

Using vibrational spectroscopy to analyse the effect of environmental aging on gel pen inks

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Abstract

Document examinations are vitally important for fraudulent investigations. During a forensic document examination, one of the major questions which arises for the examiner is: when was an ink entry made on a document? During the past half century there has been a large development in the analysis in pen inks, including the introduction of new techniques and development of methods such as the ink library approach and hyphenated chromatography. Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR) is a rapid and non-destructive technique that can objectively profile molecular changes within ink applied to document.

The aim of this study is to determine whether infrared spectroscopy can be used to calculate the age of a gel pen ink and therefore how much time has passed between an ink sample being written on a piece of paper and the sample being analysed. ATR-FTIR was used during this study as a rapid and non-destructive technique allowing multiple spectra to be produced in a short space of time, while not causing destruction to the sample.

The paper used to write ink samples on for the aging study was analysed to show consistent spectra between sheets of a single ream. This analysis was vital to determine whether all of the ink samples were to be produced onto paper which would produce the same or different spectra. As the paper provides the same spectra these differences do not need to be considered when conducting analysis between aging inks. The ink samples analysed through the drying study took 10 minutes to dry after being produced. This time frame was used as knowledge for how long the ink sample should be allowed

to dry prior to the spectrum for the ink sample being first taken as a reference point on day 0.

Through examinations, spectral peaks at 929.51cm^{-1} and 1348cm^{-1} from second derivatised data were established as the most discriminative wavenumbers for ink spectra and used as the major point of referencing ink aging. Evidence for gel pen ink aging is demonstrated from spectral data and group scatter plot correlations. Spectral data at the highly discriminating wavenumbers demonstrates differences between spectra for different lengths of aging. Correlations of ink aging are present in group scatter plots. Despite a non-linear correlation between the specific time periods, correlation are detectable over ranges of time with the major occurrence of aging present between the time periods of 4 weeks and 7 weeks.

Overall, this study presents evidence that aging of a gel pen ink can be demonstrated by the use of Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy.

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List of abbreviations

ATF	Bureau of Alcohol, Tobacco and Firearms
ATR	Attenuated Total Reflectance
ATR-FTIR	Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy
CE	Capillary Electrophoresis
EIMS	Electrospray Ionisation Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatography
GC-MS	Gas Chromatography Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IR	Infrared
RMS	Root Mean Squared
TLC	Thin Layer Chromatography
UV	Ultraviolet

Chapter 1

Introduction

1.1 Origin of the Pen

From the late Middle Ages, up until the early part of the 20th Century, the type of ink most commonly used was the iron gall ink. Iron gall inks consist of iron(II) sulphate and tannins (either tannic acid or gallic acid obtained from plant extracts or used as pure compound) in a variety of proportions. These were mixed with water, causing the tannins to break down into gallic acid or di-gallic acid, forming the ink complex [1]. When iron(II) ions were combined with organic tannin complexes the water soluble iron(II) complex is formed, giving the ink a pale grey purple colour [2-4]. Many iron gall inks are corrosive and when the ink is applied to paper the ink oxidises to become black in colour. Over time the ink will further oxidise causing a colour change from black to brown. The popularity of this type of ink has resulted in libraries and cultural institutes from all around the world holding collections of documents, manuscripts and artwork on paper and parchment which have been written with iron gall inks [5]. Iron gall inks were later improved by the creation of blue-black inks to prevent the ink corrosion, which were widely used before the introduction of ballpoint pens. [6]

The ballpoint pen has been the most popularly used type of pen during the past 60 years, however in recent years the popularity of the gel pen has greatly increased [7]. The ballpoint pen was created in 1939 by Ladislao Biro and marketed in the United States in 1945, where around fifty thousand pens were sold in a New York department store. The first ballpoint pen inks were created using oil-based solvents, but the inks

changed to using glycol based inks during the early 1950s [8]. Glycol based inks can be distinguished from oil based solvent inks by the use of a solubility test with petroleum ether, as oil based ink samples that have been on a document for less than 10 years are soluble in petroleum ether [9]. In 1955 chelated metalized dyes were used in ballpoint pen inks for the first time. These dyes are stable in light conditions and a solubility test using methanol can determine whether the ink does or does not contains the dyes. The dye most commonly found in these types of ink is blue/green copper phthalocyanine [8]. In the 1970s the roller-ball pen was introduced containing dyes similar to those found in fibre tip and porous tip pens. Writing strokes which are produced by roller ball pens can be difficult to distinguish from other inks and due to the nature of the ink, ink striations can be difficult to see. In 1978 Paper Mate and Anja created the erasable ballpoint ink, containing a rubber cement that can be erased up to a day after an ink sample has been written. 1979 saw the introduction of another new type of pen as Pentel introduced the fibre tip pen, which was soon followed by the production of the plastic nib and porous tip pens. These pens can be distinguished from fountain pens and ballpoint pens by their visual and microscopic appearance, dye colour and are generally water soluble [8]. The development of pens is summarised in Figure 1.

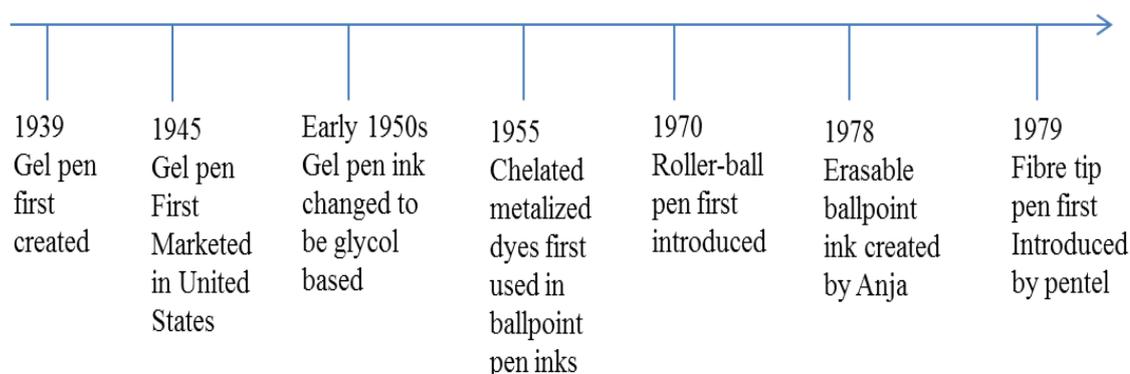


Figure 1. Development of pens

1.2 Origin of the Gel Pen

Prior to the production of the gel pen, non-ballpoint roller-ball inks were commonly used as an alternative to the ballpoint pen. The Sakura Colour Products Corporation planned to produce a pen that contained an environmentally friendly ink, free of any volatile organic compounds. The first pen which the company produced was the Ballsign pen, containing a dye-based ink. The following year the pen was changed to contain a pigment-based ink, which provides more flexibility in the choices of producible colours [10].

Gel pens were first marketed after being discovered by the Sakura Colour Products Corporation in Osaka, Japan in 1984. According to the company, “Years of research resulted in the 1982 introduction of Pigma, the first water-based pigment ink. Sakura’s revolutionary Pigma inks evolved to become the first gel ink rollerball launched as the gelly roll pen in 1984” [11]. Since being introduced, the popularity of the gel pen has increased due to the ability of the pen to produce smooth, fast and consistent ink flow and being marketed in an array of colours [12]. During the late 1980s these gel pens were first introduced into the United States and contained pigment-based inks which are difficult to analyse by Thin Layer Chromatography (TLC) due to the pigment in the ink not being soluble in the solvent, resulting in the ink not travelling across the TLC plate [13, 14].

1.3 Components of a Gel Pen

The composition of the ink used in a pen is generally kept secret by the manufacturer. This makes forensic examination difficult due to the analysis of the ink

sample being conducted with no information regarding the components and compounds that are expected to be found in the ink sample [15]. Over recent years, ink production technology has increase the range of ink compositions that are present in different types of pens throughout the world [16]. Inks which are used in gel pens are generally aqueous based, containing up to 80 % water [7, 10, 11, 17-20]. Historically the major difference between gel pens and other types of writing materials is that gel pens mainly use pigments as their colourant compared to using dyes, which are mainly found in other types of pens [12]. Dyes are colourants [21], which are soluble in the vehicle of the ink, whereas pigments are finely ground coloured particles which are insoluble in the vehicle of the ink [25]. In recent years this has changed as more dye based gel pen have been produced [22]. Inks which contain pigments can usually be created over a variety of colours [23]. The colourant of the gel pen being analysed can be determined by conducting a solubility test using methanol, as dye based inks are soluble in methanol, whereas pigments based inks are insoluble in methanol [21].

A gel pen contains a number of different components, including colouring material, the vehicle and resins. The most important of these components is the colouring material which can be made up of either dyes, pigments, or a combination of the two [24]. The structure of dyes contain mainly aromatic rings and large conjugated systems which are light sensitive and cause a slower decomposition of inks in natural environments [26]. The vehicle of the ink, which is the main liquid body [25], can contain either a single solvent, or a mixture of multiple solvents [27]. Solvents in the ink allow the ink to be applied to the paper [28]. Resins are natural or synthetic substances which are initially liquid, but over time will dry until it hardens [27]. Resins and fatty acids are added as drying agents. They can also aid with binding the ink to the paper and adjusting the viscosity of the ink [23, 28]. Gel pens may also contain a range of

non-ionic surfactants [23], lubricants, biocides, corrosion inhibitors, sequestrants, shear thinning agents, emulsifying agents, pH buffers and adjusters, polymerisation agents and pseudoplasticizers, which cause modifications to the rheological properties of the ink [29]. A manufacturer will usually add a tag into the ink in the form of a chemical marker, such as rare earth organometallic compounds and traces of optical whiteners. These tags do not vary over time and are used to signify the year in which the ink was produced. These tags are changed on an annual basis, meaning gel pens produced in the same year will all contain the same tag for identification [30-32].

Inks are produced by a company to a specification based on a variety of factors, including colour, colour density, viscosity, surface tension, water fastness, light fastness and fungal resistance. These specifications are met by controlling the chemical composition of the ink, including the type and concentration of dyes, pigments, solvents, viscosity enhancers and antifungal additives which are in the ink [33].

1.4 Document Examination

Document examination is an important area in combating fraud. Fraud is a major problem costing the private and public sectors of the UK £21.2 billion and £20.6 billion respectively in 2013 [34].

As a document examiner, the determination of when an ink sample was produced is crucial for fraud investigations. Due to this the accurate dating of an ink entry on a document has always been of high interest to forensic document examinations. [23, 35-40]. The aims of a document examination are to determine the following pieces of information about the questioned document [15]:

- Has any text been added, removed or altered to the document?
- Do multiple ink samples exhibit similar characteristics?
- What was the source of the ink sample?
- In what order were multiple inks written onto a document?
- When was an ink sample written?

The major aims of most forensic document examinations are to determine the authenticity, age and origin of an ink sample on a document [41]. When a document examination is being carried out between multiple inks, the chemical and physical properties of the inks can help provide information on whether the two inks were produced by the same manufacturer, if the inks were produced in the same production batch and the first production date of the batch of inks [37]. If additional writing has been added to certain documents then the meaning of the document can be affected, for example with wills and cheques. The forgery and alteration of a name or amount can have significant implications [23]. When analysing ink samples it is easier to characterise ink samples that are in bulk, however it is not necessarily possible to obtain a large sample size of ink, as an average 1 cm line of ink will usually only contain a maximum of 40 µg of solid material [9]. For the analysis of multiple ink samples it is best for the analysis not be carried out by comparing the first letter of a document, but to compare letters later on in the text, as the first letter of a document will often have been written with a dried pen tip and may result in differences in composition to other parts of the text [42].

When a document examination is conducted, the techniques for the examination are usually conducted in a specific order [23]. The order for a document examination is shown in Figure 2.

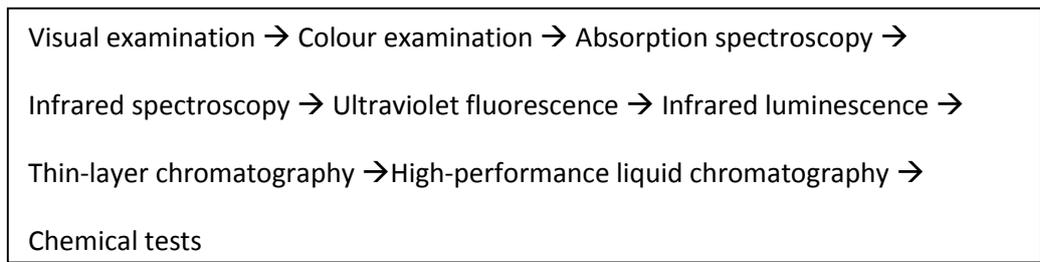


Figure 2. The stages of a document examination. Adapted from [22].

When comparing between ink samples it is a requirement to analyse both a questioned ink and a reference ink sample. During comparisons a forensic examiner will consider the concordances and discordances between the chemical profiles of the questioned and reference ink samples to evaluate whether the discordance between the two samples have arisen from plausible degradation of the sample due to environmental conditions or if the two samples are from different sources [43].

The first stage of a document examination is to determine whether the ink in the pen in question is from a ballpoint pen or a non-ballpoint pen [10]. The examiner will then begin conducting a non-destructive visual examination of the document by the use of a microscope and filtered light, using infrared and ultra-violet illuminated condition to distinguish between inks with similar appearances. The main disadvantages in the stages of visual and infrared luminescence is that the techniques have poor chemical selectivity as a number of inks will not fluoresce, meaning that spectra will not be obtainable [33]. If ink samples are unable to be distinguished from each other then it is necessary to run a TLC of the soluble dyes. This is highly discriminating and cost effective, however does damage the sample. Gel pens mainly contain insoluble pigments for their colour, so the TLC analysis is only able to confirm whether the ink is pigment or dye based [12]. Destructive techniques are generally less commonly used in

modern day document examinations, so chromatographic and electrophoresis techniques have been tested for use as modern day methods [44].

