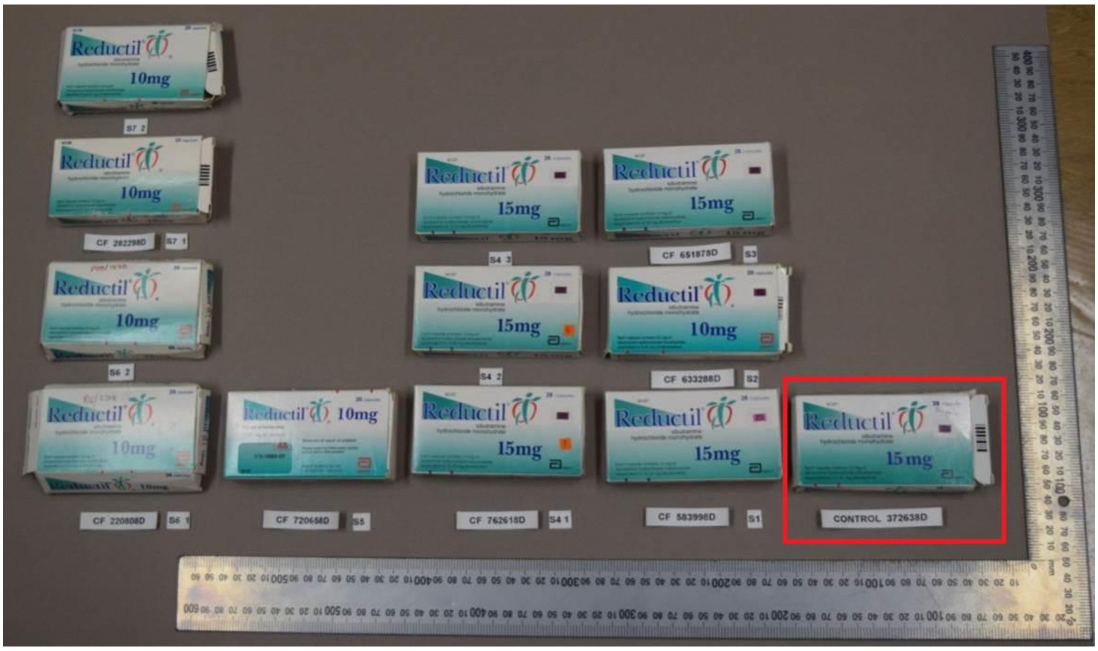


Figure 2.1 - Suspects S1 to S7 and Control C1 Carton Images

Key: Red rectangle encompasses the control carton.

Table 2.1b - Reductil Control Materials Used in the Counterfeit Investigation for Suspect Set 1

Control ID	Description	Lot and Expiry	Component (Count)	Component #
C1	Reductil 15mg Abbott Ludwigshafen, Germany For Control for Set 1 (S1 to S7) comparisons	Lot 372638D Exp 10.2007	Carton (1)	24286161

Table 2.2a - Suspect Reductil Cartons Set 2

ID	Description	Lot and Expiry	Component (Count)	Component #
S8	Reductil 15mg	Lot 273198D Exp 08-2009	Carton (4)	24286127
S9	Reductil 15mg	Lot 2011030 Exp 08.2008	Carton (2)	24286025
S10	Reductil 15mg	Lot 651878D Exp 02-2011	Carton (1)	24181172

Cartons Set 2 - Suspects S8 to S10 and control cartons:

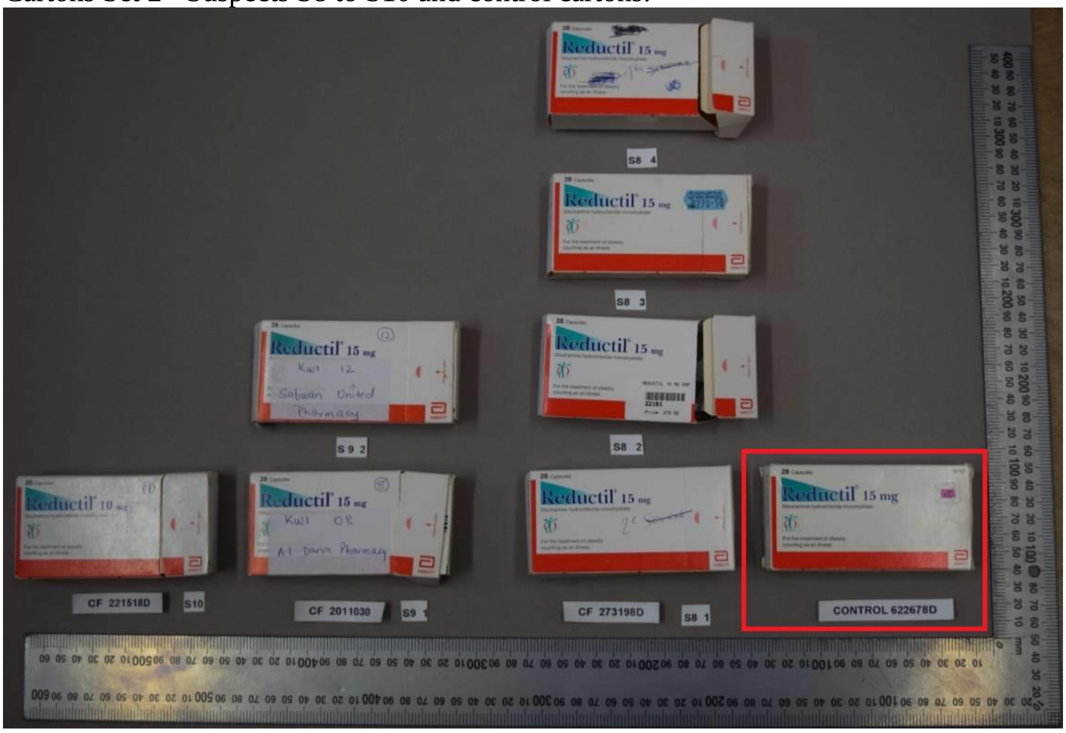


Figure 2.2 - Suspects S8 to S10 and Control C2 Carton Images
Key: Red rectangle encompasses the control carton.

Table 2.2b - Reductil Control Materials Used in the Counterfeit Investigation for Suspect Set 2

Control ID	Description	Lot and Expiry	Component (Count)	Component #
C2	Reductil 15mg Abbott Ludwigshafen, Germany For Control for Set 2 (S8 to S10) comparisons	Lot 622678 Exp 12.2010	Carton (1)	24286200

Table 2.3a - Suspect Reductil Cartons Set 3

ID	Description	Lot and Expiry	Component (Count)	Component #
S11	Reductil 15mg	Lot 250328D Exp 08.2007	Carton (2)	24286062
S12	Reductil 15mg	Lot 394068D Exp 01.2009	Carton (1)	24286160
S13	Reductil 15mg	Lot 72783 Exp 04.2011	Carton (1)	24286054*
S14	Reductil 10mg	Lot 431648D Exp 10.2008	Carton (1)	24181202
S15	Reductil 10mg	Lot 481218D Exp 20 2009	Carton (1)	No # Present
S16	Reductil 15mg	Lot 73156 Exp 03.2012	Carton (1)	24286054*

Note*: Component Number Matches Controls C3 and C4 Component Number

Cartons Set 3 - Suspects S11 to S16 and control cartons:

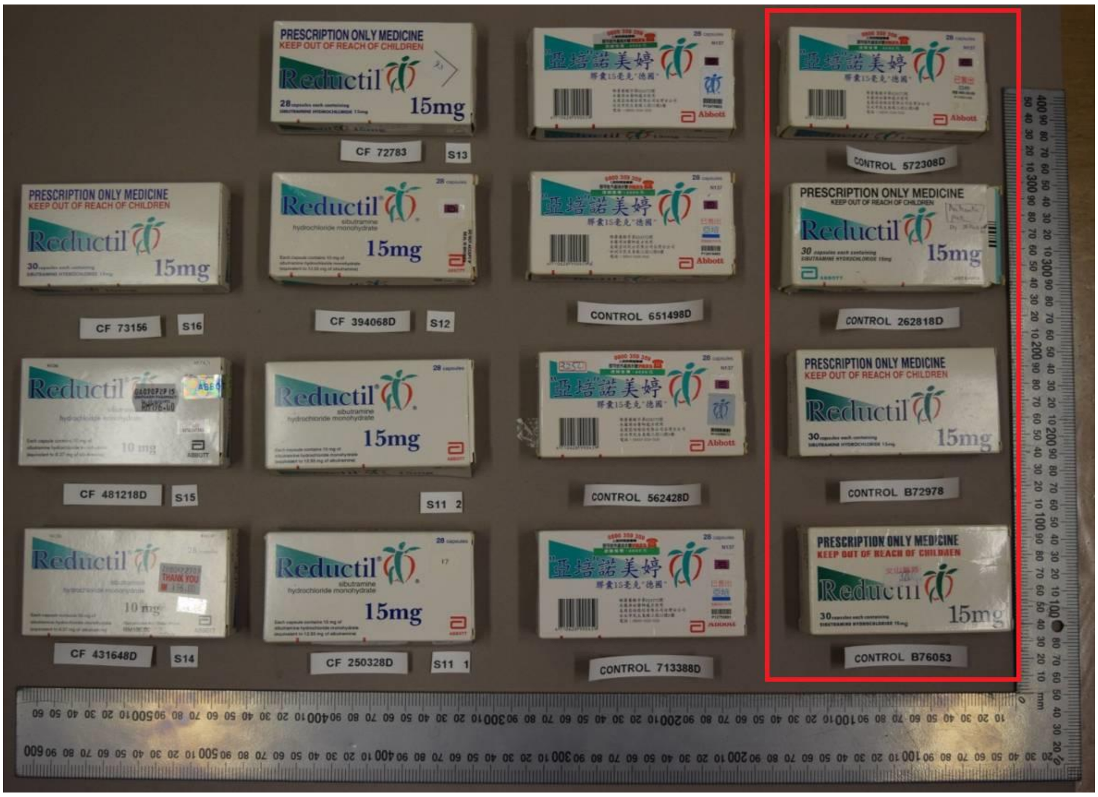


Figure 2.3 - Suspects S11 to S16 and Control C3 to C9 Carton Images

Key: Red rectangle encompasses the control cartons.

Table 2.3b - Reductil Control Materials Used in the Counterfeit Investigation for Suspect Set 3

Control ID	Description	Lot and Expiry	Component (Count)	Component #
C3	Reductil 15mg Abbott Ludwigshafen, Germany For Control for Set 3 (S11 to S16) comparisons	Lot B76053 Exp 12.2014	Carton (1)	24286054
C4		Lot B72978 Exp 12.2009	Carton (1)	24286054
C5		Lot 262818D Exp 11.2007	Carton (1)	24286058
C6		Lot 713388D Exp Unknown	Carton (1)	24286158
C7		Lot 562428D Exp 06.2010	Carton (1)	24286158
C8		Lot 651498D Exp 02.20 11	Carton (2)	24286158
C9		Lot 572308D Exp 02.2010	Carton (1)	24286158

2.3.2 Specular Reflectance FT-IR analysis

The instrument analysis settings used are detailed in Figure 2.4:

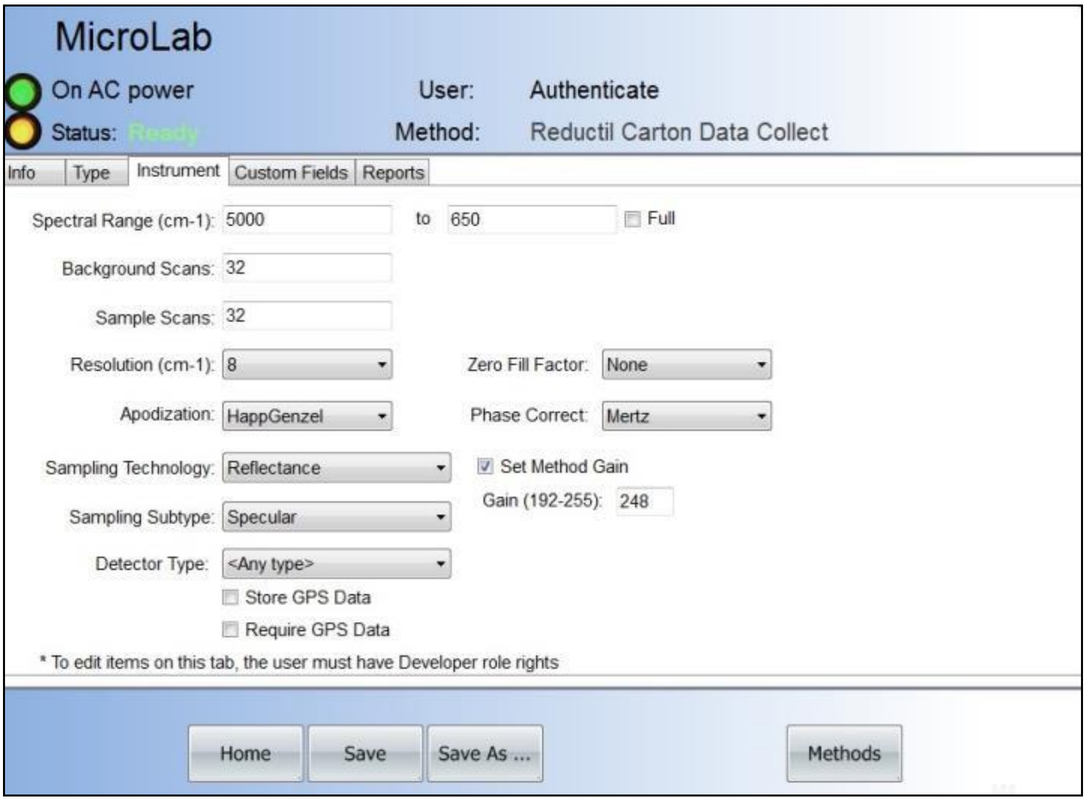
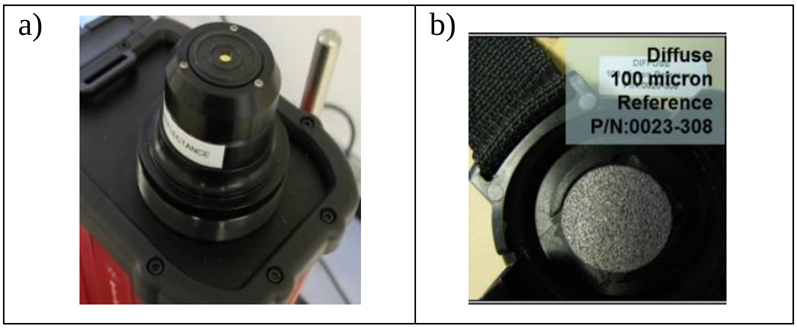


Figure 2.4 - ExoScan Instrument Settings for Reductil Carton Analysis

Prior to each analysis the ExoScan specular reflectance measuring head (Figure 2.5 a) is referenced using a diffuse 100 micron reference cap (Figure 2.5b), the reflective inner material of which is similar to a carton. Figure 2.5 c) shows the cap in place for reference measurement. Figures 2.6a and b show the ExoScan analyser in referencing and suspect analysis modes.



Figures 2.5a and b - Specular Reflectance Measuring Head and Caps - a) 45º Specular Reflectance Head with no Cap (Suspect Analysis Ready), and b) Specular Head with Cap for Referencing

Figures 2.6a to c - Docked ExoScan Analyser for Lap Top Communication with a Specular Reflectance Measuring Head in a) Referencing Mode, b) Sample Placement, and c) Suspect Analysis Mode post

System suitability was performed daily prior to analysis by first referencing a gold reflective specular mirror, and then scanning a gold specular 100 micron reference with an embedded polystyrene film (Figure 2.6a). A typical results screen shot of the passed system suitability is shown in Figure 2.7:

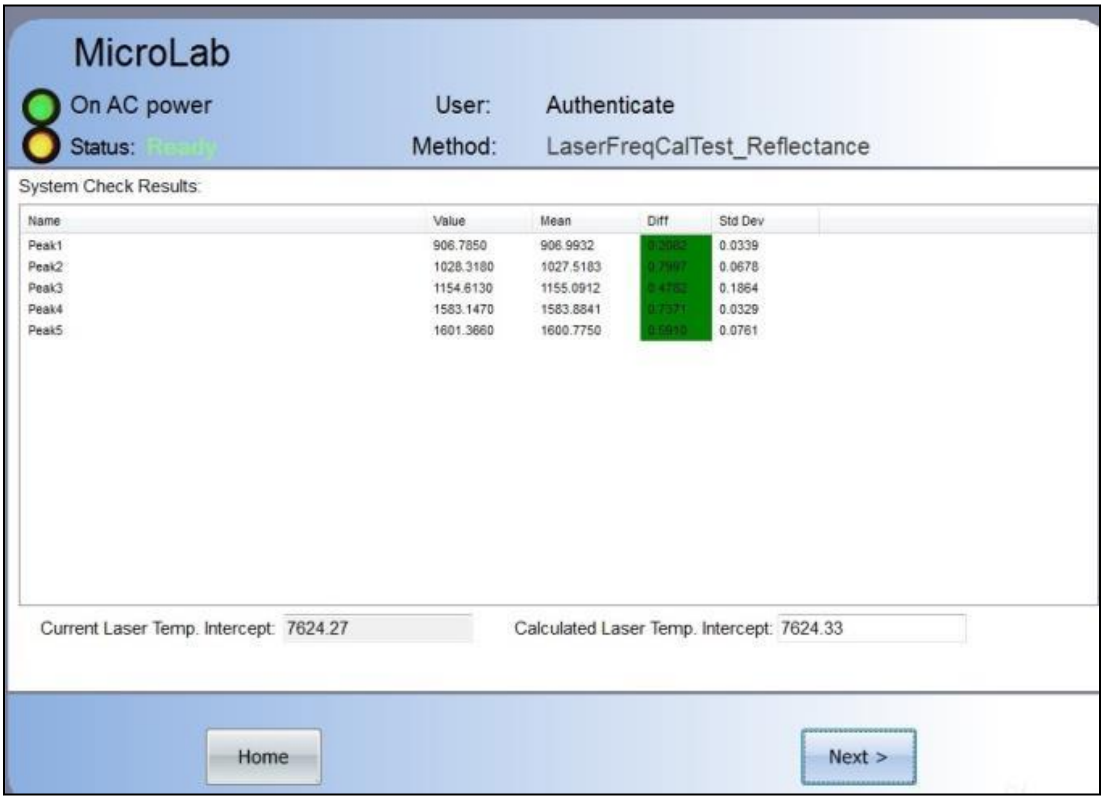


Figure 2.7 - Example System Suitability Results Page (Scanned Polystyrene)

After meeting system suitability requirements, each carton was scanned. A randomly chosen, laminated, white carton region was carefully placed on the measuring head such that a white lacquered portion of the carton was scanned within a minute, having first taken a specular 100 micron reference spectrum. A total of sixteen suspects and nine control cartons were scanned singly. As there were, at times, multiple cartons of the same batch number, twenty-five suspect spectra were obtained in total.

Suspect and control carton analysis was simply a matter of following the on screen instructions (Figure 2.8):

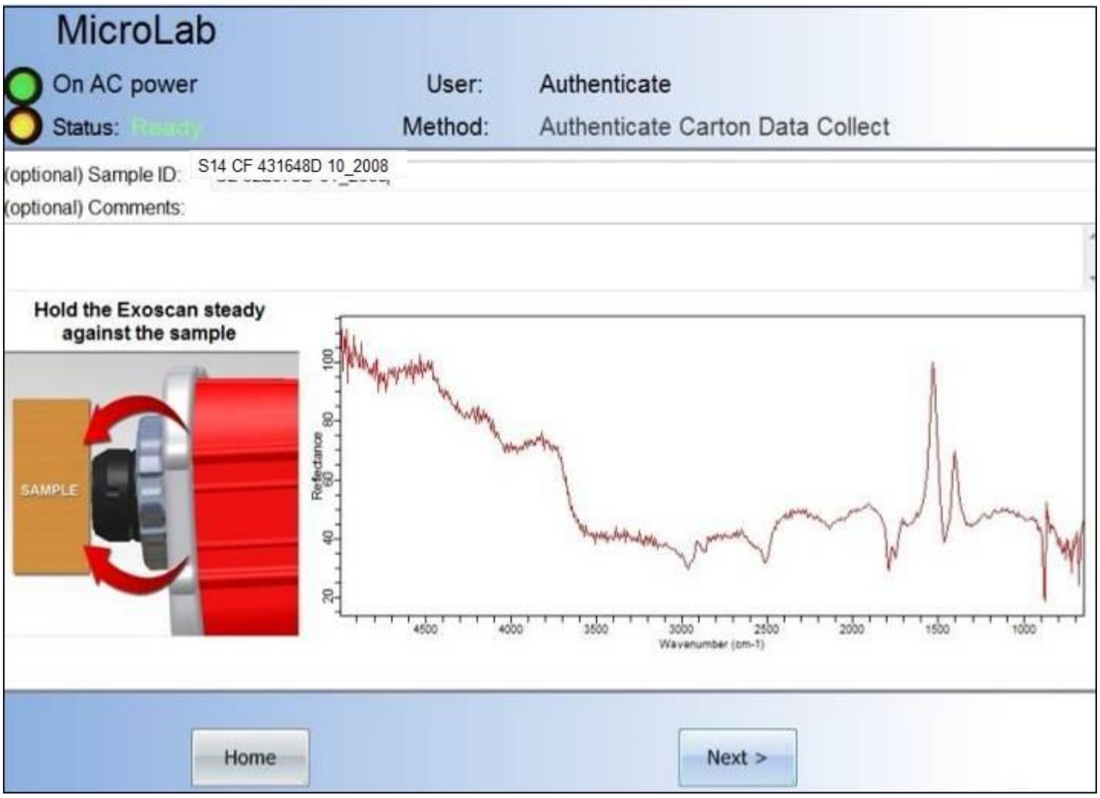


Figure 2.8 - Example Scanning Instructions Screen

A resulting example library hit screen is shown in Figure 2.9, with details page on Figure 2.10. The results page is interactive, for example, the resulting spectrum for suspect S14 has been compared with the nearest control (C5) in Figure 2.10.

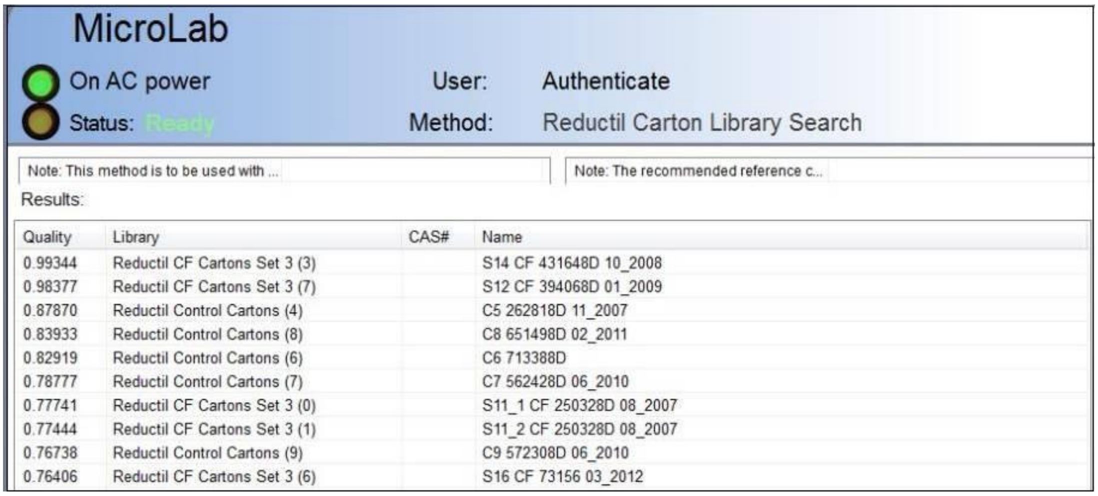


Figure 2.9 - Results from Library Scanning

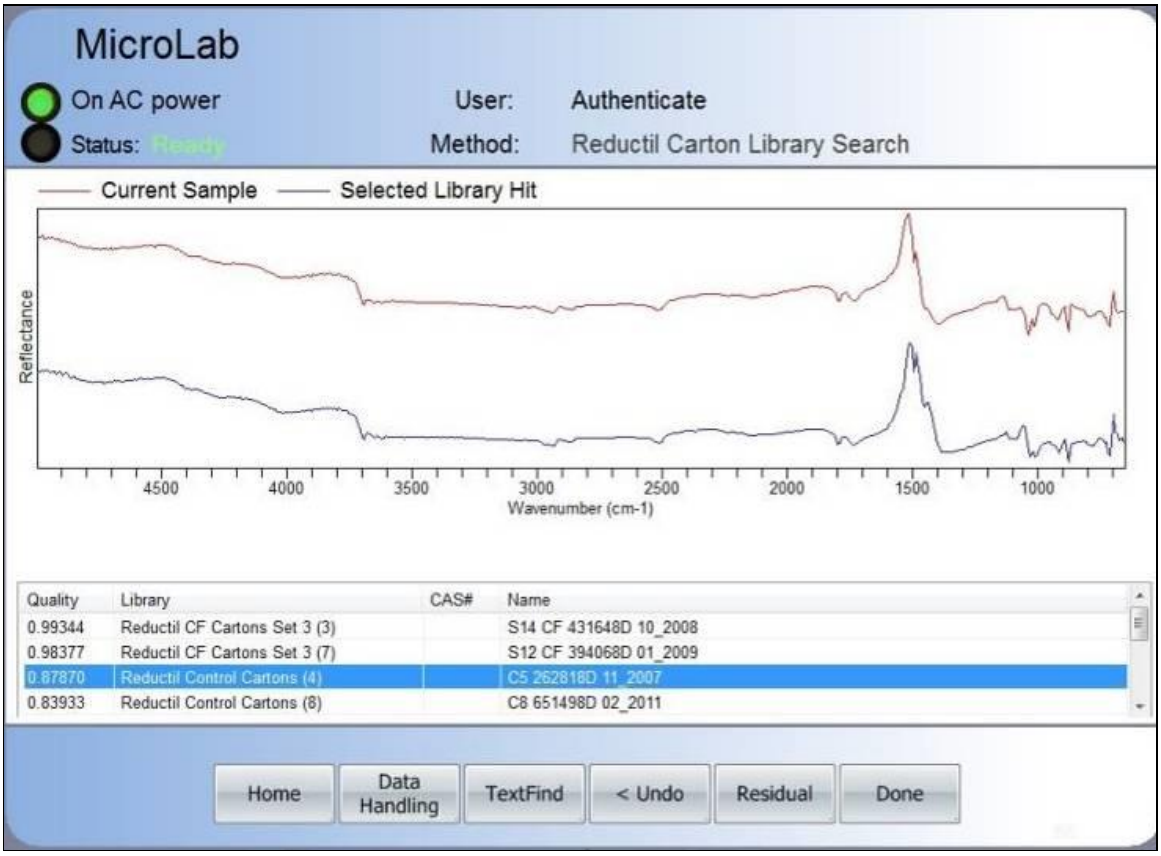


Figure 2.10 - Interactive Results Display Screenshot

2.4 Results and discussion

2.4.1 Precision

A control carton was analysed six times, removing between each analysis and replacing in a similar location on the carton (see results in Appendix A). The resulting spectra are shown in Figure 7.11 and the results are tabulated in Table 2.4 below:

Table 2.4 - Reductil Control Carton Repeatability

Replicate	*Similarity* Result
C1_1	0.9932
C1_2	0.9966
C1_3	0.9983
C1_4	0.9961
C1_5	0.9959
C1_6	0.9961
Mean	**0.9960**
CV	**0.17%**

Source Data: Appendix 1a

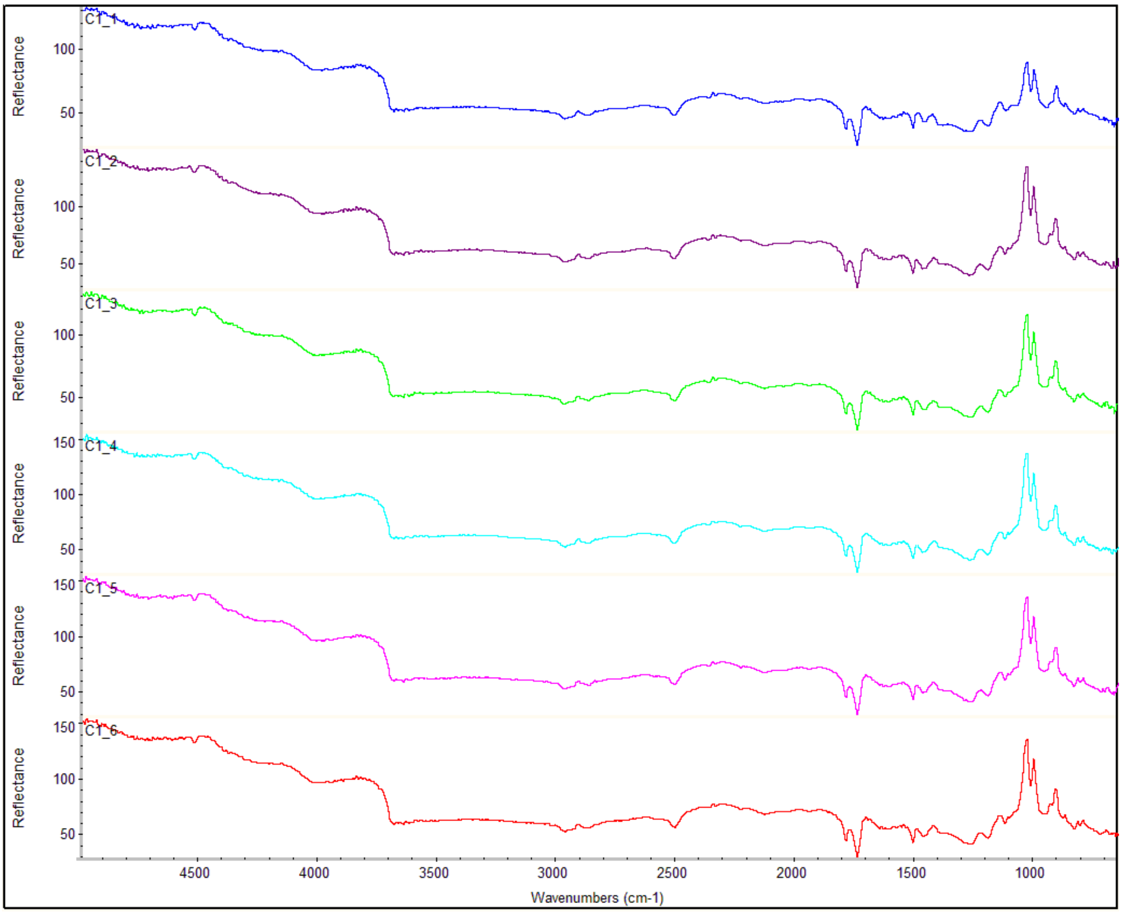


Figure 2.11 - Control C1 Carton FT-IR Repeatability Reflectance Spectral Stack

2.4.2 Set 1 – Specular Reflectance Spectra

In Figure 2.12 it was seen that the control C1 (top spectrum) was visually different to all suspects, confirming that the carton lacquers used on the suspects is not consistent with the control C1. For example, see reflectance differences around 1500cm^{-1} and 700cm^{-1} due to the lacquers (page 67).

2.4.2.1 Set 1 – Similarity Algorithm Predictions

Table 2.5 shows the success of similarity for challenged suspect and control cartons of Set 1. It was shown that they were correctly identified when scanned as unknowns (green boxes confirm similarity). Control C1 was not a second hit for any suspects, and the closest suspect to control C1 was suspect S7_1 at a similarity of 0.8101.

2.4.2.2 Set 1 – Derivative Similarity Algorithm Predictions

Table 2.6 shows the success of derivative similarity for challenged suspect and control cartons of Set 1. It was shown that eleven out of twelve cartons were correctly identified when scanned as unknowns. However, suspect S4_1 was incorrectly identified as S4_3 (identified by the red shaded box, with a derivative similarity value of 0.9352), which has exactly the same batch/ expiry.

2.4.2.3 Set 1 – Correlation Algorithm Predictions

Table 2.7 shows the success of correlation for challenged suspect and control cartons of Set 1. It was shown that they were correctly identified when scanned as unknowns (green boxes confirm similarity). Control C1 was not a second hit for any suspects, and the closest suspect to control C1 was suspect S7_1 at a correlation of 0.1899.

Reflectance FT-IR Data Set 1: Suspects S1 to S7 and Control C1

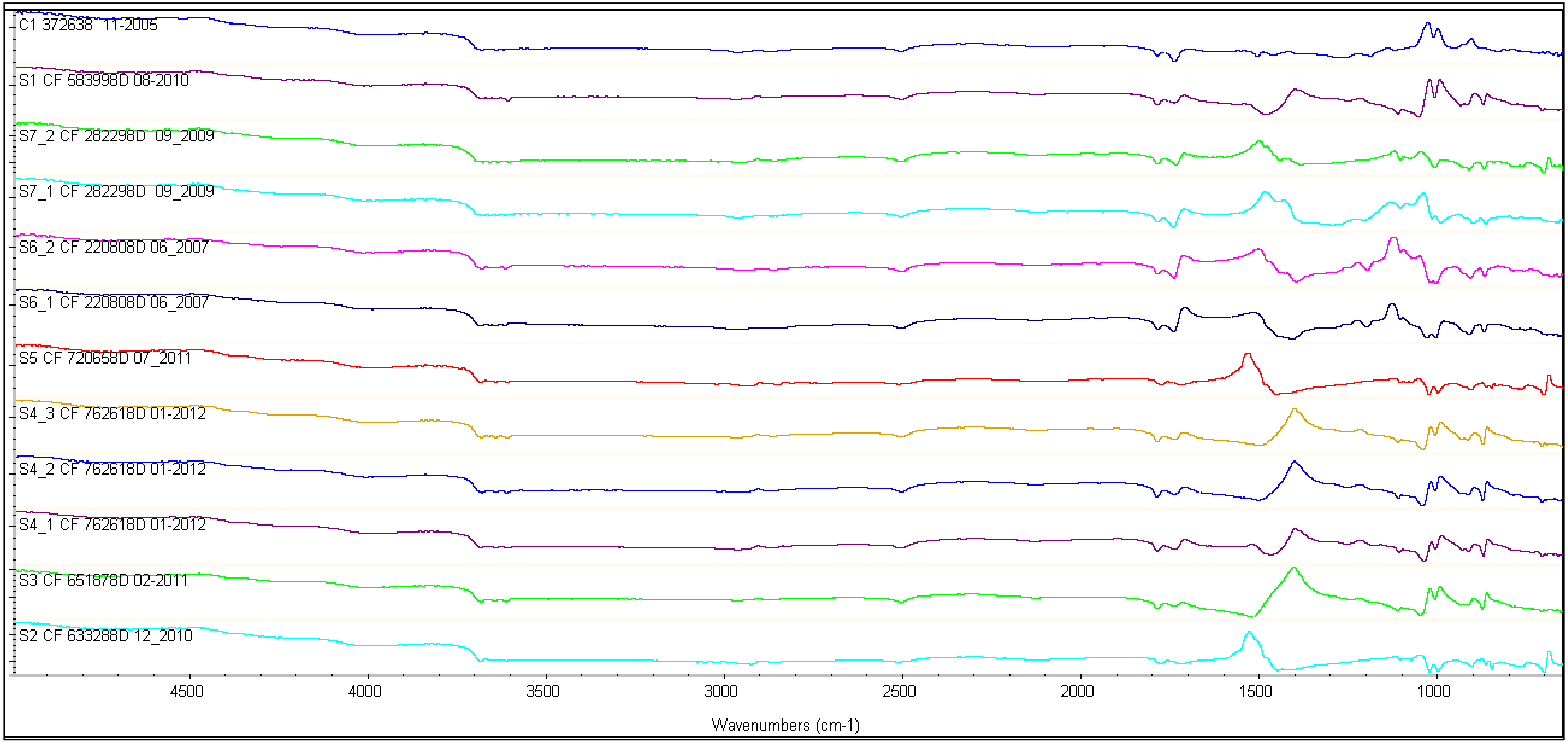


Figure 2.12 - Suspects S1 to S7 and Control C1 Carton FT-IR Reflectance Spectral Stack

2.4.2.4 Set 1 – Derivative Correlation Algorithm Predictions

Table 2.8 shows the success of derivative similarity for challenged suspect and control cartons of Set 1. It was shown that eleven out of twelve cartons were correctly identified when scanned as unknowns. However, suspect S4_1 was incorrectly identified as S4_3 (identified by the red shaded box, with a derivative correlation value of 0.0648), which has exactly the same batch/ expiry.

2.4.2.5 Set 1 – Euclidean Algorithm Predictions

Table 2.9 shows the success of Euclidean for challenged suspect and control cartons of Set 1. It was shown that they were correctly identified when scanned as unknowns (green boxes confirm similarity). Control C1 was not a second hit for any suspects, and the closest suspect to control C1 was suspect S7_2 at a Euclidean value of 0.1974.