A range of different analytical techniques have been investigated for their ability to discriminate between different inks. The discriminating power of a sample set is defined as the probability that two randomly selected samples from a data set will be different from each other. The calculation is used to provide a value for how closely a pair of samples is to each other. This is repeated for each possible pair of samples. After all of the possible pairs have been analysed with each other the samples can then be analysed to see which of the samples are closely linked to each other and which are different from each other [41]. There are advantages and disadvantages for using the discriminating power. Advantages of the technique include providing a simple number as a result which can compare how much discrimination has occurred, however discriminating power does not provide information in relation to how closely related to each other different sample sets are [28]. TLC has a discriminating power of 0.98-0.99 [45], Ultraviolet-visible (UV-Vis) spectroscopy has a discriminating power of 0.79 for blue ballpoint inks and 0.96 for black ballpoint inks [46]. Percentage reflectance micro spectrophotometry on ink in situ has a discriminating power of 0.83 and Fourier Transform infrared spectroscopy (FTIR) has a discriminating power of 0.95 for blue ballpoint pen inks and 0.82 for black ballpoint pen inks [12]. This shows an array of discriminating powers based upon the technique being used.

The storage of documents for a long period of time in stable conditions can influence the chemical composition of the inks. This is linked to the degradation of the dyes and the evaporation of volatile substances. Other factors which affect the chemical composition include exposure to daylight and alterations in humidity [47].

The most significant coverage of the earliest experiments carried out on fountain pen inks was conducted by Mitchell and described in his book: *Inks: Their composition and manufacture*, published in 1907 [48]. Mitchell later updated his work and released a second book in 1937 with the same title [49]. Prior to the 1950s, separation techniques were not used in the field of forensic ink analysis because the courts were unreceptive of destructive analytical techniques. During this time document examiners would use filter photography, alternative light sources and chemical spot tests to differentiate between ink samples [44]. During the early 1960s the first standard ink reference library was created by Werner Hoffman at the Zurich Cantonal Police Laboratory, which identifies inks and helps determine the first date that an ink was manufactured. In 1968 the first standard writing collection was established by Brunelle in the United States. This collection later became known as the Bureau of Alcohol, Tobacco and Firearms (ATF) standard ink library and contained over two thousand different samples by the end of its first year, before moving to the United States Secret Service Forensic Laboratory. During the 1970s and 1980s there was no field in the area of forensic science that had a greater impact on the detection of fraudulent documents than the examination of writing inks [8]. There has been an increase in the number of inks and products appearing on the market which have been produced by countries with emerging economies, leading to increasing diversity of available ink formulations. Forensic ink examiners therefore have to analyse a vast array of combinations between ink formulations and writing instruments when identifying the source of an ink. The diversity of available inks has a direct effect on the ability to identify the manufacturer of a sample. Another element which makes ink examinations more difficult is that certain pens from the same manufacturer may contain different ink formulations and some inks from different manufacturers may contain the same ink formulation [45],

meaning that analysed sample containing the same ink formulation may not necessarily be from the same manufacture.

1.5 Spectroscopy of Pen Ink

The materials used to write on a document can provide more information than just the text or image that can be read, so a detailed analysis of ink samples are vital to provide more information [23]. Document examinations begin with a visual examination of the sample, followed by non-destructive analysis to obtain as much information as possible without damaging the evidential value of the document [23]. Non-destructive techniques that are commonly used include Raman spectroscopy, UV-Vis spectroscopy, luminescence and FTIR spectroscopy [50]. These techniques are preferable for analysis as they are generally easier to perform, involve little or no sample preparation and allow the sample to be used for further analysis [23]. Spectroscopic methods are unable to provide all of the information that is required regarding an ink [41]. If samples cannot be distinguished from each other, then destructive techniques will be performed to provide more information about the sample. These techniques include TLC, Electrospray Ionisation Mass Spectrometry (EIMS) and High Performance Liquid Chromatography (HPLC), [50] with TLC being the most commonly used for ink analysis [8].

Differences commonly occur in the non-volatile dye components of the inks, which can be separated out from each other and analysed by the use of TLC [51]. Volatile dyes cannot be separated from each other using TLC, as when the TLC plate is drying after the technique has been completed highly volatile dyes will evaporate off

and no results will be obtainable. If an ink formulation only contains volatile dyes then differentiating between inks by TLC is not possible.

Analytical techniques that are used for the analysis of pen ink rely on a chemical variation to be present between the dyes and complimentary dye components among pen inks from different manufacturers [16]. Analysis conducted on ink samples are unable to identify the specific pen or writing material that was used to create a mark, but it is possible to identify the type of ink and ink formulations used. A possible match between samples does not necessarily mean that the samples were produced by the same pen, as it is possible that the sample was produced by a different pen containing the same ink formulation [23].

Research was conducted in 1995 to analyse the increasing number of gel pens inks on the market. Attempts were made to use spectroscopic techniques, TLC and spot tests to separate out the inks into different colours. This was possible in all inks except for black inks [52].

In order to allow more techniques to be used on an ink sample, solvent extraction is conducted to open up further avenues for analysis to be carried out, as well as increasing the resolution and intensities associated with some analytical techniques, including UV-Vis spectroscopy [16]. Figure 3 shows a schematic for the solvent extraction of ink.

Take a minimum of 1 cm length ink line or 10 plugs of ink.

Place into a 0.5 dram glass vial.

Add 20 μl of weak solvent to the vial.

Cap the vial to prevent evaporation and allow the ink to extract for 30 minutes, rotating the vial every 10 minutes.

Figure 3. Schematic for the solvent extraction of ink. Adapted from [53].

Analytical comparisons between samples stored in different conditions and on different types of paper have provided some situations where the compositions of the inks have and have not altered. Fabianska and Kunicki compared samples which were fresh, had been stored in the dark and had been stored in light conditions by optical methods and Raman spectroscopy. When observing the optical properties of the inks there were no detectable differences between samples on cream paper that had been stored in light and dark conditions. For samples on white paper, the samples which were stored in light conditions were found to have a decreased value for UV and IR luminescence in comparison to samples which had been stored in dark conditions. When the inks were analysed by Raman spectroscopy, no detectable changes were observed between the different types of ink or the colour of paper which was used [47].

1.5.1 Infrared Spectroscopy of Pen Ink

Infrared spectroscopy (IR) is a useful technique for the analysis of inks due to its non-destructive nature, minimal sample preparation, cost effectiveness and rapid analysis time [54]. Optical properties related to gel pens were found to be stable, as neither long storage times, nor the exposure to daylight caused an influence on the IR absorption or IR luminescence of the samples. Changes in the optical properties of the

inks cause a decrease in the degree of IR luminescence in the inks which are stored in daylight compared to those stored in the dark or freshly produced samples [47].

1.5.2 Fourier Transform Infrared Spectroscopy of Pen Ink

Fourier transform infrared spectroscopy (FTIR) has been used for the analysis of gel pen inks. The relative age determination using FTIR was reported for detecting the changes in dried inks over time. The ratio between the hydroxyl groups and methyl groups were measured over a period of up to 22 years and the ratio was found to decrease until levelling off after approximately 10 years [51].

Howard Humecki developed a method which used FTIR to measure three bands of the spectrum over time, the hydroxyl (-OH) band around 3300 cm^{-1} , the SP^3 alkyl (-CH) band around 2900 cm^{-1} and the carbonyl (-CO) band around 1700 cm^{-1} . Over time it was observed that the intensity of the three bands in the spectrum altered, suggesting that over time the volatile components in the inks evaporate and oxidation occurs in the inks of ballpoint pens. The mass invariant ratio of both the hydroxyl and methyl bands decrease monotonically over time, with the decreasing ratio levelling off after approximately 20 years [57]. This technique was later tested by Becker *et al.* at the Bureau of Alcohol, Tobacco and Firearms but was found to be unsuccessful. Becker used a different microscope attachment during the experimentation that Humecki has used. It is believed that due to Becker not using this attachment the optimum procedures for experimentation were not recreated, providing unsuccessful results [51].

1.6 Dating of Pens

Over time an ink will undergo a series of processes causing it to age, which will affect the composition of the ink. These processes include the evaporation of volatile substances, oxidation of parts of the ink and the hardening of resin on the surface of the paper [23]. These aging processes can be affected by environmental factors, such as temperature, light and humidity [58]. There are two types of ink age that can be calculated; the relative age and the absolute age. The relative age, establishes which ink from a set of samples on the same piece of paper was written prior to the other. For the relative age to be applied the inks need to be of the same formula. The absolute age, establishes the actual age of the ink itself, without requiring the identification of the ink formula [59].

The determination of the writing age of an ink is essential in forensic document analysis [60]. It is often an essential problem associated with forensic science, making it important to understand the aging processes of different components found in inks. When looking at the dating of ink samples, some methods can only be compared by using the relative age of ink sample [58]. The testing of the relative aging of inks can be completed by comparing the rates and extents of extraction of questioned and known dated inks in organic solvents using TLC densitometry, comparing changes in the dye concentrations by TLC or comparing volatile ink components by Gas Chromatography-Mass Spectrometry (GC-MS) [36]. Prior to a relative aging test being applied there are a set of limitations that must be applied [61]. These limitations are as follows:

- The inks must be of the same formulation.
- The ink must be compared on the same piece of paper.
- The accuracy of the aging techniques needs to be determined.

- Reliability measurements need to be conducted.
- Two comparable ink parameters must be independent of the quantity of ink that is in the sample.

The date at which an ink sample was written onto a piece of paper can be calculated if it is possible to track either the polymerisation and hardness of the resins, the loss of solvent over time or the degradation of the dyes. In order to determine the date the ink sample was written by analysing the resins, the changes in extraction efficiencies over time are studied [24]. The extraction efficiency is characterised by two concepts, the rate of extraction, which is expressed as a function of the R-ratio and the extent of the extraction, which is expressed as the extent of extraction P. The R-ratio is defined as the amount of ink that has been extracted after a period of time, t_1 , as a fraction of the extractable ink after a longer period of time, t_f . The time of t_f can be any time after t_1 , but is usually chosen to be the time when no more ink is extractable. The value of P equates to the percentage of the total amount of ink deposited onto a piece of paper which is able to be extracted after t_f minutes. Over time the value of P decreases and can be calculated by a sequential solvent extraction [62].

When investigating the aging of an ink outside of a pen there are two types of profile that should be considered. These are known as the static profile and the dynamic profile. The static profile, which is the analytical profile of an ink that includes the stable properties of the same components which do not vary over time. The comparison of static profiles can determine whether an ink displays differences in composition with another ink. The dynamic profile, which is the analytical profile of an ink that considers the processes and changes that occur in the different components of the ink after it has been placed on a piece of paper [24].

The first evidence for the attempted dating of ink was conducted in the 1920s when aging properties of iron gallotannate were demonstrated. It was found that chloride and sulphate ions migrated along the fibres in the paper, which were related to the age of the ink [35].

Gas chromatography is used for detecting volatile compounds in inks, but the use of gas chromatography is dependent on the gradual disappearance of the major vehicles contained in ballpoint pen ink formulations [63]. Research has shown that the vehicle of an ink will stay in the ink for up to a year after being written on a document. Strong solvents are used to extract volatile compounds from the ink and comparisons are made using the peak area and peak height of the gas chromatograph of volatile vehicle components. In older ink samples the relative concentration of the volatile components are generally lower.

The process of aging ink involves the decomposition of the dyes which are present in the ink. Methyl groups are lost and substituted by hydrogen atoms which cause crystal violet to decompose to methyl violet and then decompose to tetramethyl para rosaniline [30, 35]. Figure 4 shows the chemical structure of crystal violet which is commonly used in ink dye, as well as methyl violet and tetramethyl para rosaniline, which are products that crystal violet decomposes into. The concentrations of crystal violet, methyl violet and tetramethyl para rosaniline were analysed by Andrasko in 2001 over a time period of 3-4 years [64]. High performance liquid chromatography with diode array detection was used for the aging analysis. The ink was extracted with 0.2 ml of ethanol for 30 minutes at room temperature before being heated in a vial at boiling point for 30 minutes. The extract was evaporated to dryness by nitrogen steam and the resin was dissolved in methanol. It was expected that the concentration of crystal violet

would decrease and the concentration of tetramethyl para rosaniline would increase, however this was not observed [27].

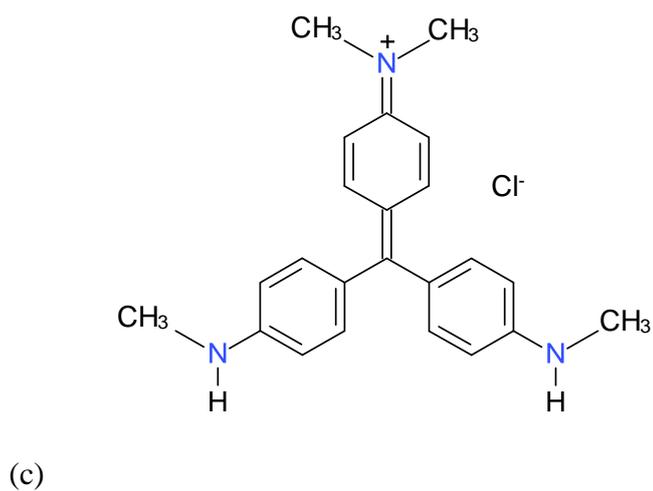
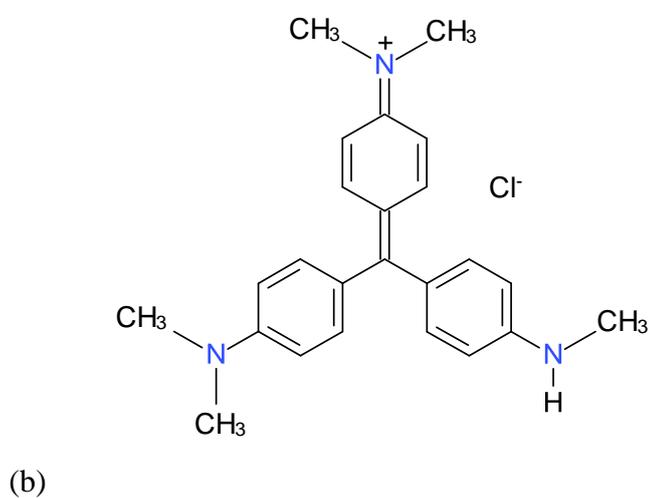
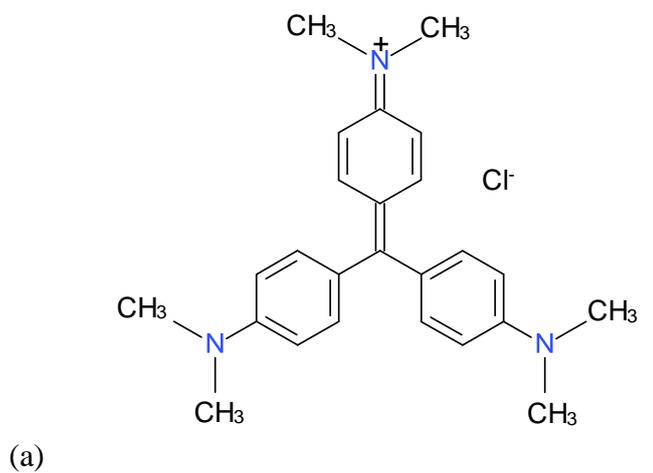


Figure 4. (a) Chemical structure of crystal violet. (b) Chemical structure of methyl violet. (c) Chemical structure of tetramethyl para rosaniline.