Note: the following key clarifies the prediction classes:

Correct Prediction

Incorrect Prediction

0.XXXX Second Closest Prediction

Table 2.5 - Reductil Cartons Set 1 Specular Reflectance Similarity Predictions (Source Data: Appendix 2a)

Carton/ Challenge	**S1**	**S2**	**S3**	**S4_1**	**S4_2**	**S4_3**	**S5**	**S6_1**	**S6_2**	**S7_1**	**S7_2**	**C1**
S1	0.9922											
S2		0.9868					0.9718				0.8681	
S3			0.9940									
S4_1				0.9983	0.9331	0.9785						
S4_2	0.8382		0.8628		0.9982							
S4_3				0.9927		0.9848						
S5		0.9606					0.9804	0.8428				
S6_1								0.9688	0.8949			
S6_2									1.0000			
S7_1										0.9964		0.8101
S7_2										0.8970	0.9900	
C1												1.0000

Table 2.6 - Reductil Cartons Specular Reflectance Set 1 Derivative Similarity Predictions (Source Data: Appendix 2c)

Carton/ Challenge	S1	S2	S3	S4_1	S4_2	S4_3	S5	S6_1	S6_2	S7_1	S7_2	C1
S1	0.9417											
S2		0.8372					0.7534					
S3	0.4374		0.8852									0.1393
S4_1				0.9299	0.8066	0.8474						
S4_2			0.6192		0.9162							
S4_3				0.9352		0.8601		0.5042				
S5		0.7248					0.8300					
S6_1								0.6792	0.5097	0.2392	0.2283	
S6_2									0.9934			
S7_1										0.8386		
S7_2											0.7322	
C1												0.9854

Table 2.7 - Reductil Cartons Specular Reflectance Set 1 Correlation Predictions Results (Source Data: Appendix 2e)

Carton/ Challenge	S1	S2	S3	S4_1	S4_2	S4_3	S5	S6_1	S6_2	S7_1	S7_2	C1
S1	0.0078											
S2		0.0133					0.0282				0.1320	
S3			0.0060									
S4_1				0.0017	0.0669	0.0215						
S4_2	0.1618		0.1372		0.0018							
S4_3				0.0073		0.0152						
S5		0.0394					0.0196	0.1572				
S6_1								0.0312	0.1052			
S6_2									0.0000			
S7_1										0.0036		0.1899
S7_2										0.1030	0.0100	
C1												0.0001

Table 2.8 - Reductil Cartons Set 1 Derivative Correlation Set 1 Predictions (Source Data: Appendix 2g)

Carton/ Challenge	**S1**	**S2**	**S3**	**S4_1**	**S4_2**	**S4_3**	**S5**	**S6_1**	**S6_2**	**S7_1**	**S7_2**	**C1**
S1	0.0583											
S2		0.1628					0.2466					
S3	0.5627		0.1148									
S4_1				0.0702	0.1934	0.1526						
S4_2			0.3808		0.0838							
S4_3				0.0648		0.1399		0.4958				
S5		0.2752					0.1700					
S6_1								0.3208	0.4903			
S6_2									0.0066	0.7608	0.7717	
S7_1										0.1614		0.8608
S7_2											0.2678	
C1												0.0146

Table 2.9 - Reductil Cartons Specular Reflectance Set 1 Euclidean Predictions (Source Data: Appendix 2i)

Carton/ Challenge	**S1**	**S2**	**S3**	**S4_1**	**S4_2**	**S4_3**	**S5**	**S6_1**	**S6_2**	**S7_1**	**S7_2**	**C1**
S1	0.0462											
S2		0.0505									0.1601	
S3			0.0514				0.0735					
S4_1				0.0184	0.1209	0.0657						
S4_2	0.2086		0.1743		0.0201							
S4_3				0.0402		0.0579						
S5		0.0882					0.0625	0.1941				
S6_1								0.0869	0.1606			
S6_2									0.0043			
S7_1										0.0271		
S7_2										0.1452	0.0430	0.1974
C1												0.0031

2.4.3 Set 2 – Specular Reflectance Spectra

In Figure 2.13 it was shown that the control C2 (top spectrum) was visually different to all suspects, confirming that the carton lacquers used on the suspects were not consistent with the control. For example, see reflectance differences around $1500cm^{-1}$ and $700cm^{-1}$ due to the lacquers. There was visual similarity between suspects S8 and S9 counterfeits.

Reflectance FT-IR Data Set 2: Suspects S8 to S10 and C2

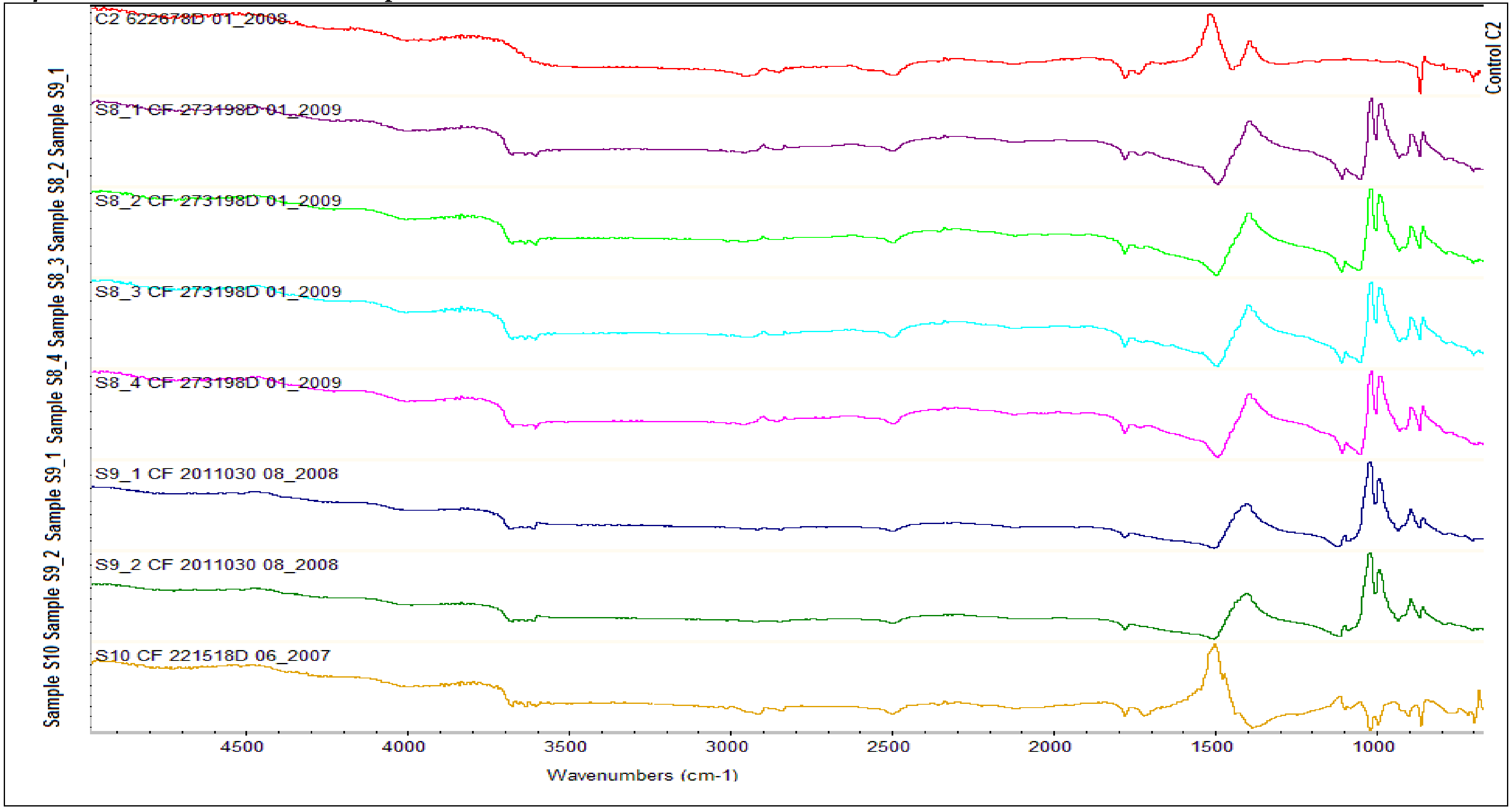


Figure 2.13 - Suspects S8 to S10 and Control C2 Carton FT-IR Reflectance Spectral Stack

2.4.3.1 Set 2 – Similarity Algorithm Predictions

Table 2.10 shows the success of similarity for challenged control and suspects of Set 2. It was shown that all suspects, apart from S8_1 were correctly identified when scanned as unknowns. Suspect S8_1 was incorrectly identified as S8_4 (having the same batch/expiry) with a correlation of 0.9924.

2.4.3.2 Set 2 – Derivative Similarity Algorithm Predictions

Table 2.11 shows the success of derivative similarity for challenged control and suspects of Set 2. Only four out of the eight cartons were correctly identified – S8_4, S9_2, S10 and C2. Three out of four S8 carton types were incorrectly identified among themselves. S9_1 was incorrectly identified as S9_2 – again these share the same Lot and expiry.

2.4.3.3 Set 2 – Correlation Algorithm Predictions

Table 2.12 shows the success of correlation for challenged suspect and control cartons of Set 2. Seven out of eight cartons were correctly identified when scanned as unknowns. Carton S8_1 was incorrectly identified as S8_4 (correlation 0.0076), both share the same Lot/ expiry.

2.4.3.4 Set 2 – Derivative Correlation Algorithm Predictions

Table 2.13 shows the success of derivative correlation for challenged control and suspects of Set 2. Only four out of the eight cartons were correctly identified – S8_4, S9_2, S10 and C2. Three out of four S8 carton types were incorrectly identified among themselves. S9_1 was incorrectly identified as S9_2 – again these share the same Lot and expiry.

2.4.3.5 Set 2 – Euclidean Algorithm Predictions

Table 2.14 shows the success of Euclidean for challenged suspect and control cartons of Set 2. Seven out of eight cartons were correctly identified when scanned as unknowns. Carton S8_1 was incorrectly identified as S8_4 (Euclidean 0.0595), both share the same Lot/ expiry.

Table 2.10 - Reductil Cartons Specular Reflectance Set 2 Similarity Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.9841	0.9940	0.9923	0.9833				
S8_2		0.9963						
S8_3			0.9923					
S8_4	0.9924			0.9943				
S9_1					0.9882	0.9963		
S9_2					0.9835	0.9999		
S10							0.9165	0.7595
C2							0.7559	0.9888

Source Data: Appendix 3a

Table 2.11 - Reductil Cartons Specular Reflectance Set 2 Derivative Similarity Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.8841	0.9141	0.9038	0.8703				
S8_2		0.9094						
S8_3			0.8392					
S8_4	0.9394			0.9148				
S9_1					0.8952	0.9110		
S9_2					0.8977	0.9859		
S10							0.9165	0.2458
C2							0.7559	0.8964

Source Data: Appendix 3c

Table 2.12 - Reductil Cartons Specular Reflectance Set 2 Correlation Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.0159	0.0060	0.0077	0.0167				
S8_2		0.0038						
S8_3			0.0077					
S8_4	0.0076			0.0057				
S9_1					0.0118	0.0037		
S9_2					0.0166	0.0001		
S10							0.0835	0.2406
C2							0.2441	0.0112

Source Data: Appendix 3e

Table 2.13 - Reductil Cartons Specular Reflectance Set 2 Derivative Correlation Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.1159	0.0860	0.0963	0.1297				
S8_2		0.0906						
S8_3			0.1608					
S8_4	0.0606			0.0853				
S9_1					0.1048	0.0890		
S9_2					0.1023	0.0141		
S10							0.1485	0.7542
C2							0.8253	0.1036

Source Data: Appendix 3g

Table 2.14 - Reductil Cartons Specular Reflectance Set 2 Euclidean Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.0719	0.0467	0.0495	0.0716				
S8_2		0.0338						
S8_3			0.0456					
S8_4	0.0595			0.0418				
S9_1					0.0631	0.0229		
S9_2					0.0691	0.0034		
S10							0.1127	0.2275
C2							0.2298	0.0486

Source Data: Appendix 3i

2.4.4 Set 3 – Specular Reflectance Spectra

In Figure 2.14 it was seen that the control C6 to C6 were extremely visually similar, as were C3 and C4. Suspects S11_1 and S11_2 were also similar.

Reflectance FT-IR Data Set 3: Suspects S11 to S16 and C4 to C9

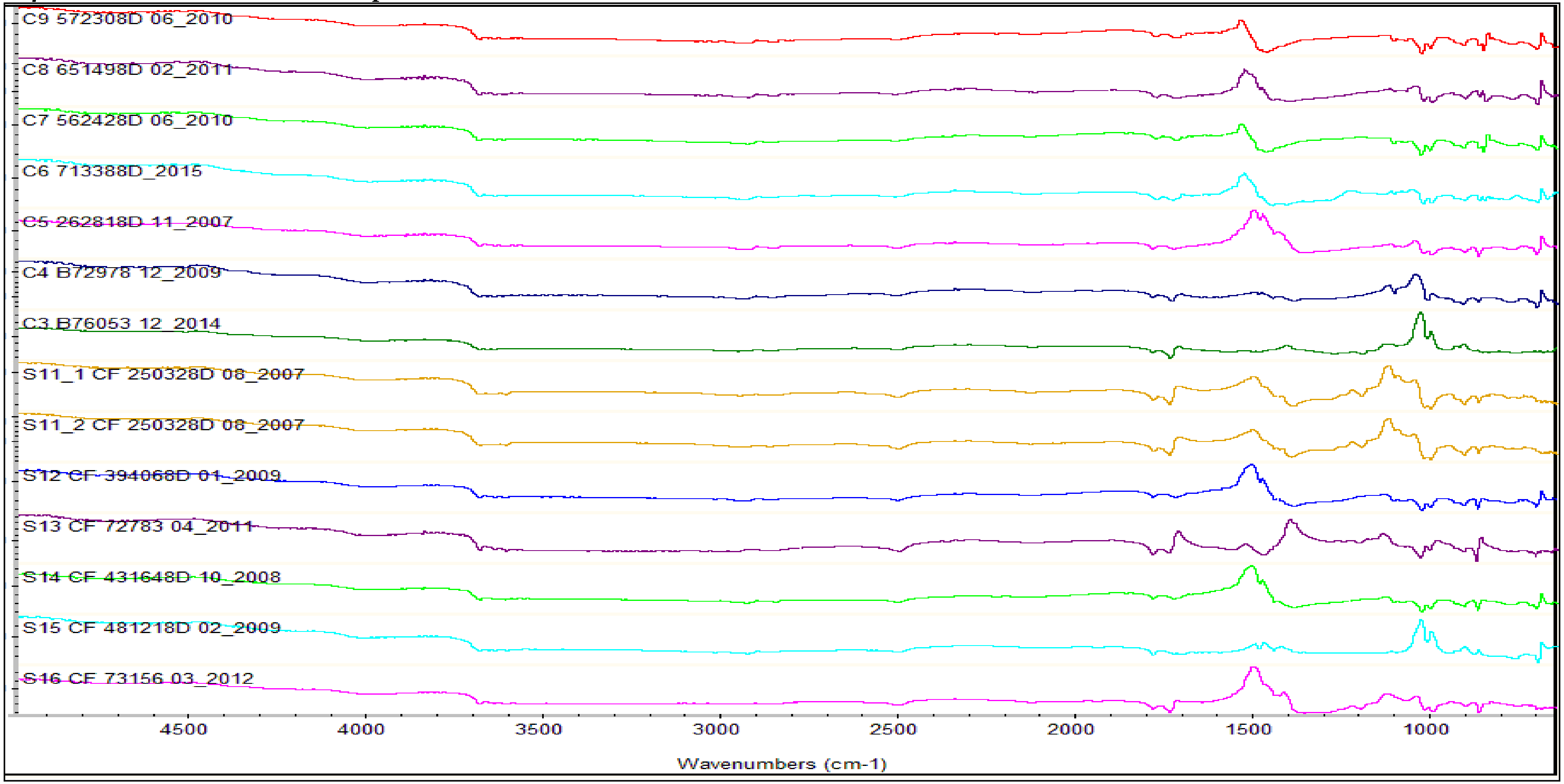


Figure 2.14 - Suspects S11 to S16 and Control C3 to C9 Carton FT-IR Reflectance Spectral Stack

2.4.4.1 Set 3 – Similarity Algorithm Predictions

Table 2.15 shows the success of similarity for challenged cartons for the suspects of Set 3. All fourteen cartons (all suspects and controls) were correctly identified.

2.4.4.2 Set 3 – Derivative Similarity Algorithm Predictions

Table 2.16 shows the success of similarity for challenged unknowns for the suspects of Set 3. Twelve out of the fourteen cartons were correctly identified. S11_1 was incorrectly identified as S11_2 (same lot/expiry) with a derivative similarity of 0.9250, and control C9 was incorrectly identified as control C7, with a derivative similarity of 0.9409. C9 and C7 do not share a common lot number.

2.4.4.3 Set 3 – Correlation Algorithm Predictions

Table 2.17 shows the success of correlation for challenged cartons for the suspects of Set 3. A total of thirteen out of fourteen cartons were correctly identified. S12 was incorrectly identified as S14 with a perfect correlation of 0.0000.

2.4.4.3 Set 3 – Derivative Correlation Algorithm Predictions

Table 2.18 shows the success of derivative correlation for challenged cartons for the suspects of Set 3. A total of thirteen out of fourteen cartons were correctly identified. S11_1 was incorrectly identified as S11_2 with a derivative correlation of 0.0900 – both these cartons share the same lot/ expiry.

2.4.3.3 Set 3 – Euclidean Algorithm Predictions

Table 2.19 shows the success of the Euclidean algorithm for challenged unknowns for the suspects of Set 3. All fourteen cartons were identified correctly.

Table 2.15 - Reductil Cartons Specular Reflectance Set 3 Similarity Predictions

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.9953	0.9861												
S11_2	0.9945	0.9952												
S12			1.0000		0.9834									
S13				0.9938										
S14			0.9863		0.9934									
S15						0.9898		0.8664						
S16							0.9943			0.8809				
C3								0.9659						
C4						0.9001			0.9984					
C5							0.8734			0.9976				
C6											1.0000		0.9732	
C7				0.7531								0.9988		0.9955
C8									0.9131		0.9730		0.9916	
C9												0.9893		0.9959

Data Source: Appendix 4a

Table 2.16 - Reductil Cartons Specular Reflectance Set 3 Derivative Similarity Predictions

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.9100	0.8505					0.5893							
S11_2	0.9250	0.9029												
S12			0.9932		0.8727									
S13				0.9247										
S14			0.8521	0.2959	0.9256									
S15						0.9110		0.1921						
S16							0.9463							
C3								0.8296						
C4						0.3972			0.8222					
C5									0.3376	0.9359				
C6											0.9922		0.6735	
C7												0.9599		0.9409
C8										0.4871	0.6447		0.9041	
C9												0.9098		0.9319

Data Source: Appendix 4c

Table 2.17 - Reductil Cartons Specular Reflectance Set 3 Correlation Predictions

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.0047	0.0139												
S11_2	0.0055	0.00482												
S12			0.0137		0.0162									
S13				0.00616										
S14			0.0000		0.0066					0.1191				
S15						0.0102		0.1336						
S16							0.0057							
C3							0.1266	0.0341						
C4									0.0016					
C5						0.0999			0.0869	0.0024				
C6											0.0000		0.0268	
C7				0.24691								0.0012		0.0041
C8											0.0270		0.0084	
C9												0.0107		0.0045

Data Source: Appendix 4e

Table 2.18 - Reductil Cartons Specular Reflectance Set 3 Derivative Correlation Predictions

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.0750	0.1495												
S11_2	0.0900	0.0971												
S12			0.0068		0.1273									
S13				0.0753										
S14			0.1479	0.7041	0.0744					0.5129				
S15						0.0890		0.8079						
S16							0.0537							
C3							0.4107	0.1704						
C4									0.1778					
C5						0.6219			0.6624	0.0641				
C6											0.0078		0.3265	
C7												0.0401		0.0681
C8											0.3553		0.0959	
C9												0.0902		0.0591

Data Source: Appendix 4g

Table 2.19 - Reductil Cartons Specular Reflectance Set 3 Euclidean Predictions

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.0335	0.0574												
S11_2	0.0399	0.0393												
S12			0.0030		0.0513									
S13				0.0360										
S14			0.0459		0.0324									
S15						0.0455		0.1990						
S16							0.0347			0.1433				
C3								0.0789						
C4						0.1379			0.0178					
C5							0.1405			0.0196				
C6											0.0020		0.0721	
C7				0.2355								0.0166		0.0311
C8									0.1308		0.0732		0.0407	
C9												0.0495		0.0302

Data Source: Appendix 4i

CHAPTER 3 – THE ANALYSIS OF COUNTERFEIT SLIMMING PILL CARTONS USING ATTENUATED TOTAL REFLECTANCE FOURIER TRANSFORM INFRA-RED SPECTROSOCPY

3.1 Introduction

This Chapter describes the analysis of counterfeit and authentic Reductil® cartons using ATR FT-IR, and comparing the outcomes of the identification algorithms available.

3.2 Background

The same sample sets that were analysed using specular reflectance (Chapter 2) were scanned using ATR FT-IR to make sets 1, 2, and 3 libraries. The cartons were then scanned one more time and challenged per identification algorithm.

3.3 Results and discussion

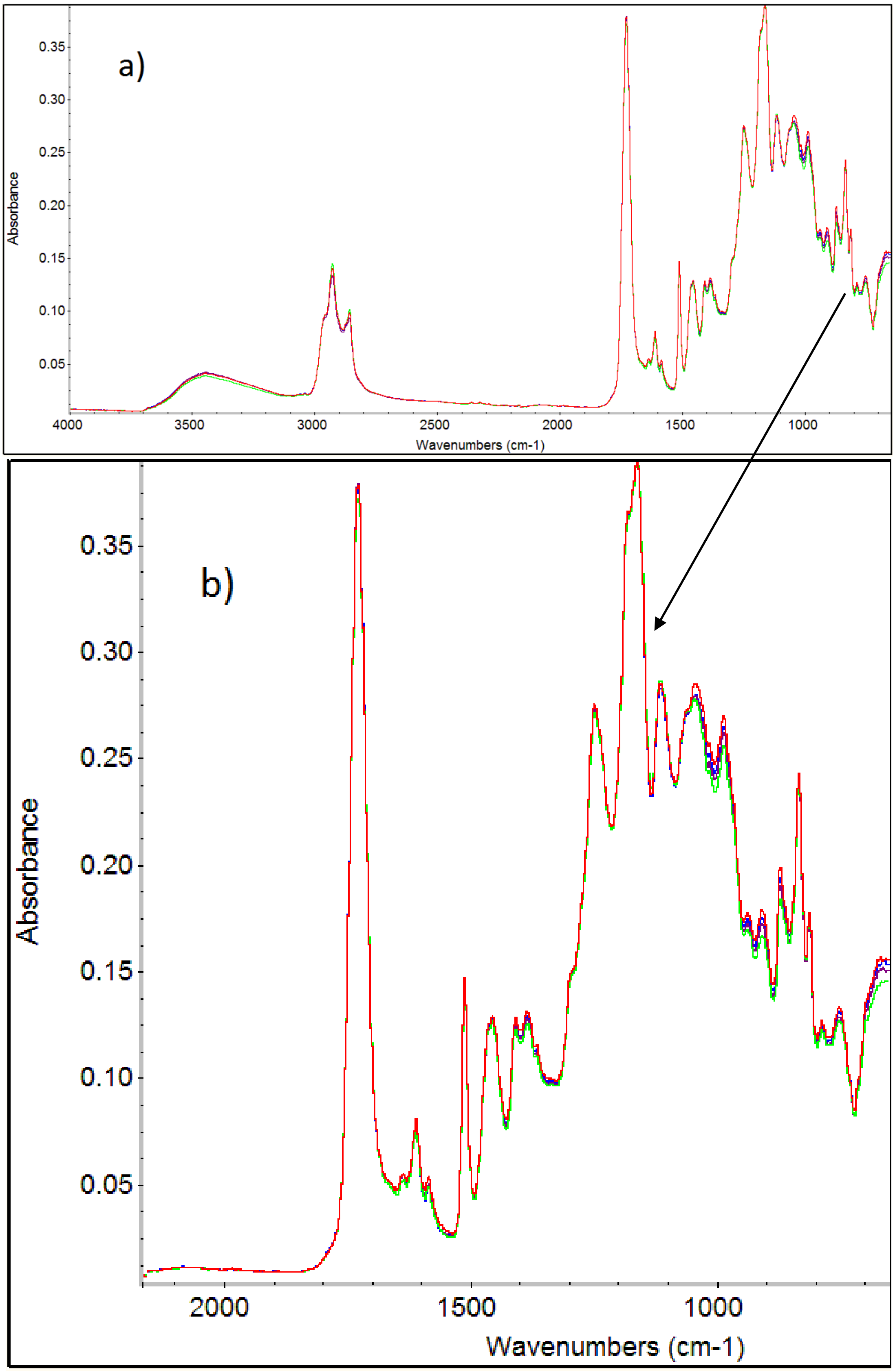
3.3.1 Precision

A control carton was analysed six times, removing between each analysis and replacing in a similar location on the carton (see results in Appendix A). The resulting spectra are shown in Figure 3.1 and the similarity predicted results are tabulated in Table 3.1.

Table 3.1 - Reductil Control Carton Repeatability

Replicate	Similarity
C1_1	0.9975
C1_2	0.9971
C1_3	0.9978
C1_4	0.9961
C1_5	0.9969
C1_6	0.9987
Mean	**0.9974**
CV	**0.08%**

Source Data: Appendix 1b



Figures 3.1a and b - Control C1 Carton FT-IR Repeatability ATR Spectral Overlays (a = full range, six spectra, and b = focus on precision in fingerprint region).

Therefore the precision of analysis using ATR was acceptable for any future analytical methodology. This was not surprising as ATR analysis only penetrates a shallow portion of the carton lacquer.

3.3.2 Set 1 – ATR Spectra

In Figure 3.2 it was seen that the control C1 (bottom spectrum) was visually different to all suspects, confirming that the carton lacquers used on the suspects is not consistent with the control C1. For example, see spectral differences around 3700 cm^{-1}, 1500 cm^{-1} and also 1150 cm^{-1}. It was shown that no suspect carton lacquer was visually similar to the control C1 carton lacquer. S7_1 and S7_2 were visually similar to each other. Also further sub-groups S4_1, S4_2 and S4_3 were spectrally similar to each other, as were S6_1 and S6_2.

FT-IR ATR Data Set 1: Suspects S1 to S7 and Control C1

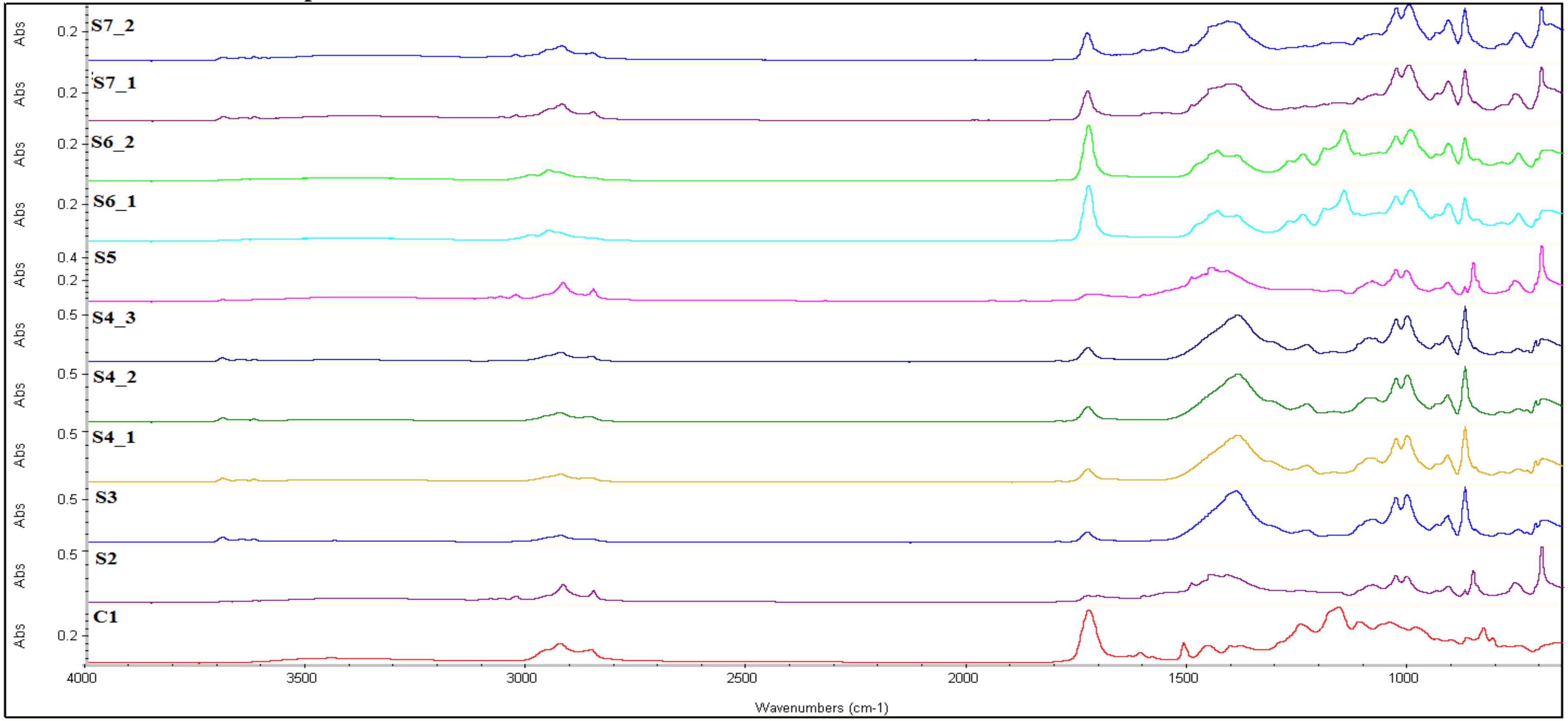


Figure 3.2 - Suspects S1 to S7 and Control C1 Carton FT-IR ATR Spectral Stack

3.3.2.1 Set 1 – Similarity Algorithm Predictions

Table 3.2 shows the success of similarity for challenged suspect and control cartons of Set 1. It was shown that eight out of twelve cartons were correctly identified. Suspect S2 was incorrectly identified as S5, S4_3 was incorrectly identified as S4_1 (same lot/ expiry), S6_2 was incorrectly identified as S6_1 (same lot/ expiry) and finally S7_2 was incorrectly identified as S7_1 (same lot/ expiry).

3.3.2.2 Set 1 – Derivative Similarity Algorithm Predictions

Table 3.3 shows the success of derivative similarity for challenged suspect and control cartons of Set 1. It was shown that nine out of twelve cartons were correctly identified. Suspect S2 was incorrectly identified as S5, S4_1 was incorrectly identified as S4_3 (same lot/ expiry), S4_2 was incorrectly identified as S4_3 (same lot/ expiry) and finally S7 was incorrectly identified as S7_1 (same lot/ expiry).

3.3.2.3 Set 1 – Correlation Algorithm Predictions

Table 3.4 shows the success of correlation for challenged suspect and control cartons of Set 1. It was shown that nine out of twelve cartons were correctly identified. Suspect S2 was incorrectly identified as S5, S6_2 was incorrectly identified as S6_1 (same lot/ expiry), and finally S7_2 was incorrectly identified as S7_1 (same lot/ expiry).

3.3.2.4 Set 1 – Derivative Correlation Algorithm Predictions

Table 3.5 shows the success of derivative similarity for challenged suspect and control cartons of Set 1. It was shown that only seven out of twelve cartons were correctly identified. Suspect S2 was incorrectly identified as S5, S4_1 was incorrectly identified as S4_3 (same lot/ expiry), S4_2 was incorrectly identified as S4_3 (same lot/ expiry), S6_2 was incorrectly identified as S6_1 (same lot/ expiry) and finally S7_2 was incorrectly identified as S7_1 (same lot/ expiry).

3.3.2.5 Set 1 – Euclidean Algorithm Predictions

Table 3.6 shows the success of Euclidean for challenged suspect and control cartons of Set 1. It was shown that only seven out of twelve cartons were correctly identified. Suspect S2 was incorrectly identified as S5, S4_2 was incorrectly identified as S4_1 (same lot/ expiry), S4_3 was incorrectly identified as S4_1 (same lot/ expiry), S6_2 was incorrectly identified as S6_1 (same lot/ expiry) and finally S7_2 was incorrectly identified as S7_1 (same lot/ expiry).

Table 3.2 - Reductil Cartons Set 1 ATR Similarity Predictions Results (Source Data: Appendix 2b)

Carton/ Challenge	S1	S2	S3	S4_1	S4_2	S4_3	S5	S6_1	S6_2	S7_1	S7_2	C1
S1	0.9997											
S2		0.9900					0.9821					
S3			0.9997									
S4_1				0.9993	0.9994	0.9994						
S4_2				0.9993	0.9994							
S4_3			0.9888			0.9991						
S5		0.9959					0.9969					
S6_1								0.9952	0.9942			
S6_2								0.9265	0.9787			0.8618
S7_1										0.9978	0.9978	
S7_2	0.9275									0.9952	0.9952	
C1												0.9995

Table 3.3 - Reductil Cartons Set 1 ATR Derivative Similarity Predictions Results (Source Data: Appendix 2d)

Carton/ Challenge	**S1**	**S2**	**S3**	**S4_1**	**S4_2**	**S4_3**	**S5**	**S6_1**	**S6_2**	**S7_1**	**S7_2**	**C1**
S1	0.9880											
S2		0.9450					0.9311					
S3	0.8983		0.9900									
S4_1				0.9855		0.9855						
S4_2					0.9852							
S4_3			0.9783	0.9870	0.9874	0.9874						
S5		0.9834					0.9789					
S6_1								0.9731				0.2728
S6_2								0.8330	0.9713			
S7_1									0.9182	0.9804		
S7_2										0.9736	0.9804	
C1											0.9736	0.9774

Table 3.4 - Reductil Cartons Set 1 ATR Correlation Predictions Results (Source Data: Appendix 2f)

Carton/ Challenge	S1	S2	S3	S4_1	S4_2	S4_3	S5	S6_1	S6_2	S7_1	S7_2	C1
S1	0.0003											
S2		0.0098					0.0179					
S3			0.0003									
S4_1				0.0007								
S4_2				0.0007	0.0006	0.0006						
S4_3			0.0112		0.0006	0.0006						
S5		0.0041					0.0031					
S6_1								0.0049	0.0058			
S6_2								0.0735	0.0212			0.1382
S7_1										0.0022	0.0022	
S7_2	0.0726									0.0048	0.0048	
C1												0.0005

Table 3.5 - Reductil Cartons Set 1 ATR Derivative Correlation Predictions Results (Source Data: Appendix 2h)

Carton/ Challenge	S1	S2	S3	S4_1	S4_2	S4_3	S5	S6_1	S6_2	S7_1	S7_2	C1
S1	0.0120											
S2		0.0550					0.0689					
S3	0.1017		0.0100									
S4_1				0.0145		0.0145						
S4_2			0.0217		0.0148							
S4_3				0.0130	0.0126	0.0126						
S5		0.0166					0.0211					
S6_1								0.0269	0.0287			0.7272
S6_2								0.1670	0.0818	0.0264		
S7_1										0.0198	0.0196	
S7_2											0.0264	
C1												0.0226

Table 3.6 - Reductil Cartons Set 1 ATR Euclidean Predictions Results (Source Data: Appendix 2j)

Carton/ Challenge	S1	S2	S3	S4_1	S4_2	S4_3	S5	S6_1	S6_2	S7_1	S7_2	C1
S1	0.0233											
S2		0.0764					0.1032					
S3			0.0191									
S4_1				0.0243	0.0239	0.0239						
S4_2				0.0243	0.0240							
S4_3			0.0927			0.0333						
S5		0.0510					0.0437					
S6_1								0.0583	0.0681			0.3157
S6_2								0.2276	0.1228			
S7_1										0.0373	0.0373	
S7_2	0.2482									0.0554	0.0554	
C1												0.0180

3.3.3 Set 2 – ATR Spectra

In Figure 3.2 it was shown that the control C2 (bottom spectrum) was visually different to all suspects, confirming that the carton lacquers used on the suspects were not consistent with the control. For example, see reflectance differences around 3700cm^{-1}, 1300cm^{-1}, and 700cm^{-1} due to the lacquers. Suspect S10 was the most visually similar to control C2 carton lacquer, however it had extra peaks at 1000cm^{-1} not present in C2.