There are three main ways in which an ink is able to be dated. These are: determining the type and manufacturer of the ink from its chemical composition, comparing an ink to a library standard and using the rate of extraction of inks by solvents from the paper [33].

Certain inks contain a dating tag in them which is able to determine the actual age of the ink, but is not able to determine the age of the ink sample on a piece of paper. Dating tags in inks can be found and analysed by the use of TLC using a solvent system made of chlorobenzene and ethyl acetate (5:1 v/v). Standard samples of tags should be run simultaneously on the same TLC plate as questioned inks. The TLC is viewed under a longwave ultraviolet light and the R_f values of the two samples are compared [37]. The first unique dating tag was added to the manufacturing process of a pen in 1975 [51].

The sequential extraction process involves the ink sample being extracted into a weak solvent until the ink has stopped dissolving. After this point the ink is then further extracted into a strong solvent until all of the remaining ink has been extracted. If the two extractions are completed with the same quantity of solvent then the percentage of extraction can be calculated by dividing the absorbance of the first extraction by the sum of the two extractions and multiplying the result by 100. The percentage result that is obtained from this calculation can be used to work out how long has passed since the ink sample has been written, as the higher the percentage of extraction the fresher the ink sample will be [51].

One of the first dating methods developed in the United States was the ink library approach [8]. Samples of questioned inks and ink samples of a known

production date were compared using analytical techniques [35, 65]. In order to counteract the limitations associated with the ink library approach, the ink tagging approach was developed at the Bureau of Alcohol Tobacco and Firearms between 1975 and 1979. Different tag and ink formulations were used each year, so if a pen was detected to contain one of these tags then the year the pen was produced could be easily determined [8].

Another approach for dating pen inks was developed in 1968 by Brunelle *et al.* involving the chemical and physical comparison between questioned inks and inks in a laboratory standard ink library, which holds over five thousand different formulations. Inks in the library can date back as far as 1958. By 1978 approximately half of the inks produced in the United States were tagged. Since the start of the date tagging approach there has been an increase in the number of inks produced outside of the United States, resulting in the number of tagged inks decreasing [51].

In 1979 Cantu used some of the research conducted by Kikicki for developing a process to estimate the age of ballpoint pen inks [61] and found that there was an observable relationship between the age of ballpoint pen ink and the rate in which the ink could be extracted from a piece of paper using weak solvent. They developed and used the solvent extraction techniques and the knowledge that the longer an ink sample has been on a piece of paper the slower the extraction process, as the ink has dried. By comparing the extraction rates of questioned ink samples and samples of a known age, it is possible to analyse the relative age to determine if the samples were written at the same or different times [2]. Cantu later modified his procedure to measure the percentage of ink extracted from solvents instead of calculating the rate of extraction. The percentage extraction is calculated by the concentration of weak solvent in the

extraction divided by the sum of the concentrations of the weak and strong solvents in the extraction, multiplied by 100 [61].

In 1985 Stewart reported a process for comparing the relative ages of ballpoint pen inks by the use of gas chromatography, based on the decrease of major vehicles in inks over a period of time. Stewart analysed fresh ink samples by gas chromatography and compared them to TLC samples of known ink samples. It was reported that the vehicle would remain in inks which have been dried on paper for up to a year after being written [63]. There have been a number of contrasting studies which have been conducted using GC/MS to determine the age of pen inks. Some studies have indicated that the dating of pen inks by GC/MS is not possible after a few days of aging [66, 67], however other studies have indicated that pen inks can be analysed over a much longer period of time [68-70].

In the same year Humicki used FTIR to observe the changes in hydroxyl and carbonyl absorption bands over time, which was believed to be linked to the loss of solvents as the ink aged. The ink was studied over a 22 year time period. The ink samples were extracted using a mixture of ethanol and pyridine, as well as pure pyridine. In all of the inks a decrease in the concentration of the hydroxyl and carbonyl bands was observed. The level of decrease was highest during the first few years, levelling off after approximately 10 years [57].

In 1987 Brunelle *et al.* reported estimating the age of ballpoint pen inks by the use of a single solvent extraction. The process involves extracting an ink using weak solvents, spotting the extracted ink onto a TLC plate and measuring the amount of the ink which was extracted densitometrically. By comparing the questioned age samples

with ink samples of known dates, the age of the ink could be estimated. The limitation with this process is that it is mass dependent, so an equal quantity of questioned and known ink is required for sample comparison [63].

In 1988 Brunelle developed the dye ratio technique, which is mass independent and estimated the age of ballpoint pen inks. Inks are extracted by the use of either strong or weak solvents, spotted onto a TLC plate and separated out using a solvent system of ethyl acetate/alcohol/water (70:35:30). The concentrations of the dye components are then measured by a TLC densitometer [71].

There are occasions when an ink of a known age is not available for comparison. In 1988 Cantu developed a method for accelerating the age of an ink sample. This allows the age of an ink to be estimated when an ink sample on the same paper with the same ink formulation is not available. Cantu heated a black ballpoint pen at 100°C for 4 minutes and found it was equivalent to aging the ink for 3 months at 20°C. Another pen was heated at 100°C for 3 days and was found to be equivalent to 68 years of aging at 22°C [62]. In order for accelerated aging to be applied to the ink sample, the ink must not have reached complete dryness. If the pen has reached this point then the pen will not undergo any changes in solubility when heated [8].

In 2005, Andrasko and Kunicki looked at the aging of ballpoint pen inks from inside the chamber of the pen. They used High Performance Liquid Chromatography combined with diode array detector to look at ink inside the chamber of a pen that had regularly been used, as well as pens which had not been used for many years. They found there was no evidence of aging that had occurred inside the chamber of a pen that had not been used related to the composition of dyes which had been found in the

chamber of a regularly used pen, however aging could be detected in inks near the tip of the chamber in pens that had not been written with for several years. It is necessary for forensic investigations to assume that the aging inside the chamber of a pen is negligible in comparison to the aging of the ink on a piece of paper [42].

Throughout the past half century there has been a large development in the analysis of pen inks. During this time the analysis has been conducted and developed, with new methods, like age accelerating, being added to the improvement of older methods using techniques including GC/MS and TLC.

1.7 Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is reliant on a compound containing covalent bonds. Almost all covalent bonds absorb radiation in the infrared region of the electromagnetic spectrum. The electromagnetic spectrum is the range of all types of light from gamma rays at the shortest wavelengths of less than 0.01 nm up to radio waves which have the longest wavelengths of greater than 10 cm [72]. Different sections of the electromagnetic spectrum are used for different types of analytical techniques. Ultraviolet and visible light are used for UV-Vis spectroscopy, infrared light is used for FTIR and radio waves are used for Nuclear Magnetic Resonance spectroscopy. Figure 5 shows the electromagnetic spectrum. The infrared section of the electromagnetic spectrum has wavelengths which occur between 0.7 μm and 100 μm , but only the area between 2.5 μm and 25 μm will cause vibrations in the molecular bonds. This is the wavenumber range used for infrared spectroscopy [73].

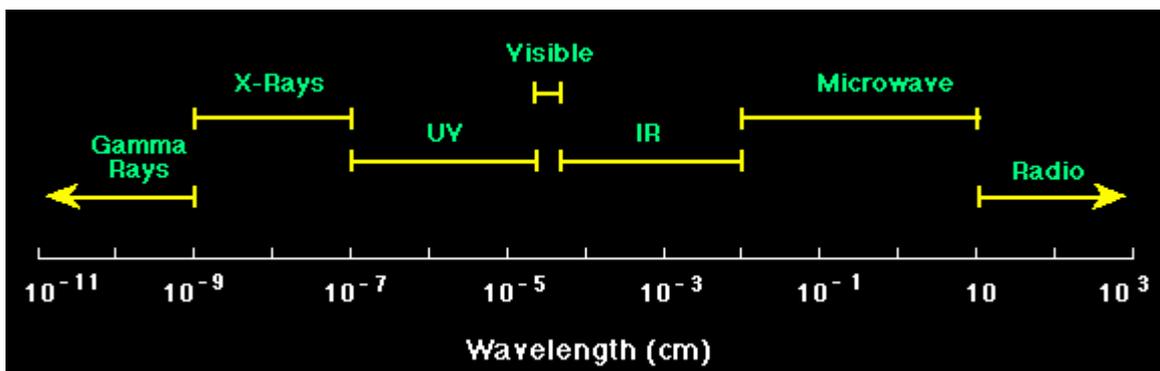


Figure 5. The electromagnetic spectrum. Replicated from [72].

Wavelength, frequency and the energy of the light can all be used as scales for the electromagnetic spectrum. These three terms can be linked between each other by equations 1.1 and 1.2

$$\nu = c/\lambda \quad \text{Equation (1.1)}$$

$$E = h\nu. \quad \text{Equation (1.2)}$$

In these equations ν = frequency in hertz (Hz), c = the speed of light in meters per second (m/s), λ = wavelength in centimeters (cm), E = energy in joules (J) and h = Planck's constant. These equations show that frequency and energy are both inversely proportional to wavelength.

Another unit commonly associated with infrared spectroscopy is wavenumber, which is represented by $\bar{\nu}$. Wavenumber is the reciprocal of wavelength and is expressed as cm^{-1} . Wavenumber can be converted to frequency by multiplying it by the speed of light in centimeters per second. These are shown in equations 1.3 and 1.4.

$$\bar{\nu} = 1/\lambda \quad \text{Equation (1.3)}$$

$$\nu = \bar{\nu} c = c/\lambda \quad \text{Equation (1.4)}$$

Wavenumber is the unit mostly used along the x-axis of an infrared spectrum. The region of the infrared section of light which can detect the vibrations of bonds is between 2.5 μm and 25 μm , which corresponds to a wavenumber range of 400 cm^{-1} to 4000 cm^{-1} . This range is used along the x-axis to show the full vibrational infrared scale.

In infrared spectroscopy the vibrations of chemical bonds cause spectral peaks. Each of the individual peaks in a spectrum is a result of a different type of bond between molecules, but the frequency can also be dependant of the type of vibration of the bond. The two main modes of vibrations are stretches and bends. There are two types of stretch known as symmetric and asymmetric stretch and four types of bend known as scissoring, wagging, rocking and twisting. These types of bond vibration are shown in Figure 6. An Asymmetrical stretch is where the two bonds stretch in opposite directions with one stretching out and the other stretching in. A symmetrical stretch is where both bonds stretch out in the same direction at the same time. A scissoring bend is where the two bonds bend in the opposite direction in the same plane towards or away from each other. A rocking bend is where the bonds bend in the same directions as each other in the same plane. A wagging bend is where the two bonds bend out of the plane in the same direction. A twisting bend is where the two bonds bend out of the plane in opposite direction [74]. The frequency of a stretching bond is greater than the frequency of a bending bond. For a CH_2 molecule a stretch bond will show on a spectrum between 2925-2850 cm^{-1} , while a bending bond will show between 1465-720 cm^{-1} depending on the type of bend. Scissoring bends have the highest wavenumber at

1465 cm^{-1} , twisting and wagging bends are between 1350-1150 cm^{-1} and rocking bends are the lowest at 720 cm^{-1} . Some molecular bonds show more than one peak on a spectrum if they have more than one type of vibration. For example a CH_3 group can show symmetrical and asymmetrical stretches so will show two stretch peaks for the same bond [73].

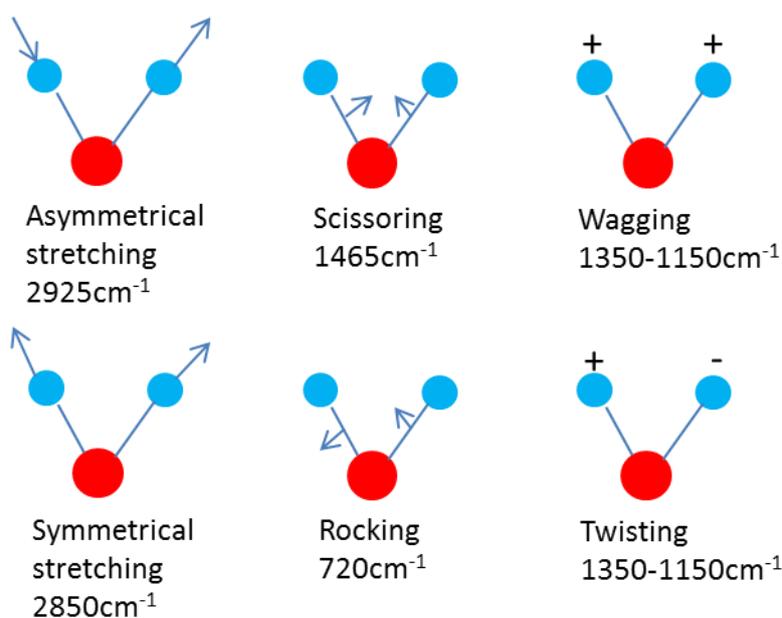


Figure 6. Stretching and bending vibrations for a CH_2 group. Replicated from [74].