ATR Data Set 2: Suspects S8 to S10 and C2

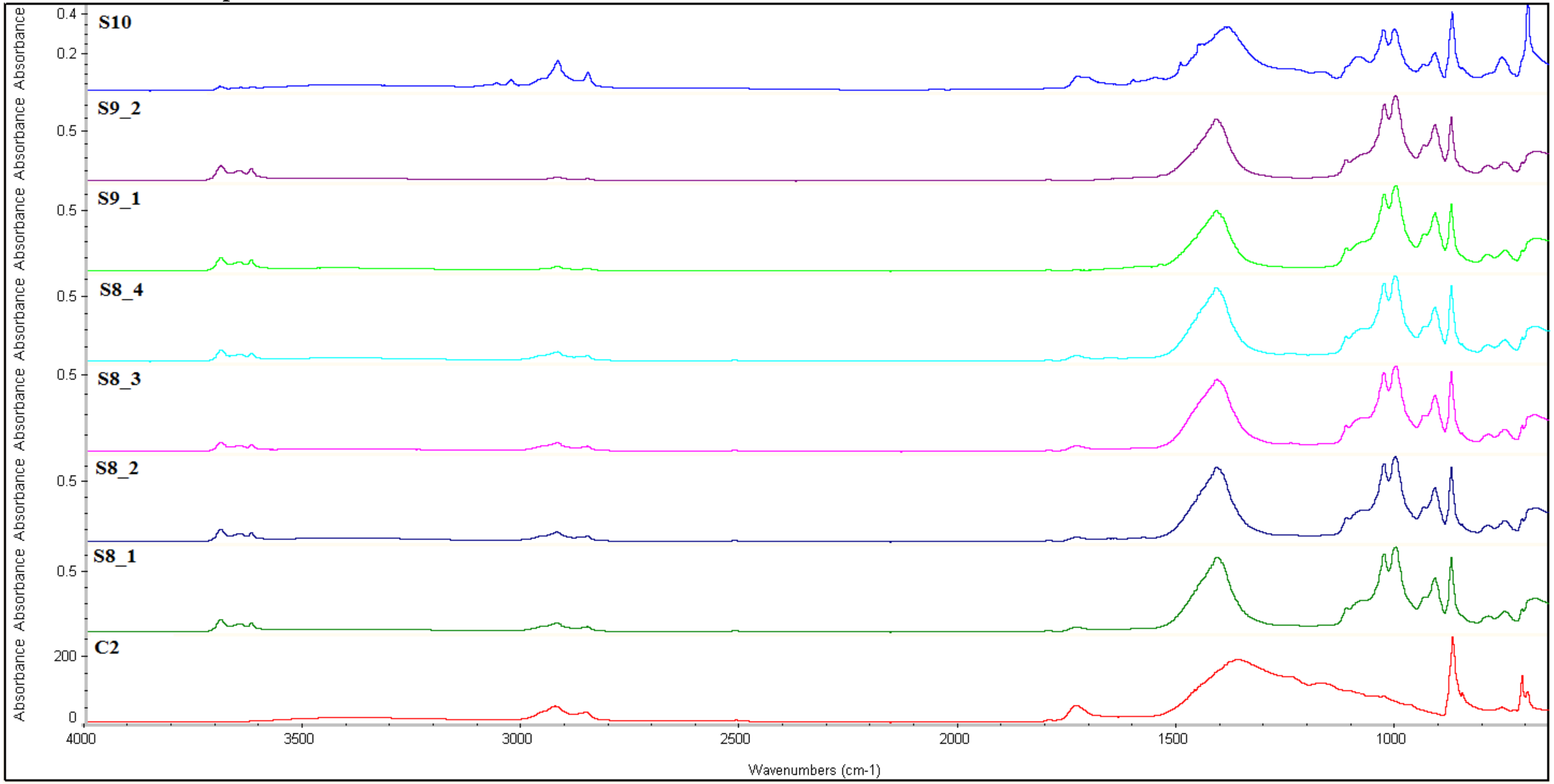


Figure 3.2 - Suspects S8 to S10 and Control C2 Carton FT-IR ATR Spectral Stack

3.3.3.1 Set 2 – Similarity Algorithm Predictions

Table 3.6 shows the success of similarity for challenged control and suspects of Set 2. It was shown that six out of ten cartons were correctly identified. Suspects S8_2 and S8_3 were both incorrectly identified as S8_1 (having the same batch/expiry).

3.3.3.2 Set 2 – Derivative Similarity Algorithm Predictions

Table 3.7 shows the success of derivative similarity for challenged control and suspects of Set 2. Six out of the eight cartons were correctly identified. S8_1 was incorrectly identified as S8_2 (same lot and expiry), and S8_3 was incorrectly identified as S8_4.

3.3.3.3 Set 2 – Correlation Algorithm Predictions

Table 3.8 shows the success of correlation for challenged suspect and control cartons of Set 2. It was shown that six out of ten cartons were correctly identified. As per Similarity outcomes, Suspects S8_2 and S8_3 were both incorrectly identified as S8_1 (having the same batch/expiry) using the correlation algorithm.

3.3.3.4 Set 2 – Derivative Correlation Algorithm Predictions

Table 3.9 shows the success of derivative correlation for challenged control and suspects of Set 2. Only four out of the eight cartons were correctly identified – S8_2, S9_2, S10 and C2. Three out of four S8 carton types were incorrectly identified among their same lot/expiry populations. S9_1 was incorrectly identified as S9_2, again these share the same lot and expiry.

3.3.3.5 Set 2 – Euclidean Algorithm Predictions

Table 3.10 shows the success of Euclidean for challenged suspect and control cartons of Set 2. Six out of eight cartons were correctly identified when scanned as unknowns. Cartons S8_2 and S8_3 were both incorrectly identified as S8_1 - all share the same lot/ expiry.

Table 3.6 - Reductil Cartons ATR Set 2 Similarity Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.9989	0.9987	0.9992					
S8_2	0.9984	0.9982		0.9992				
S8_3			0.9978				0.8366	
S8_4				0.9993				
S9_1					0.9981	0.9949		
S9_2					0.9976	0.9976		
S10							0.9986	0.6787
C2								0.9996

Source Data: Appendix 3b

Table 3.7 - Reductil Cartons ATR Set 2 Derivative Similarity Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.9849							
S8_2	0.9850	0.9863		0.9873				
S8_3			0.9865					
S8_4		0.9853	0.9867	0.9873	0.9807		0.5261	
S9_1					0.9815	0.9756		
S9_2						0.9805		
S10							0.9862	0.3878
C2								0.9893

Source Data: Appendix 3d

Table 3.8 - Reductil Cartons ATR Set 2 Correlation Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.0011	0.0013	0.0008					
S8_2	0.0016	0.0018		0.0008				
S8_3			0.0014				0.1634	
S8_4				0.0007				
S9_1					0.0020	0.0051		
S9_2					0.0024	0.0024		
S10							0.0014	0.3213
C2								0.0004

Source Data: Appendix 3f

Table 3.9 - Reductil Cartons ATR Set 2 Derivative Correlation Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.0150							
S8_2	0.0151	0.0137		0.0127				
S8_3			0.0135					
S8_4		0.0147	0.0133	0.0127			0.4740	
S9_1					0.0193	0.0244		
S9_2					0.0185	0.0195		
S10							0.0139	0.6180
C2								0.0167

Source Data: Appendix 3h

Table 3.10 - Reductil Cartons ATR Set 2 Euclidean Algorithm Predictions

Carton/ Challenge	S8_1	S8_2	S8_3	S8_4	S9_1	S9_2	S10	C2
S8_1	0.0287	0.0324	0.0247	0.0311				
S8_2	0.0383	0.0436						
S8_3			0.0330				0.3654	
S8_4				0.0227				
S9_1					0.0403			
S9_2					0.0505	0.0464		
S10						0.0633	0.0395	0.4897
C2								0.0191

Source Data: Appendix 3j

3.3.4 Set 3 – ATR Spectra

In Figure 3.3 it was seen that the control C5 to C9 were visually similar. Suspects S11_1 and S11_2 were also similar to each other.

3.3.4.1 Set 3 – Similarity Algorithm Predictions

Table 3.11 shows the success of similarity for challenged cartons for the suspects of Set 3. Thirteen out of fourteen cartons were successfully identified. Suspect carton S11_1 was incorrectly identified as S11_2 – i.e. another carton with the same lot / expiry.

ATR FT-IR Data Set 3: Suspects S11 to S16 and C4 to C9

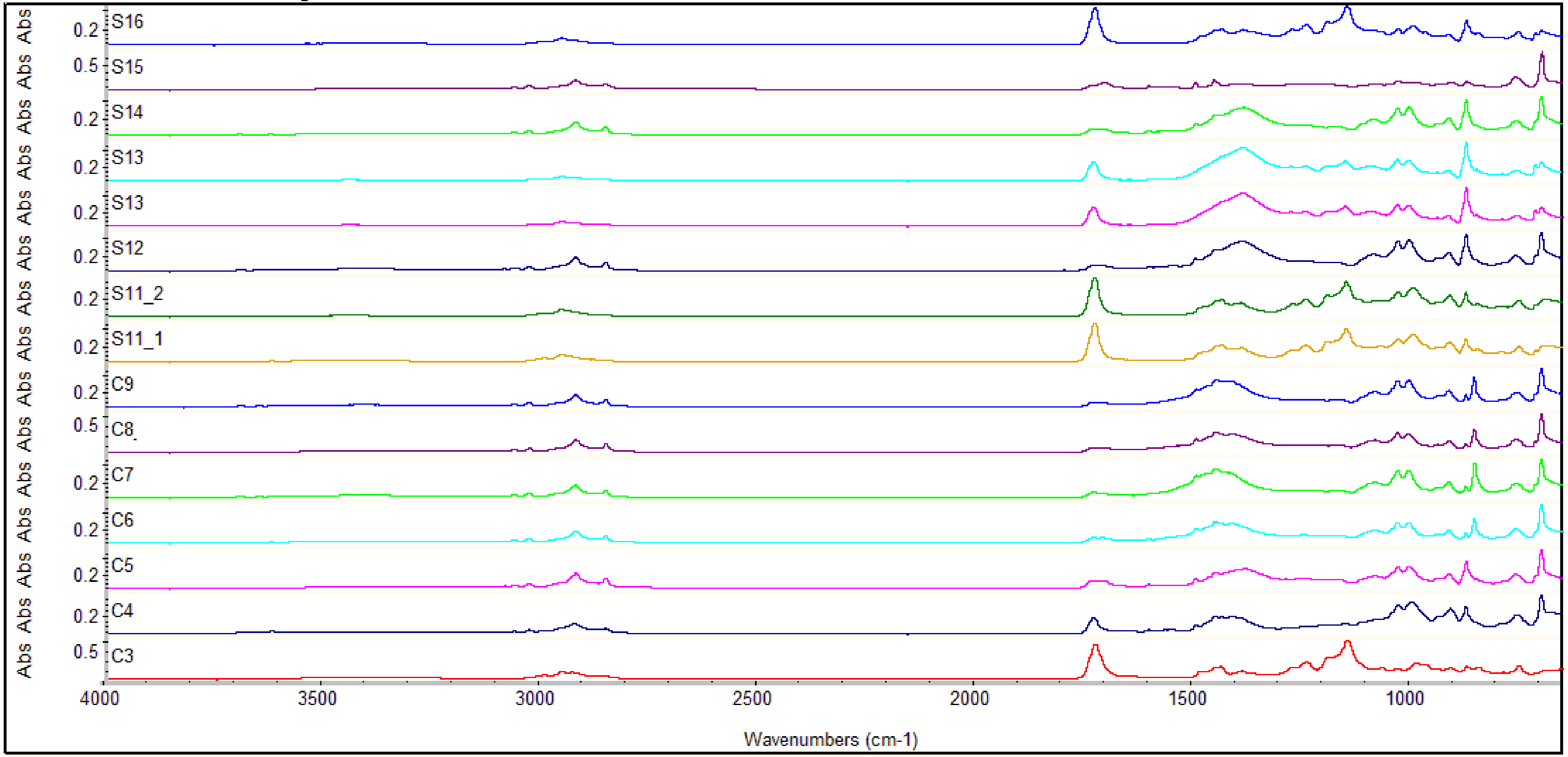


Figure 3.3 - Suspects S11 to S16 and Control C3 to C9 Carton ATR Spectral Stack

3.3.4.1 Set 3 – Similarity Algorithm Predictions

Table 3.11 shows the success of similarity for challenged cartons for the suspects of Set 3. Thirteen out of fourteen cartons were successfully identified. Suspect carton S11_1 was incorrectly identified as S11_2 – i.e. another carton with the same lot / expiry.

3.3.4.2 Set 3 – Derivative Similarity Algorithm Predictions

Table 3.12 shows the success of derivative similarity for challenged unknowns for the suspects of Set 3. Thirteen out of fourteen cartons were successfully identified. Suspect carton S11_1 was incorrectly identified as S11_2 – i.e. another carton with the same lot / expiry.

3.3.4.3 Set 3 – Correlation Algorithm Predictions

Table 3.13 shows the success of correlation for challenged cartons for the suspects of Set 3. Twelve out of fourteen cartons were correctly identified. S12 was incorrectly identified as S14. Suspect S11_1 was incorrectly identified as S11_2 (same lot / expiry).

3.3.4.4 Set 3 – Derivative Correlation Algorithm Predictions

Table 3.14 shows the success of derivative correlation for challenged cartons for the suspects of Set 3. Twelve out of fourteen cartons were correctly identified. S12 was incorrectly identified as S14. Suspect S11_1 was incorrectly identified as S11_2 (same lot / expiry).

3.3.4.5 Set 3 – Euclidean Algorithm Predictions

Table 3.15 shows the success of the Euclidean algorithm for challenged unknowns for the suspects of Set 3. Twelve out of fourteen cartons were correctly identified. S12 was incorrectly identified as S14. Suspect S11_1 was incorrectly identified as S11_2 (same lot / expiry).

Table 3.11 - Reductil Cartons ATR Set 3 Similarity Predictions Results

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.9989	0.9953												
S11_2	0.9998	0.9965												
S12			1.0000		0.9889									
S13				0.9938										
S14			0.9863		0.9964					0.9236				
S15						0.9959								
S16							0.9965	0.9236						
C3							0.9217	0.9993						
C4									0.9965		0.9964			
C5						0.7967			0.8432	0.9923				
C6											0.9977		0.9967	
C7				0.7531								0.9950		0.9952
C8													0.9988	
C9												0.9905		0.9982

Data Source: Appendix 4b

Table 3.12 - Reductil Cartons ATR Set 3 Derivative Similarity Predictions Results

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.9989	0.9953												
S11_2	0.9998	0.9965		0.6774				0.7496						
S12			1.0000		0.9899									
S13				0.9884										
S14			0.9863		0.9964									
S15						0.9959								
S16							0.9965							
C3							0.9217	0.9778						
C4									0.9744	0.8543	0.9643			
C5						0.7967			0.8208	0.9749				
C6											0.9814		0.9760	
C7												0.9708		0.9606
C8													0.9849	
C9												0.9380		0.9828

Data Source: Appendix 4d

Table 3.13 - Reductil Cartons ATR Set 3 Correlation Predictions Results

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.0114	0.0047												
S11_2	0.0002	0.0036												
S12			0.0061		0.0102									
S13				0.0005										
S14			0.0039	0.1346	0.0036					0.0764				
S15						0.0042								
S16							0.0035	0.0968						
C3							0.0783	0.0007						
C4									0.0035					
C5						0.2033			0.1568	0.0077				
C6											0.0037		0.0033	
C7												0.0050		0.0048
C8											0.0235		0.0012	
C9												0.0095		0.0018

Data Source: Appendix 4f

Table 3.14 - Reductil Cartons Set 3 ATR Derivative Correlation Predictions

Carton/ Challenge	**S11_1**	**S11_2**	**S12**	**S13**	**S14**	**S15**	**S16**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**
S11_1	0.0011	0.0047												
S11_2	0.0002	0.0036						0.2504						
S12			0.0061	0.3226	0.0102									
S13				0.0116										
S14			0.0039		0.0036									
S15						0.0042								
S16							0.0035							
C3							0.0783	0.0223						
C4									0.0256	0.1457	0.0357			
C5						0.2033			0.1792	0.0251				
C6											0.0186		0.0240	
C7												0.0292		0.0394
C8													0.0151	
C9												0.0620		0.0172

Data Source: Appendix 4h

Table 3.15 - Reductil Cartons Set 3 Euclidean Predictions Results

Carton/ Challenge	S11_1	S11_2	S12	S13	S14	S15	S16	C3	C4	C5	C6	C7	C8	C9
S11_1	0.0301	0.0603												
S11_2	0.0152	0.0494												
S12			0.0709		0.0849									
S13				0.0278										
S14			0.0579	0.3122	0.0527					0.2357				
S15						0.0557								
S16							0.0494	0.2612						
C3							0.2355	0.0253						
C4									0.0477		0.0469			
C5						0.3589			0.3208	0.0762				
C6											0.0381		0.0444	
C7												0.0579		0.0578
C8													0.0280	
C9												0.0798		0.0385

Data Source: Appendix 4j

Table 3.16 - Summary of ATR Pass Predictions

Set	Similarity	Derivative Similarity	Correlation	Derivative Correlation	Euclidean
1	8/12	9/12	9/12	7/12	7/12
2	6/8	6/8	6/8	4/8	6/8
3	13/14	13/14	12/14	12/14	12/14

CHAPTER 4 – CONCLUSIONS / RECOMMENDATIONS

Tables 4.1 and 4.2 summarize the predictions resulting from each technology and algorithm:

Table 4.1 - Comparison of ATR versus Specular Reflectance Pass Predictions

Technique	Set	Similarity	Derivative Similarity	Correlation	Derivative Correlation	Euclidean
Reflectance	1	12/12	11/12	12/12	11/12	12/12
ATR	1	8/12	9/12	9/12	7/12	7/12
Reflectance	2	7/8	4/8	7/8	4/8	7/8
ATR	2	6/8	6/8	6/8	4/8	6/8
Reflectance	3	14/14	12/14	13/14	13/14	14/14
ATR	3	13/14	13/14	12/14	12/14	12/14

Table 4.2 - Comparison of Total ATR and Total Specular Reflectance Pass Predictions

Technique	Similarity	Derivative Similarity	Correlation	Derivative Correlation	Euclidean
Reflectance	33/34	27/34	32/34	28/34	33/34
ATR	27/34	28/34	27/34	23/34	25/34

Overall, specular reflectance using either Similarity or Euclidean algorithms gave the most confident predictions for carton authentication, each achieving a total of 33 out of 34 predictions (i.e. a 97.1% confidence).

Appendixes 5a) to 5c) show the statistical comparisons between techniques using one-way analysis of variance (ANOVA - a statistical method in which the variation in a set of observations is divided into distinct components), confidence intervals (CI) and t-tests (95% confidence, for sets 1, 2 and 3 similarity, derivative similarity, and Euclidean outcomes (as these data treatments were more successful than correlation and derivative correlation outcomes). It was shown that the techniques were similar, apart from those combined with derivative similarity, which gave results significantly different between ATR and specular reflectance for Sets 1 and 2. ATR and specular reflectance results did not statistically differ for similarity data, for all three sets. Also, ATR and specular reflectance results did not statistically differ for Euclidean data, for all three sets. In both FT-IR techniques the Similarity algorithm had the highest confidence of authentication/counterfeit detection.

Appendixes 6a) to c) show the statistical comparisons for within techniques algorithms using one-way ANOVA. There was no statistical difference within the specular reflectance sample sets 1-3 except the Derivative ATR data which was statistically different. Since ATR data suggests differences within sample sets and specular reflectance does not, this calls into question the validity of ATR determinations, and again strengthens the justification for the use of specular reflectance as the preferred technique.

The final statistical comparison compared all results, from all techniques and algorithms (for example, all similarity results were pooled from both techniques) and analysed by unstacked ANOVA in Appendix 7. For Euclidean data, the reciprocal value was used to normalise the data before analysis. Similarity ATR and specular reflectance results show the most accurate counterfeit carton detection. This would appear to be the most valid algorithm. Specular reflectance mode of analysis was more capable of confirming the presence of counterfeit packaging compared with ATR. *Similarity* and *Euclidean* were found to be the most reliable identification algorithms in specular reflectance mode, whereas correlation was most suitable for ATR analysis.

Agilent has designed a specular reflectance sample interface for use with the handheld 4100 ExoScan FTIR spectrometer. The 4100 ExoScan's interface uses a lens design that illuminates the sample with normal incidents, then collects the beam collinear. Specular reflectance is a valuable FT-IR sampling technique for the analysis of lacquered thin films on reflective substrates, for the analysis of relatively thick films on reflective materials and for analysis of bulk materials where no sample preparation is preferred.

ATR is a surface measurement, and a single reflection ATR sampling technique is ideal for the identification of thick or highly-absorbing samples where small IR pathlengths are required. In many ways, a reflectance interface may be the most versatile and easiest to use of the sampling technologies for a handheld FT-IR.
Whereas ATR requires good contact with a sample, the large depth of field enables diffuse reflectance to yield good spectra without touching the sample. Obtaining good contact with ATR for powdered samples is easy when one has a lab system with a conventional pressure device that ensures good contact - not as easy when you have a handheld system and may have inconsistent pressure.