Asymmetrical chemical bonds are able to be analysed by the use of infrared spectroscopy due to them exerting a chemical dipole on each other. If a molecule is symmetrical then there will be no vibrations between the bonds resulting in the molecule not having a dipole. When infrared radiation is aimed at molecules, the molecules are excited to a higher energy state. A molecule will only absorb energy at a specific frequency and the energy change at this frequency will be a fixed quantity between 8-40 kJ/mol . Infrared radiation between 8-40 kJ/mol corresponds to the range of energy that is linked to stretches and bends between covalent bonds. When there is a match between the frequencies of both the infrared radiation and that of the stretch or

bend of the bond, the energy of the radiation increases the amplitude of the motion of the molecular bond. [73]

An infrared spectrophotometer, commonly referred to as an infrared spectrometer, is a piece of instrumentation that will provide an absorption spectrum for a compound. There are two types of infrared spectrometer that are used for analysis, dispersive and Fourier transform. A dispersive infrared spectrometer splits a beam of infrared radiation into two beams which take the same path length, one beam passes through the sample whilst the other passes through a reference sample, before joining together and passing through a monochromator. The monochromator passes the two beams of light alternatively through a detector which determines the ratio between the intensity of the two beams at varying frequencies. The ratio of these intensities is then used to determine the amount of light absorbed by the sample which is used to produce the sample spectrum [73]. A diagram showing a dispersive infrared spectrophotometer is shown in Figure 7.

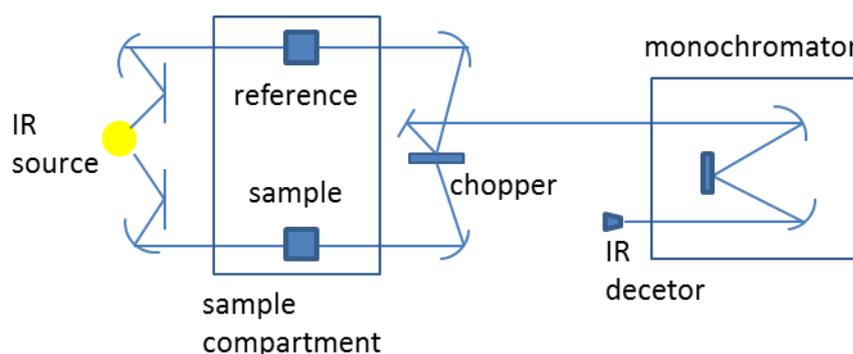


Figure 7. Schematic of a dispersive infrared spectrophotometer.

Replicated from [76]

The more commonly used type of spectrometer is a Fourier transform spectrometer. A beam of light which is emitted from a source is firstly split into two

beams by a beam splitter. These two beams of light reflect off a mirror back toward the beam splitter. These two beams take paths of different lengths with the first beam reflecting off a fixed mirror taking a path which has a fixed length and the second beam reflects off a movable mirror taking a path with an adjustable length. The two beams then recombine with each other at the beam splitter before interacting with the sample and striking the detector. The difference in the distance that the two beams travel is known as the optical path difference and if the distances between the two path lengths are the same then this is known as zero path distance [75]. An interferogram is produced, which is a plot of intensity against time. In order to convert this information into an analysable spectrum a mathematical operation called Fourier transform must be applied to the data which separates out the absorption frequencies from the interferogram and produces a spectrum showing intensity against frequency. A diagram showing a Fourier transform infrared spectrometer is shown in Figure 8. A summary of the comparisons between dispersive and Fourier transform infrared spectrometer is shown in Table 1.

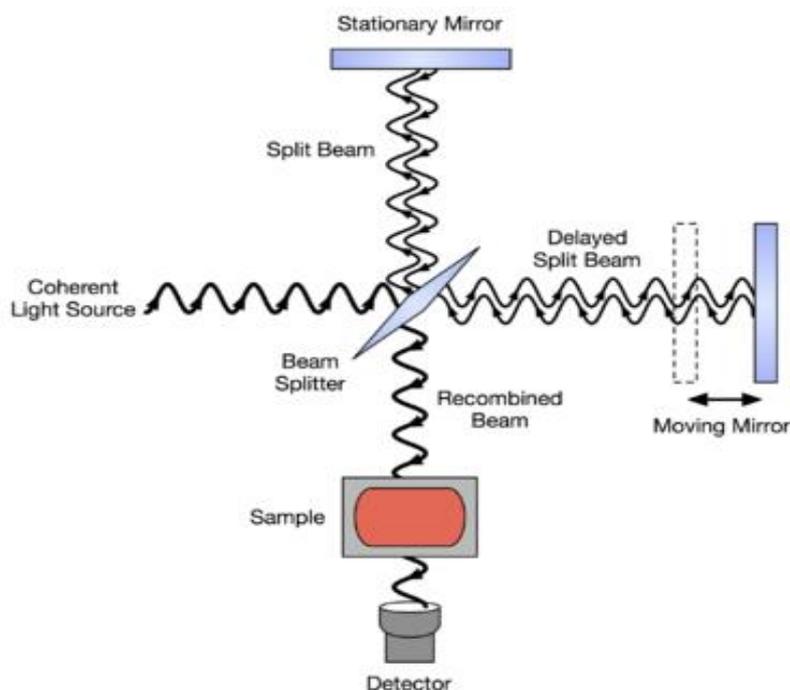


Figure 8. Schematic of a Fourier transform infrared spectrometer.

Table 1. Comparison between dispersive and Fourier transform infrared spectrophotometer.

Dispersive infrared spectrometer	Fourier transform infrared spectrometer
Beam split into two beams of equal path length.	Beam split into two beams of different path length.
One beam passes through sample before the beams are recombined.	Both beams pass through sample after the beams have been recombined.
Measures the absorption of one frequency of light at a time.	Measures the absorbance of light from a range of frequencies at one point in time.
Spectrum can be obtained straight after the detector without any mathematical operations being applied.	Fourier transform is applied to the spectral data after the light has hit the detector.

In a Fourier transform infrared spectrometer the ratio between the distances of the path lengths of the two beams of light can be used to calculate the differences in divergence between the two beams. If the two path lengths are the same length the two beams interfere constructively. If the distance of the moving mirror is altered by $\lambda/4$ then the path length will alter by $\lambda/2$. This will cause the two beams to interfere destructively. As the distance of the moving mirror is changed the intensity of the beam at the detector is altered. The intensity of the beam can be calculated by the equation 1.5.

$$I(x)=Bv(\cos(2\pi xv))$$

Equation (1.5)

$I(x)$ is the intensity of the beam at the detector, x is the displacement of the mirror in centimeters and $B(\nu)$ is the intensity of the infrared source as a function of the frequency (ν) in cm^{-1} . [77]

If a second infrared source of a different frequency is added then the equation for the intensity of the beam will change to represent the addition of the two waves together. This is shown by equation 1.6.

$$I(x) = B(\nu_1) \cos(2\pi x\nu_1) + B(\nu_2) \cos(2\pi x\nu_2) \quad \text{Equation (1.6)}$$

If more frequencies of light are added, for example in a polychromatic light source, then the total intensity of the light can be calculated from the sum of the waves using equation 1.7 which is one half of a cosine Fourier transform pair [77].

$$I(x) = \int_{-\infty}^{\infty} B(\nu) \cos(2\pi x\nu) d\nu. \quad \text{Equation (1.7)}$$

A similar approach is used by Fourier transform to convert information into an infrared spectrum. By subtracting a single frequency from polychromatic light an inverted wave will appear across the interferogram. By subtracting more frequencies more waves will appear until the interferogram shows the result of all of the frequencies being subtracted except from those absorbed by the sample. Subtracting the frequencies then results in the following equation to be used to calculate the intensity of the source as a function of the frequency. Equation 1.8 shows the second half of the cosine Fourier transform pair [77].

$$B(\nu) = \int_{-\infty}^{\infty} I(x) \cos(2\pi x\nu) dx. \quad \text{Equation (1.8)}$$

Equations 1.7 and 1.8 can both be used in combination with each other to show the relationship between the interferogram and the spectrum.

An additional application that can be added onto a FTIR is attenuated total reflectance (ATR). ATR requires a crystal to be mounted to the FTIR spectrometer. The crystal is usually made of either diamond or germanium due to them having a high refractive index. The infrared radiation is focused onto the face of the crystal. The refractive index of the crystal and angle of incidence of the light are set up so that the radiation undergoes total internal reflection causing the energy of the radiation to reflect off surface of the crystal. The crystal acts as a guide for the radiation. The radiation in the crystal causes a standing wave of radiation known as an evanescent wave. This wave is larger than crystal and penetrates beyond the surface of the crystal. When conducting analysis using ATR, the crystal is brought into contact with the sample and the sample absorbs radiation from the evanescent wave causing an infrared spectrum. The depth at which the infrared radiation penetrates into a sample can be calculated by equation 1.9.

$$DP = \frac{1}{2\pi W N_c (\sin^2 \Theta - N_{sc}^2)^{1/2}} \quad \text{Equation (1.9)}$$

In the above equation DP is the depth of penetration, W is the wavenumber, N_c is the refractive index of the crystal, Θ is the angle of incidence and N_{sc} is the ratio of the refractive index of the sample divided by the refractive index of the crystal [75].

There are two functions of infrared spectroscopy which are changeable and important for the spectroscopic data. These are resolution and the number of scans. The resolution of the spectrum determines how often a data point is collected. For example

if a spectra is run with a resolution of 4 cm^{-1} , then a data point will be collected at wavenumbers with 4 cm^{-1} intervals and if the resolution is increased then the data points will be collected more frequently. A spectrum with a higher resolution will contain a higher amount of data points and therefore will be more detailed. The number of scans conducted will also aid in the detail of the spectrum. The more scans taken will improve the detail by reducing the amount of noise of the spectrum, however this will mean that a longer length of time will be required in running the spectrum [75].

1.8 Aims of Study

During recent decades aging studies have been conducted on pen inks from a variety of types of pen using multiple techniques. Most of this research has been performed on ballpoint pen inks with a small number looking at gel pen inks and fountain pen inks. A large quantity of analytical techniques have been used during the previous research including Raman spectroscopy, FTIR Spectroscopy, Ultraviolet-visible spectroscopy, HPLC and TLC.

The main aim of the research is to determine whether infrared spectroscopy can be used to calculate the age of a gel pen ink and therefore how much time has passed between an ink sample being written on a piece of paper and the sample being analysed. The research is to include a range of different coloured pen as the majority of previously conducted research has mainly concentrated on black and blue gel pens.

Chapter 2

Materials and Methodology

This chapter describes the materials used to perform the experimentation during various stages of the project, details explaining the equipment and techniques used, as well as the methodologies conducted for the experimentation.

2.1 Materials

2.1.1 Gel Pens

Different coloured gel pens from a variety of manufacturers were purchased during September 2013. Overall, pens from five individual manufacturers were purchased, representing a range of different types of pens with a total of 15 colours across all of the manufacturers. In total 51 different pens were purchased with 45 combinations of manufacturer and colour and 6 duplications of pens which had the same manufacture and colour combination. The pens have been stored inside a locker in an office environment since being purchased. Table 2 lists all of the different pens organised by manufacturer.

Table 2. Pens used in this study listed by manufacture

Pen manufacturer	Pen Colour
Club	Black
Club	Blue
Club	Red
Club	Green

Uni-ball Signo	Black
Uni-ball Signo	Blue
Uni-ball Signo	Red
Uni-ball Signo	Green
Uni-ball Signo	Light Blue
Uni-ball Signo	Purple
Uni-ball Signo	Pink
Uni-ball Signo	Orange
Paper Mate	Black
Paper Mate	Blue
Paper Mate	Red
Paper Mate	Green
Wilko	Green
Wilko	Orange
Wilko	Pink
Wilko	Purple
Wilko	Yellow
W H Smith	Black
W H Smith	Blue
W H Smith	Light Blue
W H Smith	Green
W H Smith	Lime
W H Smith	Orange
W H Smith	Peach
W H Smith	Purple

W H Smith	Violet
W H Smith	Pink
W H Smith	Yellow
W H Smith	Gold
W H Smith	Silver
W H Smith	Brown
W H Smith	Glitter black
W H Smith	Glitter blue
W H Smith	Glitter red
W H Smith	Glitter green
W H Smith	Glitter light blue
W H Smith	Glitter orange
W H Smith	Glitter pink
W H Smith	Glitter purple
W H Smith	Glitter gold
W H Smith	Glitter silver

2.1.2 Paper

A 500 sheet ream of Vari Copy office white paper was obtained and paper from this ream was used during all stages of the project. Each sheet used during the study was randomly chosen from the ream. The ream of paper was stored in an office environment.

2.2 Infrared Spectroscopy

2.2.1 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy was used during all stages of the project, including the paper variance and drying study. A JASCO ATR-FTIR-410 was used, scanning between $4000\text{-}600\text{ cm}^{-1}$. 64 scans were conducted for each sample run, at a resolution of 4 cm^{-1} .

Figure 9 below shows an image for the instrumentation used during the preliminary experimentation.

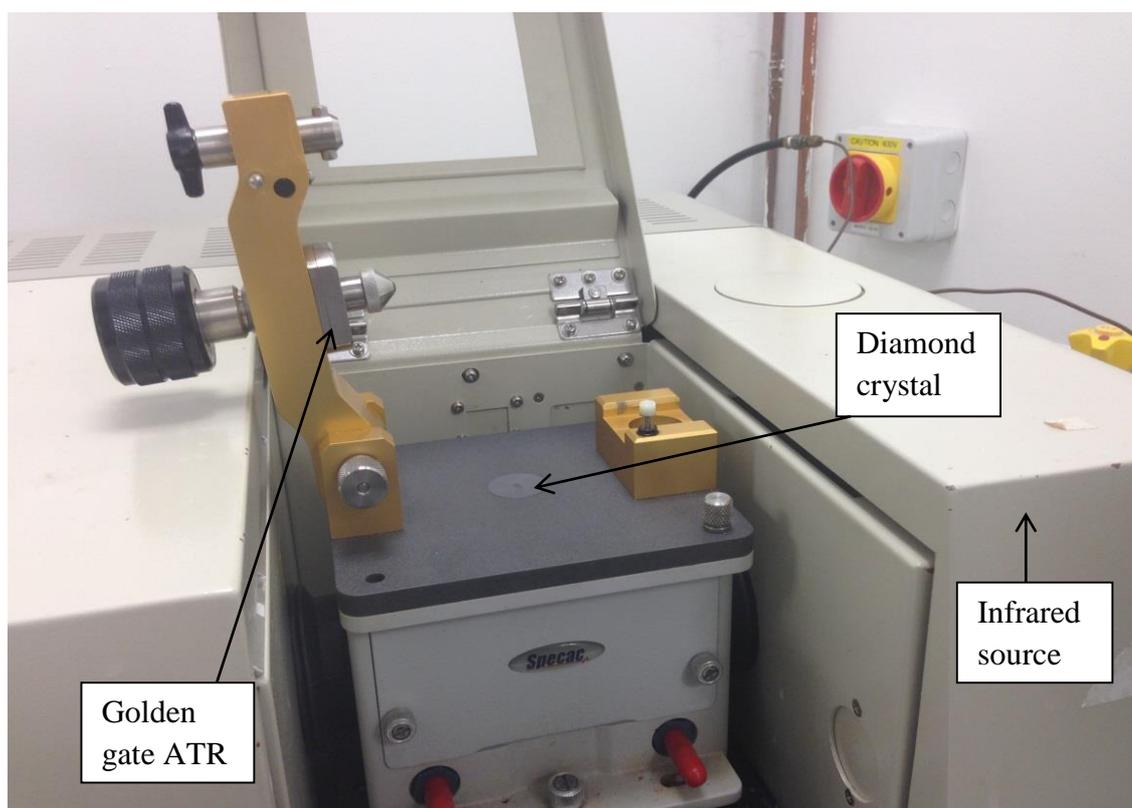


Figure 9. An image of the JASCO ATR-FTIR used during the paper variance and drying study.

2.2.2 Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy

Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) was used during all stages of the project. For the aging study an Agilent technologies Cary 670 FTIR microscope with a diamond crystal ATR attachment was used. ATR measures changes which occur in a totally internally reflected infrared beam when it comes into contact with a sample. The infrared beam is directed onto a crystal with a high refractive index at a specific angle. The internal reflectance creates an evanescent wave extending beyond the surface of the crystal. The attenuated energy from each wave is passed back to the infrared beam which exits from the opposite end of the crystal and on to the infrared detector [75]. Figure 10 shows the instrumentation used during the aging study.

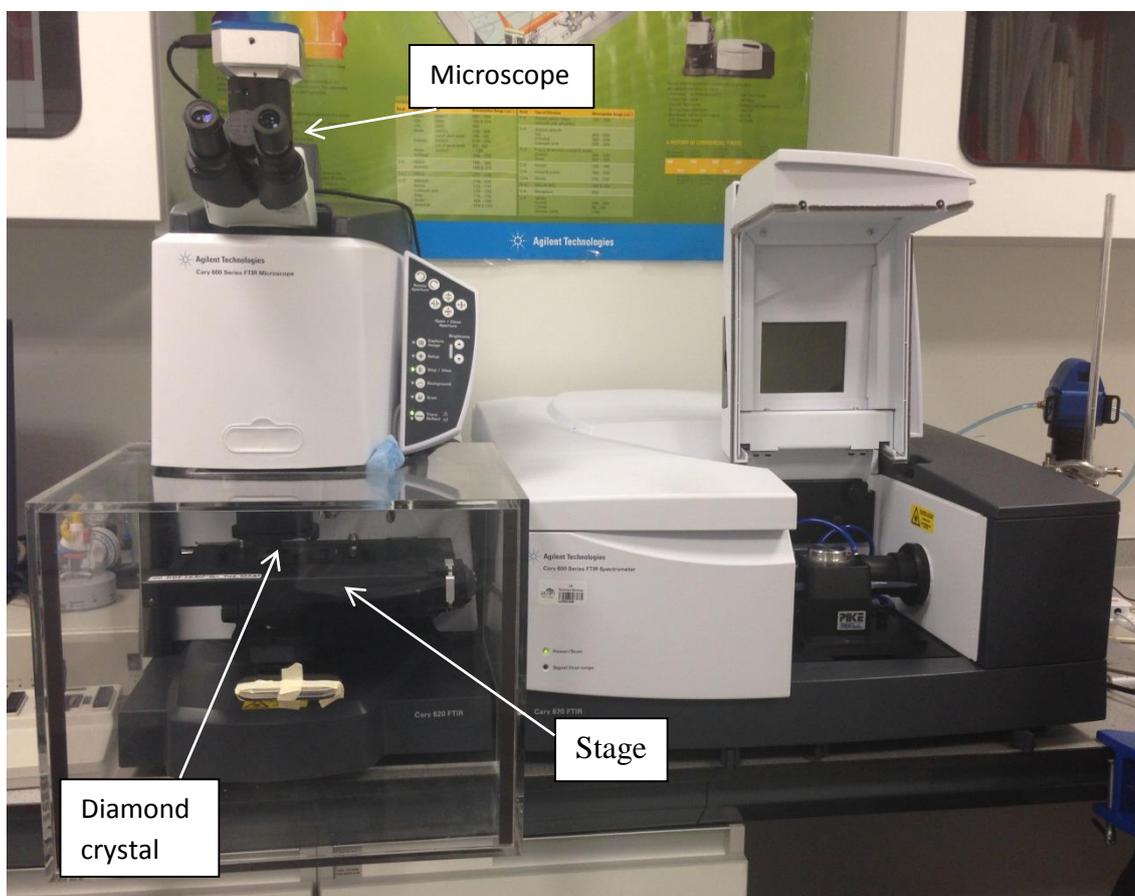


Figure 10. An image of the Agilent FTIR used during the ink aging study.

2.3 Methodology

2.3.1 Preliminary Experimentation

2.3.1.1 Paper Variance Study

The paper used during the paper variance and aging study was analysed to compare the different sheets in a single pack of paper. A pack of 500 sheets of Vari copy office white paper was obtained. From the pack, 10 sheets of paper were randomly selected, and separated into 10 parts. Spectra were collected using a JASCO FTIR spectrometer equipped with a Specac ATR single reflection diamond Golden Gate. Spectra were collected over the range of 4000-600 cm^{-1} , at a resolution of 4 cm^{-1} and over 64 co-added scans. Prior to each spectra being collected, a background absorption spectrum was collected for atmospheric correction. For each part of paper, 3 spectra were collected. After each set of 3 spectra for a single part had been collected the paper was removed and the crystal was cleaned using ethanol. In total, 300 paper spectra were collected.

2.3.1.2 Drying Study

A drying study was conducted on the gel pens to determine the length of time taken for the gel pen ink to dry. A volume of 1 μl of ink was removed from the chamber of the pen and pipetted onto a JASCO FTIR spectrometer equipped with a Specac ATR single reflection diamond Golden Gate and a spectrum was collected at time periods of 2, 4, 8, 16, 32 and 48 minutes after the ink has been placed onto the crystal. Spectra were collected over the range of 4000-600 cm^{-1} , at a resolution of 4 cm^{-1} and over 64

co-added scans. Prior to each spectrum being collected, a background absorption spectrum was collected for atmospheric correction. After all drying spectra has been collected for a single ink the ink was removed and the crystal was cleaned with ethanol. In total, 229 drying spectra were collected.

2.3.2 Aging Study

Each of the 51 pens were used to write 24 lines onto a single piece of paper, which were divided up into 8 sets of 3 lines. On the same day the ink lines were written the first set of lines were analysed, whilst the other 7 sets were stored in an office environment until they were required for analysis. Spectra were collected using an Agilent technologies Cary 600 series FTIR microscope with a microscopic diamond ATR crystal attachment. Spectra were collected in the range of 4000-600 cm^{-1} , at a resolution of 4 cm^{-1} and over 32 co-added scans. Prior to each spectra being collected, a background absorption spectrum was collected. 2 spectra were collected for each of the 3 lines in each set, and each set of lines were collected at the following time periods, 0 days, 1 day, 2 days, 1 week, 2 weeks, 4 weeks, 7 weeks and 10 weeks after the lines were written. In total 2414 spectra were collected.

2.4 Data Processing

Data were collected from the instrumentation in the form of text files. These text files were uploaded into excel spreadsheets before being imported into MATLAB and then into a spectool toolbox. After the data had been imported, pre-processing was carried out on the raw data to ease with the analysis of data. The average spectra for each set of inks were calculated and the sections of the spectrum which did not contain

important spectral data were removed from the spectra. The areas of the spectra before 850cm^{-1} , between 1560cm^{-1} and 2320cm^{-1} and after 3600cm^{-1} were set at an intensity of 0, eliminating spectral data. The section between 1560cm^{-1} and 2320cm^{-1} contained high levels of water vapour making the data in this area unable to be analysed. The areas of the spectrum before 850cm^{-1} and after 2320cm^{-1} did not contain any spectral peaks. After this stage noise reduction was carried out to improve the signal to noise ratio of the data, which was then second derivatised and vector normalised. Variable ranking was conducted for each of the spectra, determining the areas of the spectrum containing the highest differences between the spectra at each time period for the different ink samples. The areas of highest discrimination are the areas of interest to concentrate on when investigating the aging of the inks. The final stage of the pre-processing involved feature extraction and group scatter plots. The variable ranking information from the second derivatised data was used to find the wavenumbers of the most discriminating peaks to carry out feature extraction. These feature extraction points were then variably ranked to find the most discriminating spectral features for each ink, which were compared using group scatter plots.

Chapter 3

Spectral Library

This chapter displays a collection of spectra which were collected during the preliminary experimentations of the project. These include the paper variance study, drying study, dry ink study and ink discrimination. The spectra which were collected from these stages provide information to aid with the aging study. Portions of this work were presented at the 2014 SciX conference in Reno, Nevada, United States, September 2014 in a poster entitled “Using vibrational spectroscopy to analyse the composition and effect of environmental factors on gel pen ink”. (Appendix A contains the poster and the abstract accepted by the conference).

3.1 Paper Variance Study

The paper variance study was conducted to determine if all of the sheets of paper in a ream displayed the same spectrum as each other. This analysis is important in the context of the rest of the project. If the result of the analysis shows that all of the pieces and sheets of paper show the same spectrum then it is known that when different sheets of paper are being used for analysis there will be no effect from the paper that will need to be accounted for. In contrast, if it is found that there are differences between the spectra of different sheets of paper then it means during the stages of analysis the differences in the spectra caused by the paper the inks are written on will need to be considered when conducting analysis.

Overall a total of 300 spectra were collected consisting of 3 spectra of 10 different sections of 10 different sheets of paper. The raw data from the spectra were

loaded into MATLAB and the 300 spectra were plotted. A spectrum for one of these plots can be seen in Figure 11.

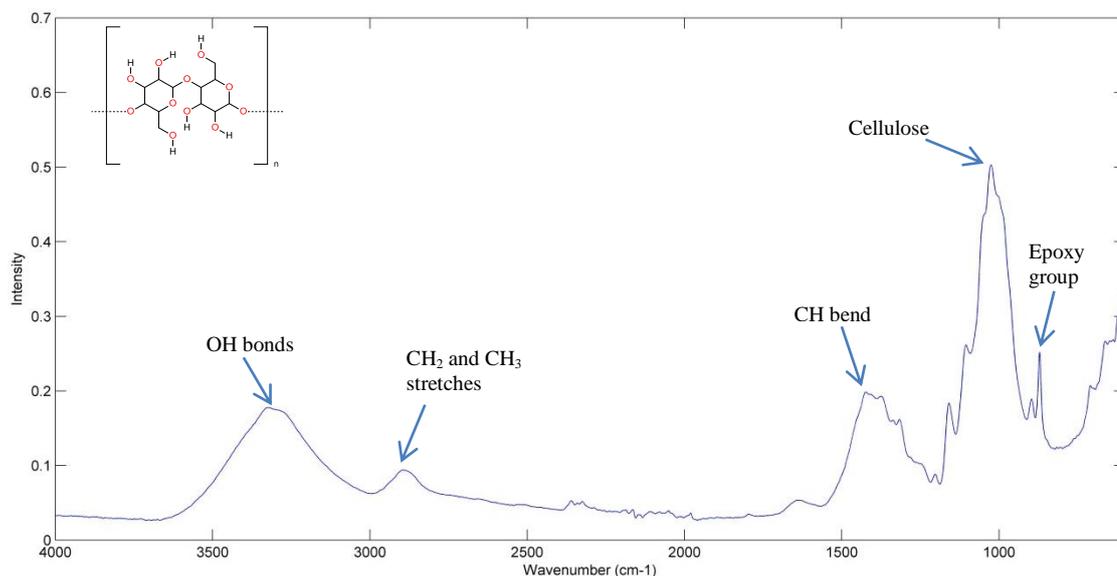


Figure 11. Spectrum of paper showing the major peaks and the structure of cellulose

A plot was created of the average spectra for all 300 spectra with error bars showing the standard deviation that is associated with each of the individual wavenumbers. The largest areas of standard deviation observable on the spectra are where the peaks are at their maximum intensity. Along the spectra the standard deviation is very low at elements of the graph where it is either flat or increase up a gradient. The analysis of the spectra shows that the variation amongst the various sheets of paper found in a single ream is very small and it can be considered that all of the sheets are the same. This is vital for the main experimentation of the project as it means that each sheet of paper that is used can be considered the same as each other, resulting in it being classed that each of the pen inks are being written onto the same surface. Table 3 shows the standard deviation of the spectra at the wavenumbers of highest intensity.

Table 3. Standard deviation at major peaks on the average paper spectrum.

Wavenumber (cm ⁻¹)	Standard deviation	Section of spectrum
870.70	0.0188	Epoxy group peak
1021.12	0.0357	Cellulose peak
1396.21	0.0215	CH bend peak
2869.56	0.0070	CH ₂ and CH ₃ stretches peak
3302.50	0.0153	OH bonds peak

Figure 12 displays the results from the paper variance study. The blue line shows the mean spectrum representing the average spectrum of all of the 300 samples. The black sections above and below the mean line shows the standard deviation of the paper samples. Data showing the standard deviation of the major peaks associated with the paper spectrum can be seen in Table 3. All of this shows that all sheets of paper are molecularly consistent, and therefore it can be assumed that all of the sheets in the ream of the paper are the same and produce the same infrared spectrum.