The precision of a reanalysed control carton removing and then presenting it to the instrument six times, was excellent for both ATR and specular reflectance. However it is anticipated that this precision would deteriorate for counterfeit cartons where the uniformity of lacquer is not as controlled as a good manufacturing process. Therefore the prediction algorithm chosen would be irrelevant as at some point the prediction would be different across the same carton.

Analysis of drug products in the field using rapid techniques requires a 99.9% pass rate. This is because the risk of false outcomes can be severe for patient safety downstream (i.e. a counterfeit batch may get into the legal supply chain or could be purchased off the internet at risk). For deployment of the specular reflectance technology in the field, a 99% pass rate could be acceptable for screening of packaging materials. This rate is acceptable for screening packaging where pressure is on customs at borders with a multitude of other works to risk assess.

Improvements to the current set up would be a smaller and lighter instrument with a long battery lifetime. Agilent technologies now market such an instrument to cope - The 4300 Handheld FTIR is lightweight, perfectly balanced and ergonomically optimized to ensure that users get superior results. The deuterated triglycine sulfate (DTGS) detector version of the 4300 is designed for frequent field deployment and at-site analysis of a wide range of materials. It is finding use in many different industrial applications/markets including aerospace, automotive, coating and paints, polymers, composites, agriculture and art conservation.

Recommendations for further works should include the proof the robustness of the technique to identify other packaging materials, including the carton and lacquer types used in the pharmaceutical industry. A first recommendation is to truly prove if lacquers are specific to artwork code, and then make corresponding libraries for identification based on these codes. Predictions could be improved by narrowing frequency range of the identification algorithm to the highest specificity to the lacquer.

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APPENDIXES

Appendix 1a - Specular Reflectance Control C1 Repeatability – Similarity Library Hits

C1_1

Quality	Library	CAS#	Name
0.99318	Reductil Control Cartons (0)		C1 372638 11-2005
0.91829	Reductil Control Cartons (2)		C3 B76053 12_2014

C1_2

Quality	Library	CAS#	Name
0.99657	Reductil Control Cartons (0)		C1 372638 11-2005
0.94770	Reductil Control Cartons (2)		C3 B76053 12_2014

C1_3

Quality	Library	CAS#	Name
0.99830	Reductil Control Cartons (0)		C1 372638 11-2005
0.94102	Reductil Control Cartons (2)		C3 B76053 12_2014

C1_4

Quality	Library	CAS#	Name
0.99611	Reductil Control Cartons (0)		C1 372638 11-2005
0.95219	Reductil Control Cartons (2)		C3 B76053 12_2014

C1_5

Quality	Library	CAS#	Name
0.99591	Reductil Control Cartons (0)		C1 372638 11-2005
0.95148	Reductil Control Cartons (2)		C3 B76053 12_2014

C1_6

Quality	Library	CAS#	Name
0.99609	Reductil Control Cartons (0)		C1 372638 11-2005
0.94896	Reductil Control Cartons (2)		C3 B76053 12_2014

Appendix 1b - ATR Control C1 Repeatability – Similarity Library Hits

C1_1

Quality	Library	CAS#	Name
0.99745	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.83573	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C1_2

Quality	Library	CAS#	Name
0.99714	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.84030	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C1_3

Quality	Library	CAS#	Name
0.99777	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.84189	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C1_4

Quality	Library	CAS#	Name
0.99613	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.84306	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C1_5

Quality	Library	CAS#	Name
0.99690	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.83754	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C1_6

Quality	Library	CAS#	Name
0.99666	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.84164	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

Appendix 2a - Specular Reflectance Similarity Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.99223	Reductil CF Cartons (0)		S1 CF 583998D 08-2010
0.83823	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S2

Quality	Library	CAS#	Name
0.98675	Reductil CF Cartons (1)		S2 CF 633288D 12_2010
0.96062	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S3

Quality	Library	CAS#	Name
0.99400	Reductil CF Cartons (2)		S3 CF 651878D 02-2011
0.86284	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S4_1

Quality	Library	CAS#	Name
0.99832	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012
0.99267	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012

S4_2

Quality	Library	CAS#	Name
0.99816	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012
0.93311	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_3

Quality	Library	CAS#	Name
0.98476	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.97848	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S5

Quality	Library	CAS#	Name
0.98044	Reductil CF Cartons (6)		S5 CF 720658D 07_2011
0.97176	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

S6_1

Quality	Library	CAS#	Name
0.96882	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007
0.84276	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S6_2

Quality	Library	CAS#	Name
0.99996	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007
0.89485	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

S7_1

Quality	Library	CAS#	Name
0.99639	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009
0.89699	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009

S7_2

Quality	Library	CAS#	Name
0.98998	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009
0.86805	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

C1

Quality	Library	CAS#	Name
0.99997	Reductil CF Cartons (13)		C1 372638D 10_2007
0.81008	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009

Appendix 2b - ATR Similarity Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.99966	CF Reductil ATR (0)		S1 CF 583998D 08_2010 ATR
0.92745	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S2

Quality	Library	CAS#	Name
0.99589	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.99003	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S3

Quality	Library	CAS#	Name
0.99967	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR
0.98883	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR

S4_1

Quality	Library	CAS#	Name
0.99929	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.99928	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_2

Quality	Library	CAS#	Name
0.99937	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.99937	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_3

Quality	Library	CAS#	Name
0.99937	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.99937	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR
0.99906	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR

S5

Quality	Library	CAS#	Name
0.99687	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.98206	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S6_1

Quality	Library	CAS#	Name
0.99515	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.92647	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S6_2

Quality	Library	CAS#	Name
0.99423	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.97876	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S7_1

Quality	Library	CAS#	Name
0.99781	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.99518	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S7_2

Quality	Library	CAS#	Name
0.99781	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.99518	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

C1

Quality	Library	CAS#	Name
0.99949	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.86176	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 2c - Specular Reflectance Derivative Similarity Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.94173	Reductil CF Cartons (0)		S1 CF 583998D 08-2010
0.43735	Reductil CF Cartons (2)		S3 CF 651878D 02-2011

S2

Quality	Library	CAS#	Name
0.83718	Reductil CF Cartons (1)		S2 CF 633288D 12_2010
0.72478	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S3

Quality	Library	CAS#	Name
0.88517	Reductil CF Cartons (2)		S3 CF 651878D 02-2011
0.61923	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S4_1

Quality	Library	CAS#	Name
0.93519	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.92985	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_2

Quality	Library	CAS#	Name
0.91620	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012
0.80659	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_3

Quality	Library	CAS#	Name
0.86011	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.84744	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S5

Quality	Library	CAS#	Name
0.82997	Reductil CF Cartons (6)		S5 CF 720658D 07_2011
0.75341	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

S6_1

Quality	Library	CAS#	Name
0.67917	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007
0.50420	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012

S6_2

Quality	Library	CAS#	Name
0.99341	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007
0.50968	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

S7_1

Quality	Library	CAS#	Name
0.83864	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009
0.23917	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007

S7_2

Quality	Library	CAS#	Name
0.73222	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009
0.22830	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

C1

Quality	Library	CAS#	Name
0.98541	Reductil CF Cartons (13)		C1 372638D 10_2007
0.13925	Reductil CF Cartons (2)		S3 CF 651878D 02-2011

Key: Red Text = Incorrect Match

Appendix 2d - ATR Derivative Similarity Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.98802	CF Reductil ATR (0)		S1 CF 583998D 08_2010 ATR
0.89828	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR

S2

Quality	Library	CAS#	Name
0.98344	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.94503	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S3

Quality	Library	CAS#	Name
0.99000	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR
0.97834	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR

S4_1

Quality	Library	CAS#	Name
0.98696	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.98548	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR

S4_2

Quality	Library	CAS#	Name
0.98744	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.98547	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.98518	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_3

Quality	Library	CAS#	Name
0.98744	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.98547	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR

S5

Quality	Library	CAS#	Name
0.97890	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.93114	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S6_1

Quality	Library	CAS#	Name
0.97307	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.83302	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S6_2

Quality	Library	CAS#	Name
0.97130	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.91822	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S7_1

Quality	Library	CAS#	Name
0.98037	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.97359	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S7_2

Quality	Library	CAS#	Name
0.98037	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.97359	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

C1

Quality	Library	CAS#	Name
0.97740	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.27282	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 2e - Specular Reflectance Correlation Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.00777	Reductil CF Cartons (0)		S1 CF 583998D 08-2010
0.16177	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S2

Quality	Library	CAS#	Name
0.01325	Reductil CF Cartons (1)		S2 CF 633288D 12_2010
0.03938	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S3

Quality	Library	CAS#	Name
0.00600	Reductil CF Cartons (2)		S3 CF 651878D 02-2011
0.13716	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S4_1

Quality	Library	CAS#	Name
0.00168	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012
0.00733	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012

S4_2

Quality	Library	CAS#	Name
0.00184	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012
0.06689	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_3

Quality	Library	CAS#	Name
0.01524	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.02152	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S5

Quality	Library	CAS#	Name
0.01956	Reductil CF Cartons (6)		S5 CF 720658D 07_2011
0.02824	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

S6_1

Quality	Library	CAS#	Name
0.03118	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007
0.15724	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S6_2

Quality	Library	CAS#	Name
0.00004	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007
0.10515	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

S7_1

Quality	Library	CAS#	Name
0.00361	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009
0.10301	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009

S7_2

Quality	Library	CAS#	Name
0.01002	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009
0.13195	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

C1

Quality	Library	CAS#	Name
0.00003	Reductil CF Cartons (13)		C1 372638D 10_2007
0.18992	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009

Appendix 2f - ATR Correlation Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.00034	CF Reductil ATR (0)		S1 CF 583998D 08_2010 ATR
0.07255	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S2

Quality	Library	CAS#	Name
0.00411	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.00997	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S3

Quality	Library	CAS#	Name
0.00033	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR
0.01117	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.01264	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR

S4_1

Quality	Library	CAS#	Name
0.00071	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.00072	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_2

Quality	Library	CAS#	Name
0.00063	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.00063	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_3

Quality	Library	CAS#	Name
0.00063	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.00063	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S5

0.00313	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.01794	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S6_1

Quality	Library	CAS#	Name
0.00485	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.07353	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S6_2

Quality	Library	CAS#	Name
0.00577	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.02124	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S7_1

Quality	Library	CAS#	Name
0.00219	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.00482	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S7_2

Quality	Library	CAS#	Name
0.00219	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.00482	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

C1

Quality	Library	CAS#	Name
0.00051	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.13824	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 2g -Specular Reflectance Derivative Correlation Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.05827	Reductil CF Cartons (0)		S1 CF 583998D 08-2010
0.56265	Reductil CF Cartons (2)		S3 CF 651878D 02-2011

S2

Quality	Library	CAS#	Name
0.16282	Reductil CF Cartons (1)		S2 CF 633288D 12_2010
0.27522	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S3

Quality	Library	CAS#	Name
0.11483	Reductil CF Cartons (2)		S3 CF 651878D 02-2011
0.38077	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S4_1

Quality	Library	CAS#	Name
0.06481	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.07015	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_2

Quality	Library	CAS#	Name
0.08380	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012
0.19341	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_3

Quality	Library	CAS#	Name
0.13989	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.15256	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S5

Quality	Library	CAS#	Name
0.17003	Reductil CF Cartons (6)		S5 CF 720658D 07_2011
0.24659	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

S6_1

Quality	Library	CAS#	Name
0.32083	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007
0.49580	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012

S6_2

Quality	Library	CAS#	Name
0.00659	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007
0.49032	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

S7_1

Quality	Library	CAS#	Name
0.16136	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009
0.76083	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007

S7_2

Quality	Library	CAS#	Name
0.26778	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009
0.77170	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

C1

Quality	Library	CAS#	Name
0.01459	Reductil CF Cartons (13)		C1 372638D 10_2007
0.86075	Reductil CF Cartons (2)		S3 CF 651878D 02-2011

Key: Red Text = Incorrect Match

Appendix 2h - ATR Derivative Correlation Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.01198	CF Reductil ATR (0)		S1 CF 583998D 08_2010 ATR
0.10172	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR

S2

Quality	Library	CAS#	Name
0.01656	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.05497	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S3

Quality	Library	CAS#	Name
0.01000	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR
0.02166	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR

S4_1

Quality	Library	CAS#	Name
0.01304	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.01452	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR

S4_2

Quality	Library	CAS#	Name
0.01256	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.01453	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.01482	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_3

Quality	Library	CAS#	Name
0.01256	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR
0.01453	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR

S5

Quality	Library	CAS#	Name
0.02110	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.06886	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S6_1

Quality	Library	CAS#	Name
0.02693	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.16698	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S6_2

Quality	Library	CAS#	Name
0.02870	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.08178	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S7_1

Quality	Library	CAS#	Name
0.01963	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.02641	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S7_2

Quality	Library	CAS#	Name
0.01963	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.02641	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

C1

Quality	Library	CAS#	Name
0.02260	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.72718	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 2i - Specular Reflectance Euclidean Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.04620	Reductil CF Cartons (0)		S1 CF 583998D 08-2010
0.20855	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S2

Quality	Library	CAS#	Name
0.05053	Reductil CF Cartons (1)		S2 CF 633288D 12_2010
0.08816	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S3

Quality	Library	CAS#	Name
0.05137	Reductil CF Cartons (2)		S3 CF 651878D 02-2011
0.17426	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012

S4_1

Quality	Library	CAS#	Name
0.01840	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012
0.04023	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012

S4_2

Quality	Library	CAS#	Name
0.02010	Reductil CF Cartons (4)		S4_2 CF 762618D 01-2012
0.12093	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S4_3

Quality	Library	CAS#	Name
0.05785	Reductil CF Cartons (12)		S4_3 CF 762618D 01_2012
0.06569	Reductil CF Cartons (11)		S4_1 CF 762618D 01-2012

S5

Quality	Library	CAS#	Name
0.06254	Reductil CF Cartons (6)		S5 CF 720658D 07_2011
0.07345	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

S6_1

Quality	Library	CAS#	Name
0.08692	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007
0.19406	Reductil CF Cartons (6)		S5 CF 720658D 07_2011

S6_2

Quality	Library	CAS#	Name
0.00428	Reductil CF Cartons (8)		S6_2 CF 220808D 06_2007
0.16064	Reductil CF Cartons (7)		S6_1 CF 220808D 06_2007

S7_1

Quality	Library	CAS#	Name
0.02714	Reductil CF Cartons (9)		S7_1 CF 282298D 09_2009
0.14521	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009

S7_2

Quality	Library	CAS#	Name
0.04299	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009
0.16011	Reductil CF Cartons (1)		S2 CF 633288D 12_2010

C1

Quality	Library	CAS#	Name
0.00312	Reductil CF Cartons (13)		C1 372638D 10_2007
0.19737	Reductil CF Cartons (10)		S7_2 CF 282298D 09_2009

Appendix 2j - ATR Euclidean Library Hits for Suspect Set 1

S1

Quality	Library	CAS#	Name
0.02332	CF Reductil ATR (0)		S1 CF 583998D 08_2010 ATR
0.24823	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S2

Quality	Library	CAS#	Name
0.05101	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.07644	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S3

Quality	Library	CAS#	Name
0.01909	CF Reductil ATR (2)		S3 CF 651878D 02_2011 ATR
0.09274	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR

S4_1

Quality	Library	CAS#	Name
0.02428	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.02432	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_2

Quality	Library	CAS#	Name
0.02390	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.02398	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR

S4_3

Quality	Library	CAS#	Name
0.02390	CF Reductil ATR (13)		S4_1 CF 762618D 01_2012 ATR
0.02398	CF Reductil ATR (14)		S4_2 CF 762618D 01_2012 ATR
0.03332	CF Reductil ATR (15)		S4_3 CF 762618D 01_2012 ATR

S5

Quality	Library	CAS#	Name
0.04369	CF Reductil ATR (1)		S5 CF 720658D 07_2011 ATR
0.10322	CF Reductil ATR (3)		S2 CF 633288D 12_2010 ATR

S6_1

Quality	Library	CAS#	Name
0.05830	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.22761	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S6_2

Quality	Library	CAS#	Name
0.06812	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR
0.12283	CF Reductil ATR (12)		S6_2 CF 220808D 06_2007 ATR

S7_1

Quality	Library	CAS#	Name
0.03731	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.05535	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

S7_2

Quality	Library	CAS#	Name
0.03731	CF Reductil ATR (10)		S7_1 CF 282298D 09_2009 ATR
0.05535	CF Reductil ATR (9)		S7_2 CF 282298D 09_2009 ATR

C1

Quality	Library	CAS#	Name
0.01797	Control Reductil ATR (6)		C1 372638D 10_2007 ATR
0.31574	CF Reductil ATR (11)		S6_1 CF 220808D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 3a - Specular Reflectance Similarity Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.99240	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.98413	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_2

Quality	Library	CAS#	Name
0.99625	Reductil CF Cartons Set 2 (1)		S8_2 CF 273198D 01_2009
0.99403	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_3

Quality	Library	CAS#	Name
0.99231	Reductil CF Cartons Set 2 (2)		S8_3 CF 273198D 01_2009
0.99228	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_4

Quality	Library	CAS#	Name
0.99428	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.98328	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S9_1

Quality	Library	CAS#	Name
0.98817	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008
0.98345	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008

S9_2

Quality	Library	CAS#	Name
0.99994	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.99627	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S10

Quality	Library	CAS#	Name
0.91649	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007
0.75589	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008

C2

Quality	Library	CAS#	Name
0.98878	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008
0.75945	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007

Key: Red Text = Incorrect Match

Appendix 3b - ATR Similarity Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.99893	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.99842	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S8_2

Quality	Library	CAS#	Name
0.99873	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.99818	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S8_3

Quality	Library	CAS#	Name
0.99922	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.99859	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.99782	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR

S8_4

Quality	Library	CAS#	Name
0.99933	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.99921	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S9_1

Quality	Library	CAS#	Name
0.99805	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR
0.99763	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR

S9_2

Quality	Library	CAS#	Name
0.99756	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.99489	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S10

Quality	Library	CAS#	Name
0.99860	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR
0.83664	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR

C2

Quality	Library	CAS#	Name
0.99963	Control Reductil ATR (5)		C2 622768D 12_2010 ATR
0.67866	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 3c - Specular Reflectance Derivative Similarity Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.93936	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.88414	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_2

Quality	Library	CAS#	Name
0.91405	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009
0.90938	Reductil CF Cartons Set 2 (1)		S8_2 CF 273198D 01_2009

S8_3

Quality	Library	CAS#	Name
0.90375	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009
0.88850	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.83922	Reductil CF Cartons Set 2 (2)		S8_3 CF 273198D 01_2009

S8_4

Quality	Library	CAS#	Name
0.91475	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.87026	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S9_1

Quality	Library	CAS#	Name
0.89766	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.89524	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S9_2

Quality	Library	CAS#	Name
0.98587	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.91099	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S10

Quality	Library	CAS#	Name
0.91649	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007
0.75589	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008

C2

Quality	Library	CAS#	Name
0.89638	Reductil Control Cartons (1)		C2 622678D 01_2008
0.24582	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007