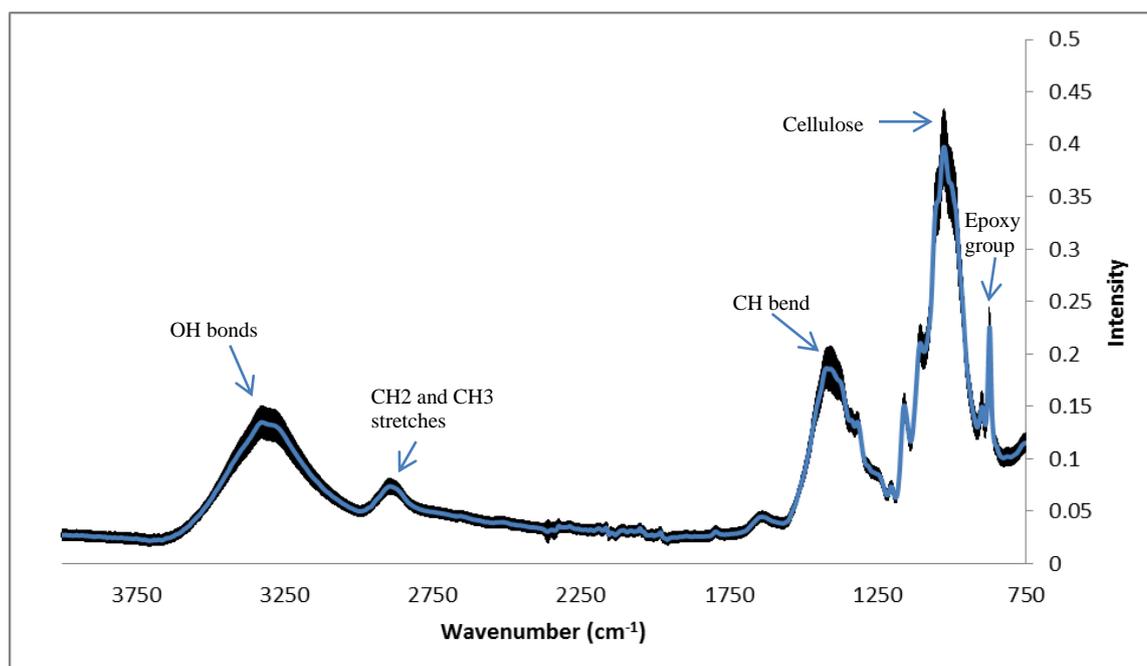


Figure 12. Average paper spectrum showing the mean and standard deviation of the paper.

3.2 Analysis of Pure Ink Samples

3.2.1 Drying Study

The first groups of pens used for the drying study were analysed over a time period of 48 minutes with spectra taken at 6 different times (2 minutes, 4 minutes, 8 minutes, 16 minutes, 32 minutes and 48 minutes). After the first sets of pens had been analysed for this study it was determined that the ink took approximately 20 minutes to dry. The next group of pens were then analysed over a 20 minute time period at 4 different times (2 minutes, 6 minutes, 12 minutes and 20 minutes). After further analysis it was found that 1 μ l ink took 10 minutes to dry. The final group of inks were analysed over a 10 minute time period, with spectra being taken at 3 time periods (2 minutes, 6 minutes and 10 minutes).

A drying study for each of the pen inks were performed to provide information related to two different areas. The first is to determine the length of time taken for a 1 μ l sample of a gel pen ink to dry so that during the main stage of the experimentation the length of time the ink should be left to dry before taking the spectrum on day 0 is known. The other information to be obtained from this stage is to create a database with spectra of each individual pen that is being used.

Figure 13 shows an example for the drying of the ink from a blue papermate gel pen that was analysed and Table 4 shows the peaks which are present in the ink spectra and the functional groups which the peaks correspond to.

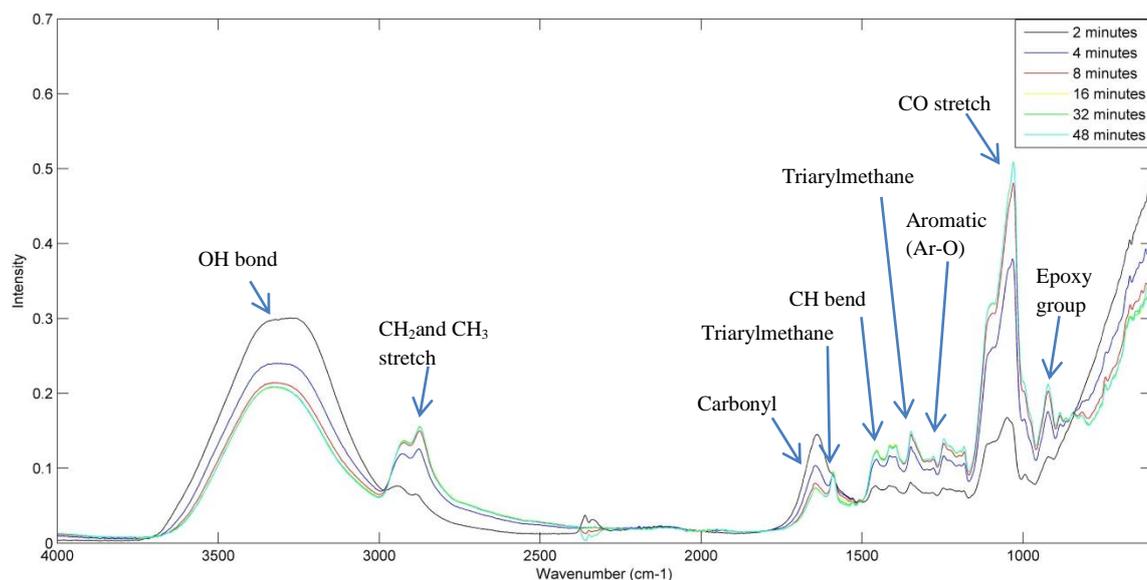


Figure 13. Spectra showing the drying of a Papermate blue ink.

The ink was dried and analysed over a period of 48 minutes. The 6 different spectra are overlaid to show the changes in the spectra over time. Different sections of the spectrum alter in different ways as the ink dries. For the peaks at 1020 cm^{-1} , 2870 cm^{-1} and the range of peaks between 1100 cm^{-1} and 1450 cm^{-1} , as the ink dries the intensity of the peaks increases. In contrast, for the peaks at 1650 cm^{-1} and 3300 cm^{-1} , as the ink dries the intensity of the peak decreases.

Table 4. Peaks which are present in the dried ink spectra.

Wavenumber (cm ⁻¹)	Functional group
3400	OH broad
2900	CH ₂ and CH ₃ stretch
1630	Carbonyl
1590	Triarylmethane
1400	CH bend
1340	Triarylmethane
1240	Aromatic (Ar-O)
1180	Triarylmethane
1030	CO stretch
920	Terminal epoxy

Appendix B contains spectra for the drying study which was conducted on each of the inks. The spectrum for each individual ink shows the set of spectra which were collected at each time period together for comparison. Comparisons between inks show drying in all of the inks, with larger changes in the intensity between the first and last spectrum for some of the inks. This is most present in the WHSmith glitter inks.

3.2.2 Dry Ink

During the preliminary experimentation a spectrum was collected for each of the inks once they had dried. This was taken from the last spectrum that was collected during the drying study producing a library of spectra for all of the inks used during the project. This provides a spectrum for each of the pure inks which are being used without

the influences and peaks from the paper. An example of one of the dry ink spectra is represented in Figure 14.

Appendix C contains a collection of spectra showing the spectrum of each ink which had been allowed to dry. Comparisons between the different ink samples shows main differences in two separate areas of the spectra. The shapes and peaks in the set of peaks between 1150 cm^{-1} and 1800 cm^{-1} and the shape and ratio of the double peak around 2900 cm^{-1} .

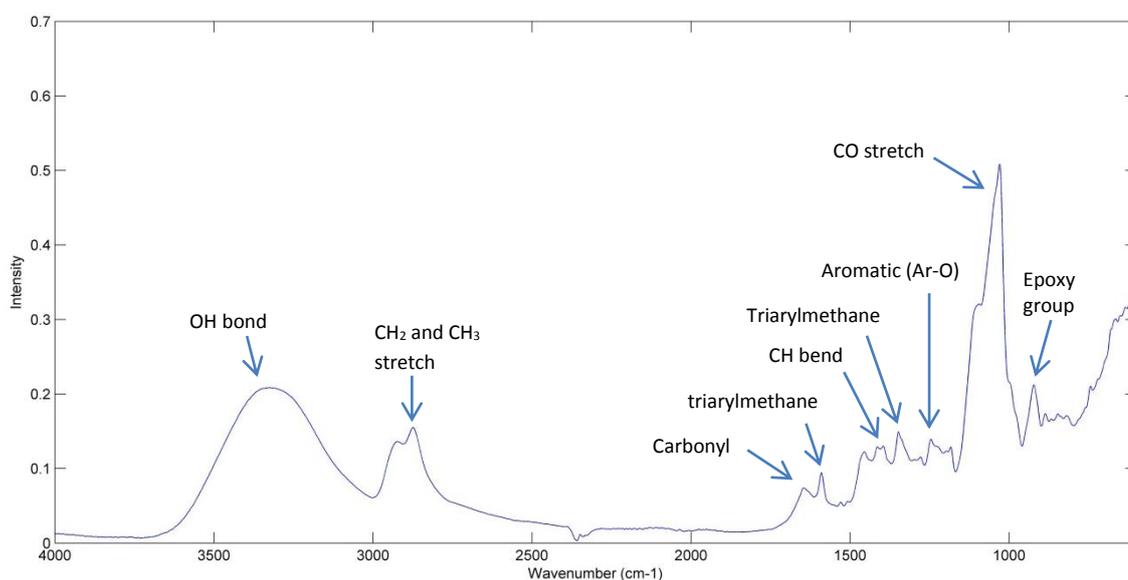


Figure 14. Spectrum of dry ink showing the major peaks of a dry papermate blue ink.

3.3 Ink Discrimination

Once the drying study had been completed a set of spectra were collected for each of the inks being used in the study. For each ink there was a set of spectra showing the stages of drying for the ink with a final spectrum showing the pure spectrum of the dried ink. There was also a range of spectra for the paper which is to be used for the study. Comparisons are to be made between the dried ink spectrum, average paper

spectrum and the spectrum of the ink when written onto paper. Appendix D contains a collection of spectra for each of the inks comparing the spectrum of the dry ink sample, the spectrum of the paper and the spectrum of the ink when it had been written onto a piece of paper. Figure 15 shows an example for one of these comparison spectra. There are similarities and differences that can be observed between all three of the spectra to determine where the peaks have come from.

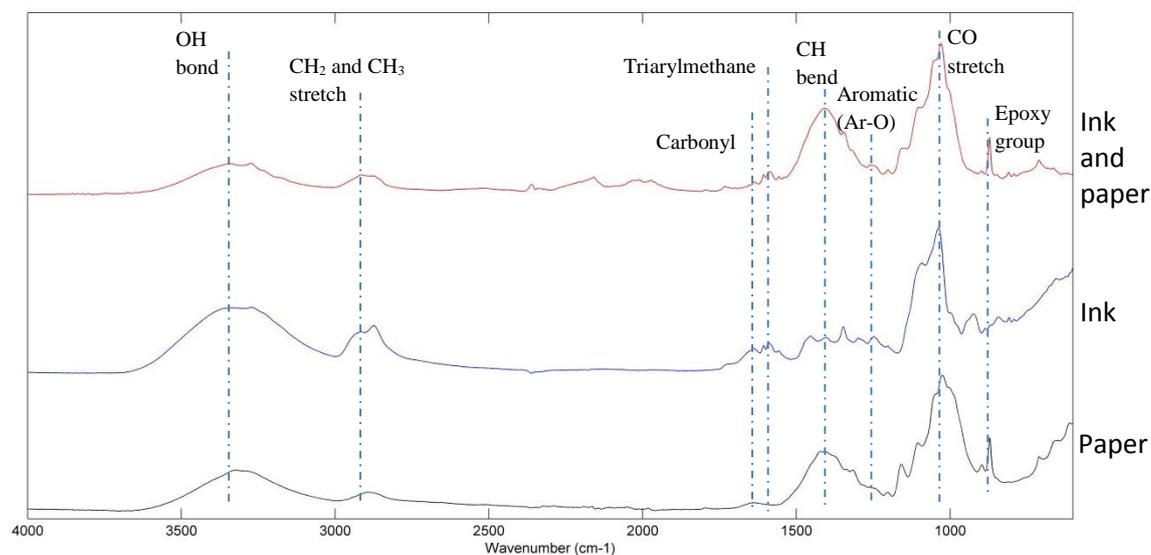


Figure 15. Spectrum comparing paper, dry ink and ink deposited onto paper.

For the example in Figure 15 the majority of the peaks in the red spectrum show elements which can be seen to originate from the paper spectra compared to the pure ink spectra. Looking at the peaks in the red spectra the peak at 872 cm^{-1} is sharp resembling the paper spectra. The peak at 1030 cm^{-1} shows elements of both the paper and dry ink spectra. All of the spectra have a large peak at 1030 cm^{-1} , but all have differences on the left hand side of the peak where shoulders of the peak which are present in both the paper and dry ink spectra can be seen on the spectra of the ink on paper. The peaks at 1408 cm^{-1} and 2890 cm^{-1} are both present in just the paper spectra and ink on paper spectra, whilst the small peak around 1590 cm^{-1} has a shape present in both the dry ink

and ink on paper spectra. This shows that analysis conducted on ink written on paper shows parts of the spectrum associated with just the paper and just the ink, so discrimination can be observed.

The spectral library has produced a collection of spectra containing an average spectrum for the sheets of paper used during the project. The drying study established that an 1 μl sample of gel pen ink took 10 minutes for the pure ink sample to fully dry and produced a full collection of a dry spectrum for each of the inks used.

Chapter 4

Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy for the Analysis of Environmental Factors on Inks

This chapter explains the results achieved throughout the main aging study of the project to determine if ATR-FTIR can be used to provide information on the effect of environmental factors on a gel pen ink sample. This chapter provides details describing the development of the spectra through the stages of data pre-processing to a stage where the spectral data is interpreted. Portions of this work were presented at the 2014 SciX conference in Reno, Nevada United States, September 2014 in a poster entitled “Using vibrational spectroscopy to analyse the composition and effect of environmental factors on gel pen ink”. (Appendix A contains the poster and the abstract accepted by the conference).

4.1 Pre-processing

The ink aging study is the major section of the project looking into demonstrating if infrared spectroscopy can be used to determine the age of an ink sample. To begin the data analysis, vector normalisation was conducted on the data. Vector normalisation is a process which converts the unit length of a vector to the value of 1. This occurs at the peak with the highest intensity, converting the intensity of the highest peak to be the same value in all of the spectra. Vector normalisation was carried out on the average spectra at each time period for a single pen and plotted on the same spectrum. The vector normalisation aligned each of the spectra based on the peak with the highest intensity at 1030 cm^{-1} . An example of one of these plots is shown in Figure 16.

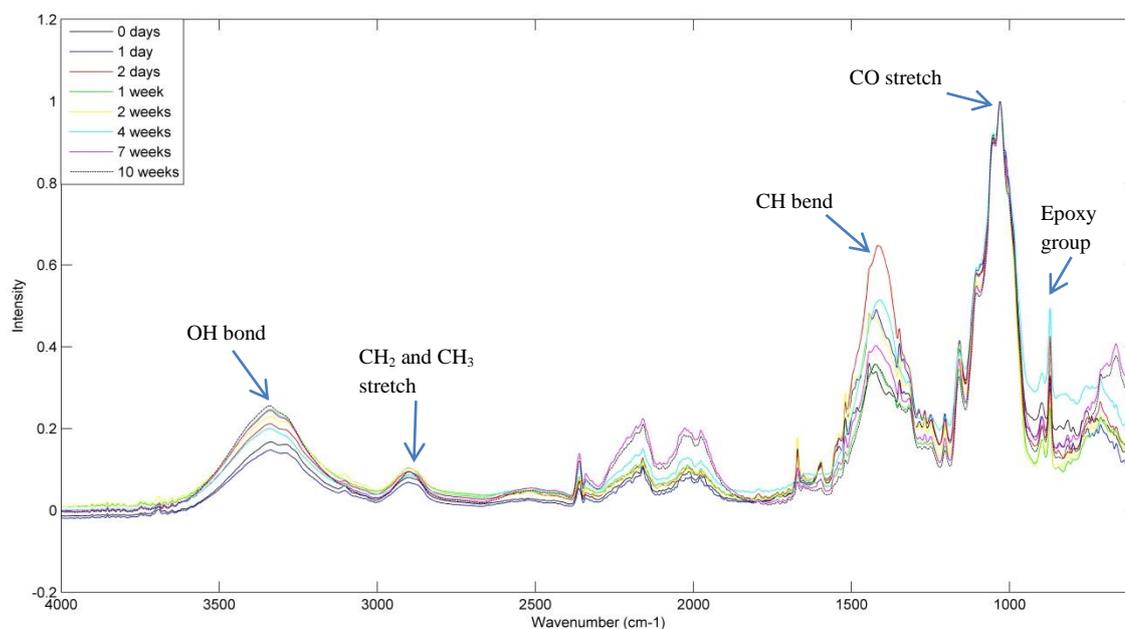


Figure 16. Ink aging spectra after vector normalisation.

For the analysis during the ink aging study, each time period of aging is represented by a specific colour of spectrum. From looking at the spectra in Figure 16 it can be seen that vector normalisation of the data results in the spectra having different baselines, making the analysis of the spectra difficult. This required further pre-processing to be conducted on the data prior to results for the aging study being determined. The pre-processing stages of the average spectra involved noise reduction, second derivatisation, vector normalisation and then variable ranking.

An example of a spectrum after the pre-processing had been conducted is shown in Figure 17. Variable ranking of all of the inks was conducted and the top 30 most discriminating peaks from each of the individual pens were compared with each other to find the peaks in the spectra that were the most commonly discriminating.

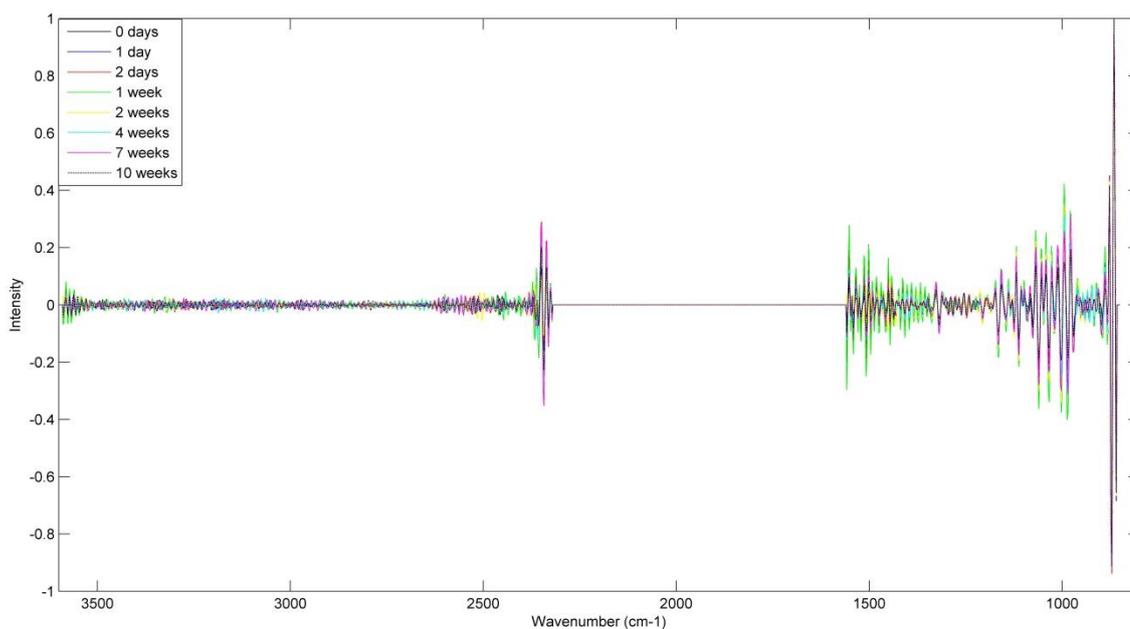


Figure 17. A spectrum after noise reduction, second derivatisation, vector normalisation and variable ranking have been conducted

4.2 Variable Ranking

Table 5 shows the peaks in the spectra which were found to be in the top 30 most discriminating peaks for the highest number of inks, and the number of inks in which these peaks were the most discriminatory. If a wavenumber is present in the top 30 variable ranking then this wavenumber is one of the most discriminating wavenumbers for the spectrum of that ink and the wavenumbers in the top 30 for the most inks are the wavenumbers showing the most consistent spectral variation. These peaks are the areas in the spectra in which the spectra over the 8 different time periods will be the most different from each other, and will therefore be the sections and peaks in the spectrum to observe any changes and alterations between the different ink spectra over the time periods. The two peaks which are the most discriminating are the peaks at 929.51 cm^{-1} and 1348 cm^{-1} , these wavenumbers are present in the top 30 variable ranking for 69% and 59% of the inks respectively. The peak at 929.51 cm^{-1} corresponds

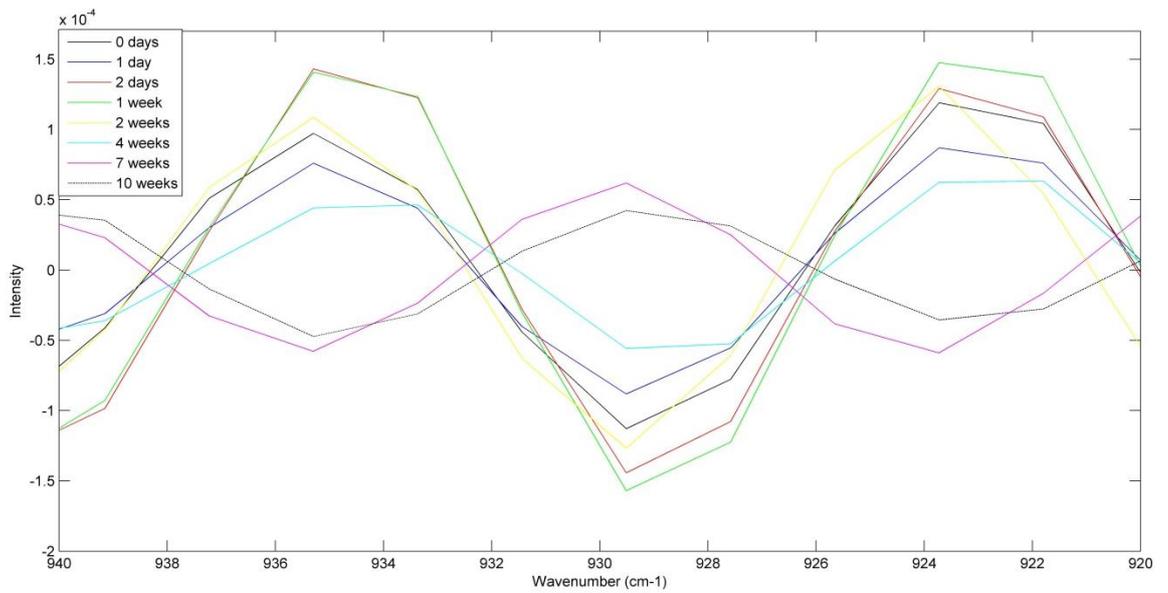
to the terminal epoxy functional group in the ink and the peak at 1348 cm^{-1} corresponds to the one of the triarylmethane functional groups in the ink. Both of these wavenumbers are linked to parts of the ink spectrum. Despite the paper spectrum also containing an epoxy group, this peak is present at a lower wavenumber (870 cm^{-1}).

Table 5. Most highly discriminating peaks in the inks

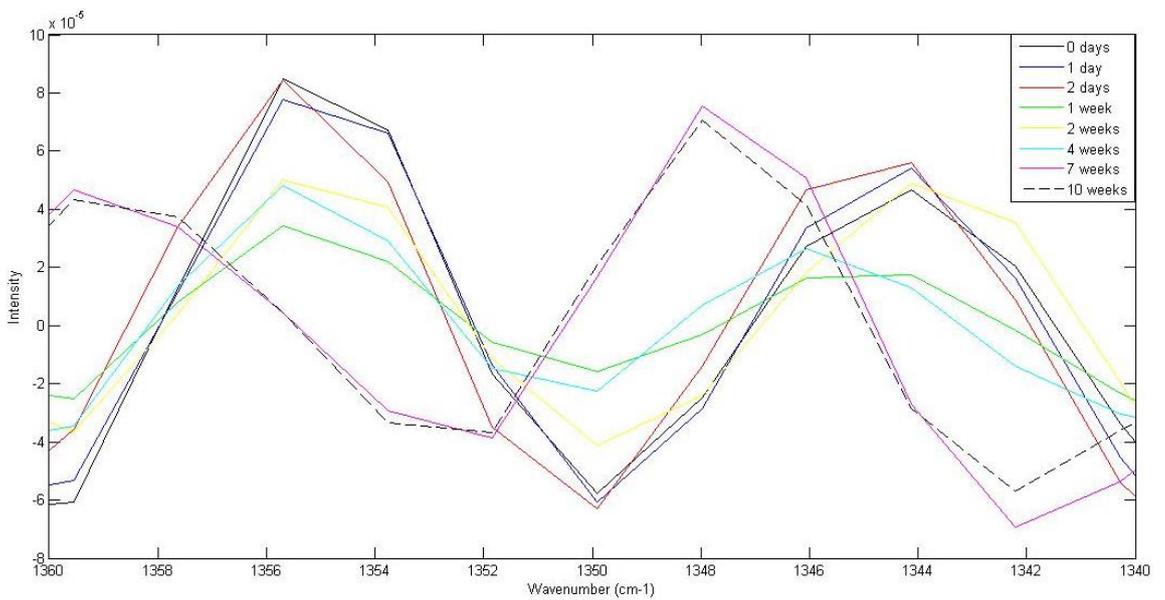
Wavenumber (cm^{-1})	Number of inks in top 30 variable ranking (out of 51)	Functional group
929.51	35	Terminal epoxy
1348	30	Triarylmethane
1344.1	30	Triarylmethane
923.73	28	Terminal epoxy
912.15	27	Terminal epoxy
1272.8	26	Aromatic (Ar-O)
1349.9	26	Triarylmethane
917.94	25	Terminal epoxy
1290.1	25	Aromatic (Ar-O)

Figure 18 contains the spectra of a Uni-ball Signo black ink sample over time at some of the most highly discriminating points of the spectrum. Figure 18a shows the spectrum over a wavenumber range of 922 cm^{-1} to 940 cm^{-1} . From the spectrum correlation between aging and the spectrum can be observed. Each of the second derivatised spectra from 0 days to 2 weeks all have a similar shape, with a high negative gradient becoming shallower just before the wavenumber of 929.51 cm^{-1} and then sharply peaking upwards. The spectrum at 4 weeks features a flattening of the spectrum before the wavenumber at 929.51 cm^{-1} . The spectra for 7 weeks and 10 weeks has a

different shape with the intensity of the spectrum increasing prior to the wavenumber at 929.51 cm^{-1} before decreasing after the peak, which is a contrast to the spectra from 0 days to 4 weeks. Figure 18b shows the spectrum over a wavenumber range of 1342 cm^{-1} to 1360 cm^{-1} . The spectra from 0 days to 2 days contain a sharp increase in intensity at the point of 1348 cm^{-1} . This is also the case for the spectrum at the 2 week time period. The two spectra for 1 week and 4 weeks have a shallower increase in the intensity compared to the time period of 0 days to 2 days. This correlation shows non-linearity between the spectra from 1 week to 4 weeks, with the spectrum at 2 week showing a large negative gradient. The spectra for 7 weeks and 10 weeks show a vast contrast with the spectra of lower time, with a decrease in the spectral intensity up until the peak at 1348 cm^{-1} , before the intensity increases.