Key: Red Text = Incorrect Match

Appendix 3d - ATR Derivative Similarity Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.98496	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR
0.98488	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR

S8_2

Quality	Library	CAS#	Name
0.98631	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATF
0.98529	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATF

S8_3

Quality	Library	CAS#	Name
0.98670	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.98647	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR

S8_4

Quality	Library	CAS#	Name
0.98732	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR
0.98729	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

S9_1

Quality	Library	CAS#	Name
0.98148	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.98069	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S9_2

Quality	Library	CAS#	Name
0.98053	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.97563	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S10

Quality	Library	CAS#	Name
0.98615	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR
0.52605	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

C2

Quality	Library	CAS#	Name
0.98927	CF Reductil ATR 2 (17)		C2 622768D 12_2010 ATR_2015-
0.38782	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 3e - Specular Reflectance Correlation Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.00760	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.01587	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_2

Quality	Library	CAS#	Name
0.00375	Reductil CF Cartons Set 2 (1)		S8_2 CF 273198D 01_2009
0.00597	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_3

Quality	Library	CAS#	Name
0.00769	Reductil CF Cartons Set 2 (2)		S8_3 CF 273198D 01_2009
0.00772	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_4

Quality	Library	CAS#	Name
0.00572	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.01672	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S9_1

Quality	Library	CAS#	Name
0.01183	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008
0.01655	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008

S9_2

Quality	Library	CAS#	Name
0.00006	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.00373	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S10

Quality	Library	CAS#	Name
0.08351	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007
0.24411	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008

C2

Quality	Library	CAS#	Name
0.01122	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008
0.24055	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007

Key: Red Text = Incorrect Match

Appendix 3f - ATR Correlation Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.00107	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.00158	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S8_2

Quality	Library	CAS#	Name
0.00127	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.00182	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S8_3

Quality	Library	CAS#	Name
0.00078	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.00141	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

S8_4

Quality	Library	CAS#	Name
0.00067	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.00079	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S9_1

Quality	Library	CAS#	Name
0.00195	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR
0.00237	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR

S9_2

Quality	Library	CAS#	Name
0.00244	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.00511	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S10

Quality	Library	CAS#	Name
0.00140	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR
0.16336	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR

C2

Quality	Library	CAS#	Name
0.00037	Control Reductil ATR (5)		C2 622768D 12_2010 ATR
0.32134	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 3g -Specular Reflectance Derivative Correlation Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.06064	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.11586	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_2

Quality	Library	CAS#	Name
0.08595	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009
0.09062	Reductil CF Cartons Set 2 (1)		S8_2 CF 273198D 01_2009

S8_3

Quality	Library	CAS#	Name
0.09625	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009
0.11150	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.16078	Reductil CF Cartons Set 2 (2)		S8_3 CF 273198D 01_2009

S8_4

Quality	Library	CAS#	Name
0.08525	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.12974	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S9_1

Quality	Library	CAS#	Name
0.10234	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.10476	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S9_2

Quality	Library	CAS#	Name
0.01413	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.08901	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S10

Quality	Library	CAS#	Name
0.14848	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007
0.82526	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008

C2

Quality	Library	CAS#	Name
0.10362	Reductil Control Cartons (1)		C2 622678D 01_2008
0.75418	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007

Key: Red Text = Incorrect Match

Appendix 3h - ATR Derivative Correlation Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.01504	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR
0.01512	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR

S8_2

Quality	Library	CAS#	Name
0.01369	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR
0.01471	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

S8_3

Quality	Library	CAS#	Name
0.01330	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.01353	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR

S8_4

Quality	Library	CAS#	Name
0.01268	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR
0.01271	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

S9_1

Quality	Library	CAS#	Name
0.01852	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.01931	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S9_2

Quality	Library	CAS#	Name
0.01947	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.02437	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S10

Quality	Library	CAS#	Name
0.01385	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR
0.47395	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

C2

Quality	Library	CAS#	Name
0.01672	Control Reductil ATR (5)		C2 622768D 12_2010 ATR
0.61803	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 3i - Specular Reflectance Euclidean Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.05947	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.07194	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_2

Quality	Library	CAS#	Name
0.03383	Reductil CF Cartons Set 2 (1)		S8_2 CF 273198D 01_2009
0.04672	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_3

Quality	Library	CAS#	Name
0.04560	Reductil CF Cartons Set 2 (2)		S8_3 CF 273198D 01_2009
0.04948	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S8_4

Quality	Library	CAS#	Name
0.04175	Reductil CF Cartons Set 2 (3)		S8_4 CF 273198D 01_2009
0.07159	Reductil CF Cartons Set 2 (0)		S8_1 CF 273198D 01_2009

S9_1

Quality	Library	CAS#	Name
0.06312	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008
0.06914	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008

S9_2

Quality	Library	CAS#	Name
0.00338	Reductil CF Cartons Set 2 (5)		S9_2 CF 2011030 08_2008
0.02288	Reductil CF Cartons Set 2 (4)		S9_1 CF 2011030 08_2008

S10

Quality	Library	CAS#	Name
0.11266	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007
0.22982	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008

C2

Quality	Library	CAS#	Name
0.04858	Reductil CF Cartons Set 2 (7)		C2 622678D 01_2008
0.22748	Reductil CF Cartons Set 2 (6)		S10 CF 221518D 06_2007

Appendix 3j - ATR Euclidean Library Hits for Suspect Set 2

S8_1

Quality	Library	CAS#	Name
0.02873	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.03826	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S8_2

Quality	Library	CAS#	Name
0.03238	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.03940	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR
0.04024	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.04355	CF Reductil ATR 2 (4)		S8_2 CF 273198D 01_2009 ATR

S8_3

Quality	Library	CAS#	Name
0.02471	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR
0.03299	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR

S8_4

Quality	Library	CAS#	Name
0.02269	CF Reductil ATR 2 (6)		S8_4 CF 273198D 01_2009 ATR
0.03111	CF Reductil ATR 2 (3)		S8_1 CF 273198D 01_2009 ATR

S9_1

Quality	Library	CAS#	Name
0.04034	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR
0.05045	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR

S9_2

Quality	Library	CAS#	Name
0.04639	CF Reductil ATR 2 (2)		S9_2 CF 2011030 08_2008 ATR
0.06334	CF Reductil ATR 2 (1)		S9_1 CF 2011030 08_2008 ATR

S10

Quality	Library	CAS#	Name
0.03952	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR
0.36541	CF Reductil ATR 2 (5)		S8_3 CF 273198D 01_2009 ATR

C2

Quality	Library	CAS#	Name
0.01911	Control Reductil ATR (5)		C2 622768D 12_2010 ATR
0.48973	CF Reductil ATR 2 (0)		S10 CF 221518D 06_2007 ATR

Key: Red Text = Incorrect Match

Appendix 4a - Specular Reflectance Similarity Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.99526	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007
0.99452	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007

S11_2

Quality	Library	CAS#	Name
0.99518	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.98607	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S12

Quality	Library	CAS#	Name
0.99996	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009
0.98632	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S13

Quality	Library	CAS#	Name
0.99384	Reductil CF Cartons Set 3 (2)		S13 CF 72783 04_2011
0.75309	Reductil CF Cartons Set 3 (12)		C7 562428D 62_2010

S14

Quality	Library	CAS#	Name
0.99344	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008
0.98377	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009

S15

Quality	Library	CAS#	Name
0.98979	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009
0.90008	Reductil Control Cartons (3)		C4 B72978 12_2009

S16

Quality	Library	CAS#	Name
0.99429	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012
0.87343	Reductil Control Cartons (4)		C5 262818D 11_2007

C3

Quality	Library	CAS#	Name
0.96586	Reductil CF Cartons Set 3 (8)		C3 B76053 12_2014
0.86639	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009

C4

Quality	Library	CAS#	Name
0.99842	Reductil Control Cartons (3)		C4 B72978 12_2009
0.91311	Reductil Control Cartons (8)		C8 651498D 02_2011

C5

Quality	Library	CAS#	Name
0.99760	Reductil Control Cartons (4)		C5 262818D 11_2007
0.88087	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012

C6

Quality	Library	CAS#	Name
0.99998	Reductil Control Cartons (6)		C6 713388D
0.97300	Reductil Control Cartons (8)		C8 651498D 02_2011

C7

Quality	Library	CAS#	Name
0.99884	Reductil Control Cartons (7)		C7 562428D 06_2010
0.98930	Reductil Control Cartons (9)		C9 572308D 06_2010

C8

Quality	Library	CAS#	Name
0.99157	Reductil Control Cartons (8)		C8 651498D 02_2011
0.97320	Reductil Control Cartons (6)		C6 713388D

C9

Quality	Library	CAS#	Name
0.99591	Reductil Control Cartons (9)		C9 572308D 06_2010
0.99546	Reductil Control Cartons (7)		C7 562428D 06_2010

Appendix 4b - ATR Similarity Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.99978	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.99886	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S11_2

Quality	Library	CAS#	Name
0.99645	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.99528	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S12

Quality	Library	CAS#	Name
0.99996	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009
0.98632	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S13

Quality	Library	CAS#	Name
0.99384	Reductil CF Cartons Set 3 (2)		S13 CF 72783 04_2011
0.75309	Reductil CF Cartons Set 3 (12)		C7 562428D 62_2010

S14

Quality	Library	CAS#	Name
0.99637	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.98985	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S15

Quality	Library	CAS#	Name
0.99585	CF Reductil ATR 3 (4)		S15 CF 418218D 02_2009 ATR
0.79673	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

S16

Quality	Library	CAS#	Name
0.99647	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR
0.92166	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C3

Quality	Library	CAS#	Name
0.99930	Control Reductil ATR (2)		C3 B76053 12_2014 ATR
0.90322	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR

C4

Quality	Library	CAS#	Name
0.99651	Control Reductil ATR (1)		C4 B72978 12_2009 ATR
0.84324	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

C5

Quality	Library	CAS#	Name
0.99227	Control Reductil ATR (0)		C5 262818D 11_2007 ATR
0.92357	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR

C6

Quality	Library	CAS#	Name
0.99765	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.99635	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C7

Quality	Library	CAS#	Name
0.99502	Control Reductil ATR (4)		C7 562428D 06_2010 ATR
0.99047	Control Reductil ATR (8)		C9 572308D 02_2010 ATR

C8

Quality	Library	CAS#	Name
0.99878	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.99672	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C9

Quality	Library	CAS#	Name
0.99819	Control Reductil ATR (8)		C9 572308D 02_2010 ATR
0.99518	Control Reductil ATR (4)		C7 562428D 06_2010 ATR

Key: Red Text = Incorrect Match

Appendix 4c - Specular Reflectance Derivative Similarity Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.92497	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.90997	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S11_2

Quality	Library	CAS#	Name
0.90292	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.85048	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S12

Quality	Library	CAS#	Name
0.99316	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009
0.85213	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S13

Quality	Library	CAS#	Name
0.92471	Reductil CF Cartons Set 3 (2)		S13 CF 72783 04_2011
0.29587	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S14

Quality	Library	CAS#	Name
0.92556	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008
0.87274	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009

S15

Quality	Library	CAS#	Name
0.91096	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009
0.39724	Reductil CF Cartons Set 3 (9)		C4 B72978 12_2009

S16

Quality	Library	CAS#	Name
0.94627	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012
0.58931	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

C3

Quality	Library	CAS#	Name
0.82957	Reductil CF Cartons Set 3 (8)		C3 B76053 12_2014
0.19213	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009

C4

Quality	Library	CAS#	Name
0.82220	Reductil Control Cartons (3)		C4 B72978 12_2009
0.33757	Reductil Control Cartons (4)		C5 262818D 11_2007

C5

Quality	Library	CAS#	Name
0.93587	Reductil Control Cartons (4)		C5 262818D 11_2007
0.48713	Reductil Control Cartons (8)		C8 651498D 02_2011

C6

Quality	Library	CAS#	Name
0.99220	Reductil Control Cartons (6)		C6 713388D
0.64469	Reductil Control Cartons (8)		C8 651498D 02_2011

C7

Quality	Library	CAS#	Name
0.95987	Reductil Control Cartons (7)		C7 562428D 06_2010
0.90984	Reductil Control Cartons (9)		C9 572308D 06_2010

C8

Quality	Library	CAS#	Name
0.90410	Reductil Control Cartons (8)		C8 651498D 02_2011
0.67347	Reductil Control Cartons (6)		C6 713388D

C9

Quality	Library	CAS#	Name
0.94088	Reductil Control Cartons (7)		C7 562428D 06_2010
0.93194	Reductil Control Cartons (9)		C9 572308D 06_2010

Appendix 4d - ATR Derivative Similarity Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.99978	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.99886	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S11_2

Quality	Library	CAS#	Name
0.99645	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.99528	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S12

Quality	Library	CAS#	Name
0.05787	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.07092	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S13

Quality	Library	CAS#	Name
0.98837	CF Reductil ATR 3 (1)		S13 CF 72783 04_2011 ATR
0.67743	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S14

Quality	Library	CAS#	Name
0.99637	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.98985	CF Reductil ATR 3 (3)		S12 CF 394068D 01 2009 ATR

S15

Quality	Library	CAS#	Name
0.99585	CF Reductil ATR 3 (4)		S15 CF 418218D 02_2009 ATR
0.79673	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

S16

Quality	Library	CAS#	Name
0.99647	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR
0.92166	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C3

Quality	Library	CAS#	Name
0.97771	Control Reductil ATR (2)		C3 B76053 12_2014 ATR
0.74962	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR

C4

Quality	Library	CAS#	Name
0.97438	Control Reductil ATR (1)		C4 B72978 12_2009 ATR
0.82083	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

C5

Quality	Library	CAS#	Name
0.97489	Control Reductil ATR (0)		C5 262818D 11_2007 ATR
0.85434	Control Reductil ATR (1)		C4 B72978 12_2009 ATR

C6

Quality	Library	CAS#	Name
0.98143	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.96432	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C7

Quality	Library	CAS#	Name
0.97081	Control Reductil ATR (4)		C7 562428D 06_2010 ATR
0.93803	Control Reductil ATR (8)		C9 572308D 02_2010 ATR

C8

Quality	Library	CAS#	Name
0.98488	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.97600	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C9

Quality	Library	CAS#	Name
0.98280	Control Reductil ATR (8)		C9 572308D 02_2010 ATR
0.96059	Control Reductil ATR (4)		C7 562428D 06_2010 ATR

Key: Red Text = Incorrect Match

Appendix 4e - Specular Reflectance Correlation Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.00474	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007
0.00648	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007

S11_2

Quality	Library	CAS#	Name
0.00482	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.01393	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S12

Quality	Library	CAS#	Name
0.00004	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009
0.01368	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S13

Quality	Library	CAS#	Name
0.00616	Reductil CF Cartons Set 3 (2)		S13 CF 72783 04_2011
0.24691	Reductil CF Cartons Set 3 (12)		C7 562428D 62_2010

S14

Quality	Library	CAS#	Name
0.00656	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008
0.01623	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009

S15

Quality	Library	CAS#	Name
0.01021	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009
0.09992	Reductil Control Cartons (3)		C4 B72978 12_2009

S16

Quality	Library	CAS#	Name
0.00571	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012
0.12657	Reductil Control Cartons (4)		C5 262818D 11_2007

C3

Quality	Library	CAS#	Name
0.03414	Reductil CF Cartons Set 3 (8)		C3 B76053 12_2014
0.13361	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009

C4

Quality	Library	CAS#	Name
0.00158	Reductil Control Cartons (3)		C4 B72978 12_2009
0.08689	Reductil Control Cartons (8)		C8 651498D 02_2011

C5

Quality	Library	CAS#	Name
0.00240	Reductil Control Cartons (4)		C5 262818D 11_2007
0.11913	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012

C6

Quality	Library	CAS#	Name
0.00002	Reductil Control Cartons (6)		C6 713388D
0.02700	Reductil Control Cartons (8)		C8 651498D 02_2011

C7

Quality	Library	CAS#	Name
0.00116	Reductil Control Cartons (7)		C7 562428D 06_2010
0.01070	Reductil Control Cartons (9)		C9 572308D 06_2010

C8

Quality	Library	CAS#	Name
0.00843	Reductil Control Cartons (8)		C8 651498D 02_201
0.02680	Reductil Control Cartons (6)		C6 713388D

C9

Quality	Library	CAS#	Name
0.00409	Reductil Control Cartons (9)		C9 572308D 06_2010
0.00454	Reductil Control Cartons (7)		C7 562428D 06_2010

Appendix 4f - ATR Correlation Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.00022	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.00114	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S11_2

Quality	Library	CAS#	Name
0.00355	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.00472	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S12

Quality	Library	CAS#	Name
0.00385	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.00610	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S13

Quality	Library	CAS#	Name
0.00048	CF Reductil ATR 3 (1)		S13 CF 72783 04_2011 ATR
0.13458	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR

S14

Quality	Library	CAS#	Name
0.00363	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.01015	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S15

Quality	Library	CAS#	Name
0.00415	CF Reductil ATR 3 (4)		S15 CF 418218D 02_2009 ATR
0.20327	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

S16

Quality	Library	CAS#	Name
0.00353	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR
0.07834	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C3

Quality	Library	CAS#	Name
0.00070	Control Reductil ATR (2)		C3 B76053 12_2014 ATR
0.09678	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR

C4

Quality	Library	CAS#	Name
0.00349	Control Reductil ATR (1)		C4 B72978 12_2009 ATR
0.15676	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

C5

Quality	Library	CAS#	Name
0.00773	Control Reductil ATR (0)		C5 262818D 11_2007 ATR
0.07643	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR

C6

Quality	Library	CAS#	Name
0.00235	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.00365	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C7

Quality	Library	CAS#	Name
0.00498	Control Reductil ATR (4)		C7 562428D 06_2010 ATR
0.00953	Control Reductil ATR (8)		C9 572308D 02_2010 ATR

C8

Quality	Library	CAS#	Name
0.00122	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.00328	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C9

Quality	Library	CAS#	Name
0.00181	Control Reductil ATR (8)		C9 572308D 02_2010 ATR
0.00482	Control Reductil ATR (4)		C7 562428D 06_2010 ATR

Key: Red Text = Incorrect Match

Appendix 4g -Specular Reflectance Derivative Correlation Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.07503	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.09003	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S11_2

Quality	Library	CAS#	Name
0.09708	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.14952	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S12

Quality	Library	CAS#	Name
0.00684	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009
0.14787	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S13

Quality	Library	CAS#	Name
0.07529	Reductil CF Cartons Set 3 (2)		S13 CF 72783 04_2011
0.70413	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S14

Quality	Library	CAS#	Name
0.07444	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008
0.12726	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009

S15

Quality	Library	CAS#	Name
0.08904	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009
0.62188	Reductil Control Cartons (3)		C4 B72978 12_2009

S16

Quality	Library	CAS#	Name
0.05373	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012
0.41069	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

C3

Quality	Library	CAS#	Name
0.17043	Reductil CF Cartons Set 3 (8)		C3 B76053 12_2014
0.80787	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009

C4

Quality	Library	CAS#	Name
0.17780	Reductil Control Cartons (3)		C4 B72978 12_2009
0.66243	Reductil Control Cartons (4)		C5 262818D 11_2007

C5

Quality	Library	CAS#	Name
0.06413	Reductil Control Cartons (4)		C5 262818D 11_2007
0.51287	Reductil Control Cartons (8)		C8 651498D 02_2011

C6

Quality	Library	CAS#	Name
0.00780	Reductil Control Cartons (6)		C6 713388D
0.35531	Reductil Control Cartons (8)		C8 651498D 02 2011

C7

Quality	Library	CAS#	Name
0.04013	Reductil Control Cartons (7)		C7 562428D 06_2010
0.09016	Reductil Control Cartons (9)		C9 572308D 06_2010

C8

Quality	Library	CAS#	Name
0.09590	Reductil Control Cartons (8)		C8 651498D 02_2011
0.32653	Reductil Control Cartons (6)		C6 713388D

C9

Quality	Library	CAS#	Name
0.05912	Reductil Control Cartons (7)		C7 562428D 06_2010
0.06806	Reductil Control Cartons (9)		C9 572308D 06_2010

Key: Red Text = Incorrect Match

Appendix 4h - ATR Derivative Correlation Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.00022	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.00114	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S11_2

Quality	Library	CAS#	Name
0.00355	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.00472	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S12

Quality	Library	CAS#	Name
0.00385	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.00610	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S13

Quality	Library	CAS#	Name
0.01163	CF Reductil ATR 3 (1)		S13 CF 72783 04_2011 ATR
0.32257	CF Reductil ATR 3 (3)		S12 CF 394068D 01 2009 ATR

S14

Quality	Library	CAS#	Name
0.00363	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.01015	CF Reductil ATR 3 (3)		S12 CF 394068D 01 2009 ATR

S15

Quality	Library	CAS#	Name
0.00415	CF Reductil ATR 3 (4)		S15 CF 418218D 02_2009 ATR
0.20327	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

S16

Quality	Library	CAS#	Name
0.00353	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR
0.07834	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C3

Quality	Library	CAS#	Name
0.02229	Control Reductil ATR (2)		C3 B76053 12_2014 ATR
0.25038	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR

C4

Quality	Library	CAS#	Name
0.02562	Control Reductil ATR (1)		C4 B72978 12_2009 ATR
0.17917	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

C5

Quality	Library	CAS#	Name
0.02511	Control Reductil ATR (0)		C5 262818D 11_2007 ATR
0.14566	Control Reductil ATR (1)		C4 B72978 12_2009 ATR

C6

Quality	Library	CAS#	Name
0.01857	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.03568	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C7

Quality	Library	CAS#	Name
0.02919	Control Reductil ATR (4)		C7 562428D 06_2010 ATR
0.06197	Control Reductil ATR (8)		C9 572308D 02_2010 ATR

C8

Quality	Library	CAS#	Name
0.01512	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.02400	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C9

Quality	Library	CAS#	Name
0.01720	Control Reductil ATR (8)		C9 572308D 02_2010 ATR
0.03941	Control Reductil ATR (4)		C7 562428D 06 2010 ATR

Key: Red Text = Incorrect Match

Appendix 4i - Specular Reflectance Euclidean Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.03348	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007
0.03985	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007

S11_2

Quality	Library	CAS#	Name
0.03930	Reductil CF Cartons Set 3 (1)		S11_2 CF 250328D 08_2007
0.05738	Reductil CF Cartons Set 3 (0)		S11_1 CF 250328D 08_2007

S12

Quality	Library	CAS#	Name
0.00302	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009
0.04586	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008

S13

Quality	Library	CAS#	Name
0.03595	Reductil CF Cartons Set 3 (2)		S13 CF 72783 04_2011
0.23548	Reductil CF Cartons Set 3 (12)		C7 562428D 62_2010

S14

Quality	Library	CAS#	Name
0.03242	Reductil CF Cartons Set 3 (3)		S14 CF 431648D 10_2008
0.05134	Reductil CF Cartons Set 3 (7)		S12 CF 394068D 01_2009

S15

Quality	Library	CAS#	Name
0.04547	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009
0.13792	Reductil Control Cartons (3)		C4 B72978 12_2009

S16

Quality	Library	CAS#	Name
0.03468	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012
0.14051	Reductil Control Cartons (4)		C5 262818D 11_2007

C3

Quality	Library	CAS#	Name
0.07885	Reductil CF Cartons Set 3 (8)		C3 B76053 12_2014
0.19898	Reductil CF Cartons Set 3 (5)		S15 CF 481218D 02_2009

C4

Quality	Library	CAS#	Name
0.01775	Reductil Control Cartons (3)		C4 B72978 12_2009
0.13076	Reductil Control Cartons (8)		C8 651498D 02_2011

C5

Quality	Library	CAS#	Name
0.01957	Reductil Control Cartons (4)		C5 262818D 11_2007
0.14326	Reductil CF Cartons Set 3 (6)		S16 CF 73156 03_2012

C6

Quality	Library	CAS#	Name
0.00200	Reductil Control Cartons (6)		C6 713388D
0.07321	Reductil Control Cartons (8)		C8 651498D 02_2011

C7

Quality	Library	CAS#	Name
0.01661	Reductil Control Cartons (7)		C7 562428D 06_2010
0.04947	Reductil Control Cartons (9)		C9 572308D 06_2010

C8

Quality	Library	CAS#	Name
0.04067	Reductil Control Cartons (8)		C8 651498D 02_2011
0.07205	Reductil Control Cartons (6)		C6 713388D

C9

Quality	Library	CAS#	Name
0.03017	Reductil Control Cartons (9)		C9 572308D 06_2010
0.03110	Reductil Control Cartons (7)		C7 562428D 06_2010

Appendix 4j - ATR Euclidean Library Hits for Suspect Set 3

S11_1

Quality	Library	CAS#	Name
0.01518	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.03008	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S11_2

Quality	Library	CAS#	Name
0.04940	CF Reductil ATR 3 (8)		S11_2 CF 250328D 08_2007 ATR
0.06031	CF Reductil ATR 3 (7)		S11_1 CF 250328D 08_2007 ATR

S12

Quality	Library	CAS#	Name
0.05787	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.07092	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S13

Quality	Library	CAS#	Name
0.02776	CF Reductil ATR 3 (1)		S13 CF 72783 04_2011 ATR
0.31215	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR

S14

Quality	Library	CAS#	Name
0.05274	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR
0.08494	CF Reductil ATR 3 (3)		S12 CF 394068D 01_2009 ATR

S15

Quality	Library	CAS#	Name
0.05568	CF Reductil ATR 3 (4)		S15 CF 418218D 02_2009 ATR
0.35894	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

S16

Quality	Library	CAS#	Name
0.04937	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR
0.23553	Control Reductil ATR (2)		C3 B76053 12_2014 ATR

C3

Quality	Library	CAS#	Name
0.02530	Control Reductil ATR (2)		C3 B76053 12_2014 ATR
0.26121	CF Reductil ATR 3 (2)		S16 CF 73156 03_2012 ATR

C4

Quality	Library	CAS#	Name
0.04769	Control Reductil ATR (1)		C4 B72978 12_2009 ATR
0.32075	Control Reductil ATR (0)		C5 262818D 11_2007 ATR

C5

Quality	Library	CAS#	Name
0.07615	Control Reductil ATR (0)		C5 262818D 11_2007 ATR
0.23569	CF Reductil ATR 3 (0)		S14 CF 431648D 10_2008 ATR

C6

Quality	Library	CAS#	Name
0.03807	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.04689	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C7

Quality	Library	CAS#	Name
0.05790	Control Reductil ATR (4)		C7 562428D 06_2010 ATR
0.07979	Control Reductil ATR (8)		C9 572308D 02_2010 ATR

C8

Quality	Library	CAS#	Name
0.02798	Control Reductil ATR (7)		C8 651498D 02_2011 ATR
0.04435	Control Reductil ATR (9)		C6 713388D 12_2010 ATR

C9

Quality	Library	CAS#	Name
0.03854	Control Reductil ATR (8)		C9 572308D 02_2010 ATR
0.05780	Control Reductil ATR (4)		C7 562428D 06_2010 ATR

Key: Red Text = Incorrect Match

Appendix 5a - Techniques Statistical Comparisons Set 1

(Similarity, Derivative Similarity, and Euclidean Only)

One-way ANOVA, Paired T test and CI: Set 1 Sim SR results, Set 1 Sim ATR

```
                       Individual 95% CIs For Mean Based on Pooled StDev
Level                  -----+---------+---------+---------+----
Set 1 Sim SR results   (-----------*-----------)
Set 1 Sim ATR Results               (-----------*-----------)
                       -----+---------+---------+---------+----
                          0.9880    0.9920    0.9960    1.0000
Pooled StDev = 0.00792
95% CI for mean difference: (-0.01235, 0.00225)
T-Test of mean difference = 0 (vs not = 0): T-Value = -1.52  P-Value = 0.156
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

One-way ANOVA, Paired T test and CI: Set 1 Der Sim SR results, Set 1 Der Sim ATR

```
                          Individual 95% CIs For Mean Based on Pooled StDev
Level                     ----+---------+---------+---------+-----
Set 1 Der Sim SR Results  (-------*-------)
Set 1 Der Sim ATR Result                        (-------*-------)
                          ----+---------+---------+---------+-----
                            0.850     0.900     0.950     1.000

Pooled StDev = 0.0676
95% CI for mean difference: (-0.1688, -0.0502)
T-Test of mean difference = 0 (vs not = 0): T-Value = -4.06  P-Value = 0.002
P Value is < 0.05
Conclusion is that there is a statistical difference between techniques.
```

One-way ANOVA, Paired T test and CI: Set 1 Euclid SR results, Set 1 Euclid ATR

```
                     Individual 95% CIs For Mean Based on Pooled StDev
Level                  -------+---------+---------+---------+--
Set 1 Euc SR Results   (----------------*----------------)
Set 1 Euc ATR Results       (----------------*---------------)
                       -------+---------+---------+---------+--
                            0.030     0.040     0.050     0.060
Pooled StDev = 0.02799
95% CI for mean difference: (-0.0312, 0.0205)
T-Test of mean difference = 0 (vs not = 0): T-Value = -0.46  P-Value = 0.656
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

Appendix 5b - Techniques Statistical Comparisons Set 2

(Similarity, Derivative Similarity, and Euclidean Only)

One-way ANOVA, Paired T test and CI: Set 2 Sim SR results, Set 2 Sim ATR

```
                       Individual 95% CIs For Mean Based on Pooled StDev
Level                  ---+---------+---------+---------+------
Set 2 Sim SR results   (-----------*-----------)
Set 2 Sim ATR Results               (-----------*-----------)
                       ---+---------+---------+---------+------
                        0.972     0.984     0.996     1.008
Pooled StDev = 0.0192
95% CI for mean difference: (-0.03875, 0.00682)
T-Test of mean difference = 0 (vs not = 0): T-Value = -1.66  P-Value = 0.142
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

One-way ANOVA, Paired T test and CI: Set 2 Der Sim SR results, Set 2 Der Sim ATR

```
                          Individual 95% CIs For Mean Based on Pooled StDev
Level                     --------+---------+---------+---------+-
Set 2 Der Sim SR Results  (------*-----)
Set 2 Der Sim ATR Result                        (------*-----)
                          --------+---------+---------+---------+-
                                0.910     0.945     0.980     1.015
Pooled StDev = 0.0290
95% CI for mean difference: (-0.1156, -0.0446)
T-Test of mean difference = 0 (vs not = 0): T-Value = -5.33  P-Value = 0.001
P Value is < 0.05
Conclusion is that there is a statistical difference between techniques.
```

One-way ANOVA, Paired T test and CI: Set 2 Euclid SR results, Set 2 Euclid

```
                       Individual 95% CIs For Mean Based on Pooled StDev
Level                  ---------+---------+---------+---------+
Set 2 Euc SR Results               (-----------*-----------)
Set 2 Euc ATR Results  (-----------*-----------)
                       ---------+---------+---------+---------+
                              0.030     0.045     0.060     0.075

Pooled StDev = 0.02352
95% CI for mean difference: (-0.0104, 0.0473)
T-Test of mean difference = 0 (vs not = 0): T-Value = 1.51  P-Value = 0.175
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

Appendix 5c - Techniques Statistical Comparisons Set 3

(Similarity, Derivative Similarity, and Euclidean Only)

One-way ANOVA, Paired T test and CI: Set 3 Sim SR results, Set 3 Sim ATR

```
Individual 95% CIs For Mean Based on Pooled StDev
Level                     +---------+---------+---------+---------
Set 3Sim SR results       (-------------*--------------)
Set 3 Sim ATR Results               (--------------*-------------)
                          +---------+---------+---------+---------
                        0.9900    0.9925    0.9950    0.9975


95% CI for mean difference: (-0.00833, 0.00321)
T-Test of mean difference = 0 (vs not = 0): T-Value = -0.96  P-Value = 0.356
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

One-way ANOVA, Paired T test and CI: Set 3 Der Sim SR results, Set 3 Der Sim ATR

```
Individual 95% CIs For Mean Based on Pooled StDev
Level                      ----+---------+---------+---------+-----
Set 3 Der Sim SR Results   (----------------*-----------------)
Set 3 Der Sim ATR Result    (----------------*-----------------)
                           ----+---------+---------+---------+-----
                             0.840     0.900     0.960     1.020

Pooled StDev = 0.1916
95% CI for mean difference: (-0.1623, 0.1519)
T-Test of mean difference = 0 (vs not = 0): T-Value = -0.07  P-Value = 0.944
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

One-way ANOVA, Paired T test and CI: Set 3 Euclid SR results, Set 3 Euclid

```
Individual 95% CIs For Mean Based on Pooled StDev
Level                   ---------+---------+---------+---------+
Set 3 Euc SR Results    (---------*--------)
Set 3 Euc ATR Results                   (--------*---------)
                        ---------+---------+---------+---------+
                               0.030     0.040     0.050     0.060
Pooled StDev = 0.01770
95% CI for mean difference: (-0.03333, 0.00226)
T-Test of mean difference = 0 (vs not = 0): T-Value = -1.89  P-Value = 0.082
P Value is > 0.05
Conclusion is that there is no statistical difference between techniques.
```

Appendix 6a - Within Specular Reflectance Statistical Comparison of Sets by One-way ANOVA

Similarity

```
Individual 95% CIs For Mean Based on Pooled StDev
Level    N     Mean    StDev  -------+---------+---------+---------+--
Set 1   12  0.99587  0.00612  (----------*----------)
Set 2    8  0.99851  0.00071          (------------*------------)
Set 3   14  0.99613  0.00407    (----------*--------)
                              -------+---------+---------+---------+--
                                   0.9950    0.9975    1.0000    1.0025

Pooled StDev = 0.00451, P = 0.398
P Value is > 0.05
Conclusion is that there is no statistical difference between the predicted sets.
```

Derivative Similarity

```
Individual 95% CIs For Mean Based on Pooled StDev
Level    N     Mean    StDev  ---+---------+---------+---------+------
Set 1   12  0.86909  0.09476  (-----------*-----------)
Set 2    8  0.90519  0.04093          (-------------*-------------)
Set 3   14  0.92068  0.04943                  (---------*----------)
                              ---+---------+---------+---------+------
                               0.840     0.875     0.910     0.945

Pooled StDev = 0.06774, P = 0.164
Since P Value is > 0.05
Conclusion is that there is no statistical difference between the predicted sets.
```

Euclidean

```
Individual 95% CIs For Mean Based on Pooled StDev
Level    N     Mean    StDev  --------+---------+---------+---------+-
Set 1   12  0.03928  0.02518       (---------*---------)
Set 2    8  0.05261  0.03174             (-----------*-----------)
Set 3   14  0.03073  0.01932  (-------*--------)
                              --------+---------+---------+---------+-
                                    0.030     0.045     0.060     0.075

Pooled StDev = 0.02467, P = 0.152

Since P Value is > 0.05
Conclusion is that there is no statistical difference between the predicted sets.
```

Appendix 6b - Within ATR Statistical Comparison of Sets by One-way ANOVA

Similarity

```
Individual 95% CIs For Mean Based on Pooled StDev
Level    N     Mean    StDev  -------+---------+---------+---------+--
Set 1   12  0.99587  0.00612  (----------*----------)
Set 2    8  0.99851  0.00071          (------------*------------)
Set 3   14  0.99613  0.00407    (----------*--------)
                              -------+---------+---------+---------+--
                                   0.9950    0.9975    1.0000    1.0025

Pooled StDev = 0.00451, P = 0.398
P Value is > 0.05
Conclusion is that there is no statistical difference between the predicted sets.
```

Derivative Similarity

```
                              Individual 95% CIs For Mean Based on Pooled StDev
Level    N     Mean    StDev  --------+---------+---------+---------+-
Set 1   12  0.97855  0.01209  (-----*-----)
Set 2    8  0.98531  0.00295          (-------*------)
Set 3   14  0.99646  0.00305                            (-----*----)
                              --------+---------+---------+---------+-
                                    0.9800    0.9870    0.9940    1.0010

Pooled StDev = 0.00760, P = 0.000
P Value is < 0.05
Conclusion is that there is a statistical difference between the predicted sets.
```

Euclidean

```
Individual 95% CIs For Mean Based on Pooled StDev
Level    N     Mean    StDev   -+---------+---------+---------+--------
Set 1   12  0.04466  0.03054               (------------*-----------)
Set 2    8  0.03416  0.00996   (--------------*---------------)
Set 3   14  0.04626  0.01592                  (----------*-----------)
                               -+---------+---------+---------+--------
                              0.020     0.030     0.040     0.050

Pooled StDev = 0.02144, P = 0.426
P Value is > 0.05
Conclusion is that there is no statistical difference between the predicted sets.
```

Appendix 7 - Assessment of All Sets Across All Algorithms by Unstacked ANOVA

Using all sample sets and the Euclidean data reciprocal (to allow correlation precision to 1)

One-way ANOVA: All Sim SR r, All Sim ATR , All Der Sim , All Der Sim , ...

```
Source   DF       SS       MS      F      P
Factor    5  0.22394  0.04479  42.52  0.000
Error   198  0.20854  0.00105
Total   203  0.43248

S = 0.03245   R-Sq = 51.78%   R-Sq(adj) = 50.56%


Level                       N    Mean   StDev
All Sim SR results         34  0.9900  0.0153
All Sim ATR Results        34  0.9966  0.0045
All Der Sim SR Results     34  0.8988  0.0696
All Der Sim ATR Results    34  0.9875  0.0109
All Euc SR Rec             34  0.9611  0.0254
All Euc ATR Rec            34  0.9571  0.0214

Individual 95% CIs For Mean Based on Pooled StDev
Level                      ----+---------+---------+---------+-----
All Sim SR results                                (---*---)
All Sim ATR Results                                  (--*---)
All Der Sim SR Results     (---*--)
All Der Sim ATR Results                           (--*---)
All Euc SR Rec                                 (--*---)
All Euc ATR Rec                              (---*---)
                           ----+---------+---------+---------+-----
                             0.900     0.930     0.960     0.990

Pooled StDev = 0.0325
```