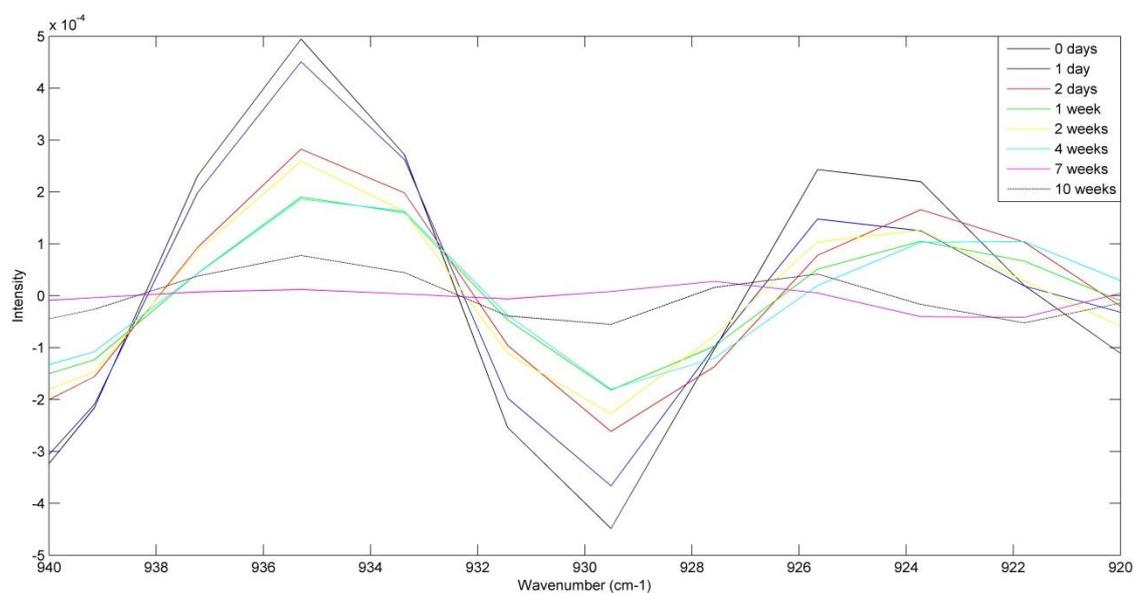
(a)



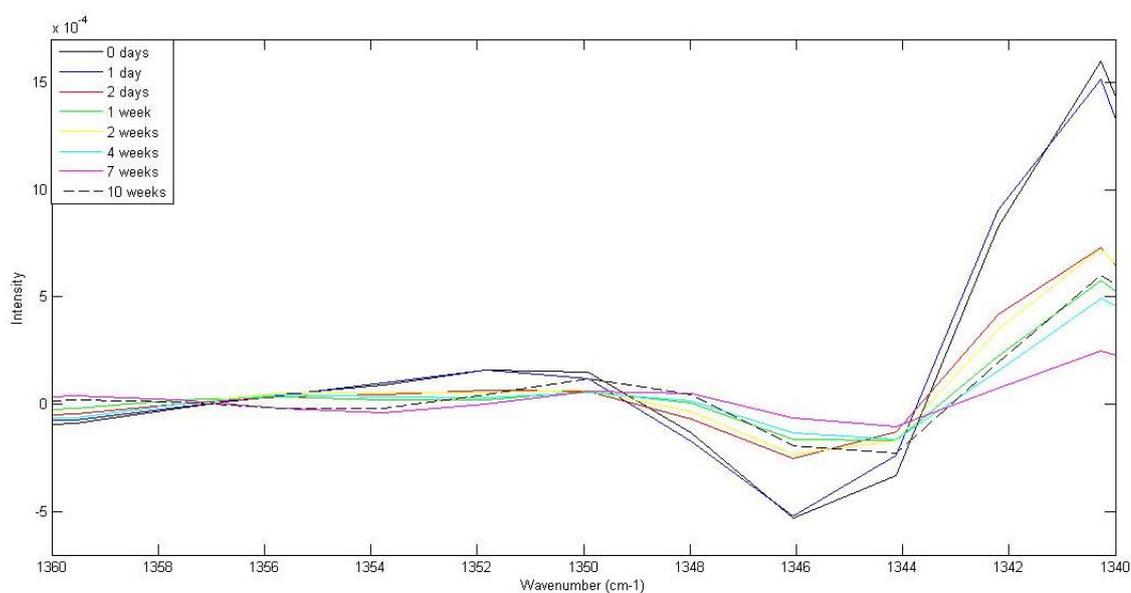
(b)

Figure 18. (a) Spectra of the Uni-ball Signo black ink aging over a wavenumber range of 922 cm^{-1} to 940 cm^{-1} . (b) Spectra of the Uni-ball Signo black ink aging over a wavenumber range of 1342 cm^{-1} to 1360 cm^{-1} .

Figure 19 contains the spectra of a Uni-ball Signo blue ink sample over time at some of the most highly discriminating points of the spectrum. Figure 19a shows the spectrum of the peak over a wavenumber range of 920 cm^{-1} to 940 cm^{-1} . The spectra for the time periods of 0 days and 1 day are a straight line of increasing intensity, with no alteration in the shape and direction of the spectra at the wavenumber of 929.51 cm^{-1} . The spectra for 2 days to 4 weeks contain a small kink in their spectrum at the point of 929.51 cm^{-1} , where the gradient of the spectrum becomes shallower. For the later spectra at 7 weeks and 10 weeks the spectrum is reasonably flat, with only small peaks and changes. Figure 19b contains the spectra over a wavenumber range of 1340 cm^{-1} to 1358 cm^{-1} . The spectra for each of the time periods are very similar to each other, with each spectrum showing a steady decrease in the intensity of the spectrum. The spectra for 0 days and 1 day have a larger gradient in comparison to the remainder of the spectra and have a noticeably larger intensity at the wavenumber of 1346.1 cm^{-1} . In the area of the spectra at 1346.1 cm^{-1} the spectra from 0 days to 2 days are increasing in intensity up until this point. For the spectra from 1 week this section of the spectra is generally flat.



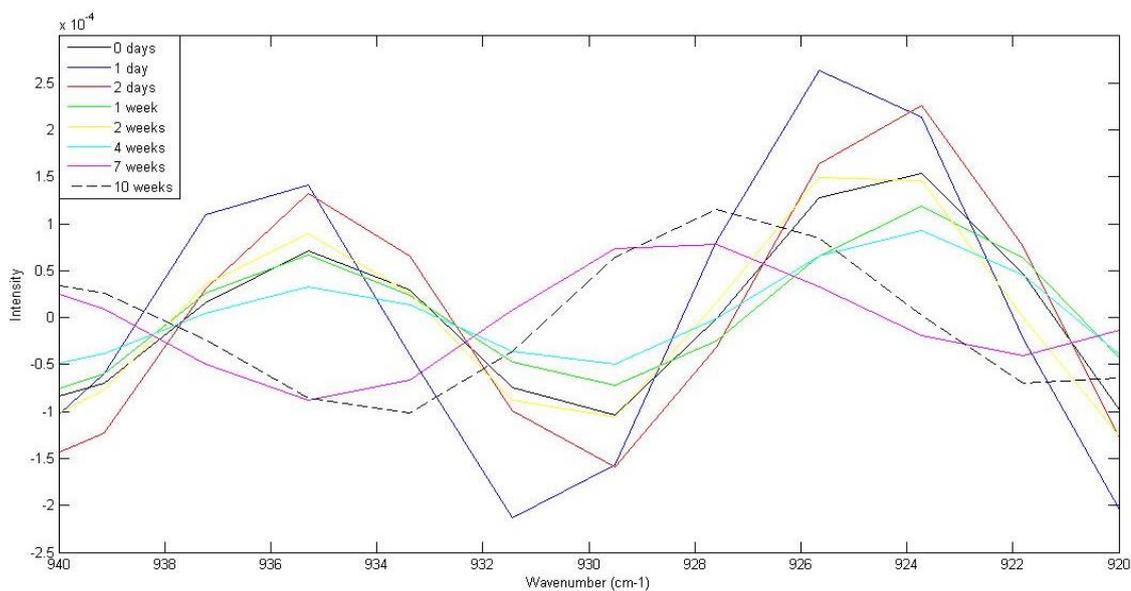
(a)



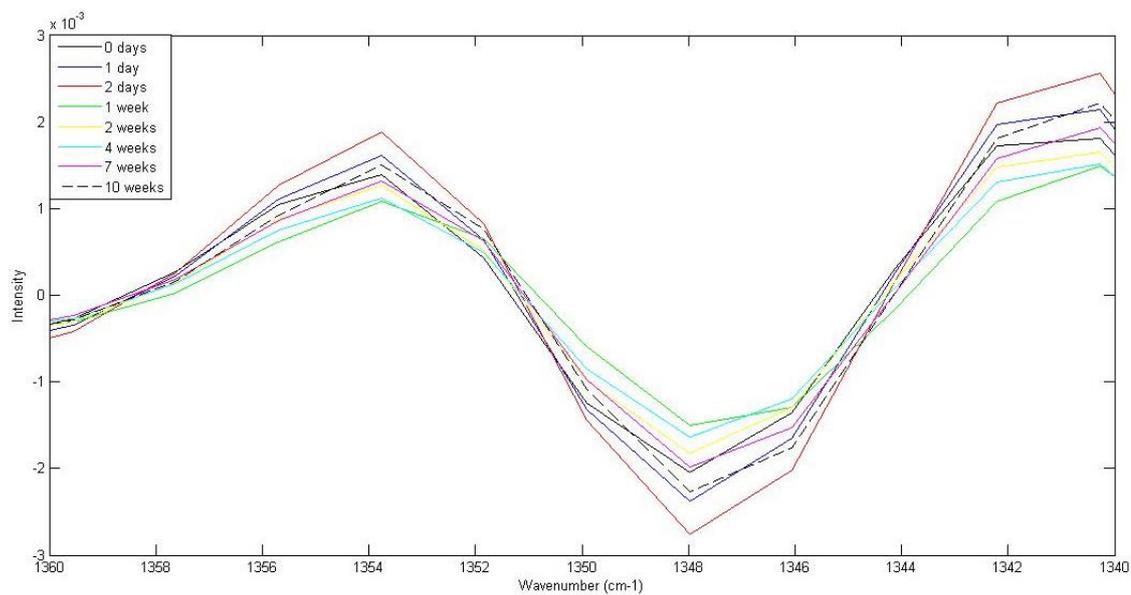
(b)

Figure 19. (a) Spectra of the Uni-ball Signo blue ink aging over a wavenumber range of 920 cm⁻¹ to 940 cm⁻¹. (b) Spectra of the Uni-ball Signo blue ink aging over a wavenumber range of 1340 cm⁻¹ to 1358 cm⁻¹.

Figure 20 contains the spectra of a Uni-ball Signo red ink sample over time at some of the most highly discriminating points of the spectrum. Figure 20a shows the spectrum over a wavenumber range of 922 cm^{-1} to 942 cm^{-1} . The spectra between 0 days and 4 weeks all follow the same generic shape, with a negative gradient prior to this wavenumber before changing to a positive gradient after this wavenumber has been reached. The only exception to this is the spectra after 1 day where the spectrum continues with a shallower negative gradient. The spectrum for the earlier time periods also has less of a kink in the spectrum at the point at 927.58 cm^{-1} . The spectra representing 7 weeks and 10 weeks show spectra contrasting to the earlier time periods as the peak of the spectra at these times is a positive peak compared to a trough for the earlier time periods. Figure 20b shows the spectrum over a wavenumber range of 1340 cm^{-1} to 1358 cm^{-1} . In these spectra there is no clear observable difference between all of the spectra to show evidence of aging for the ink.



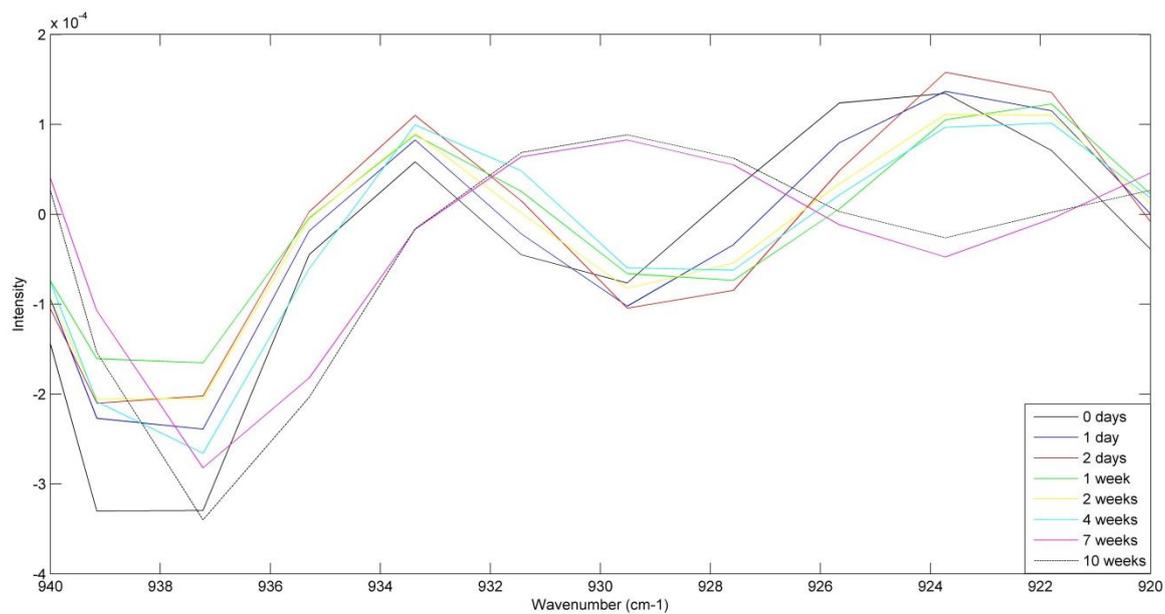
(a)



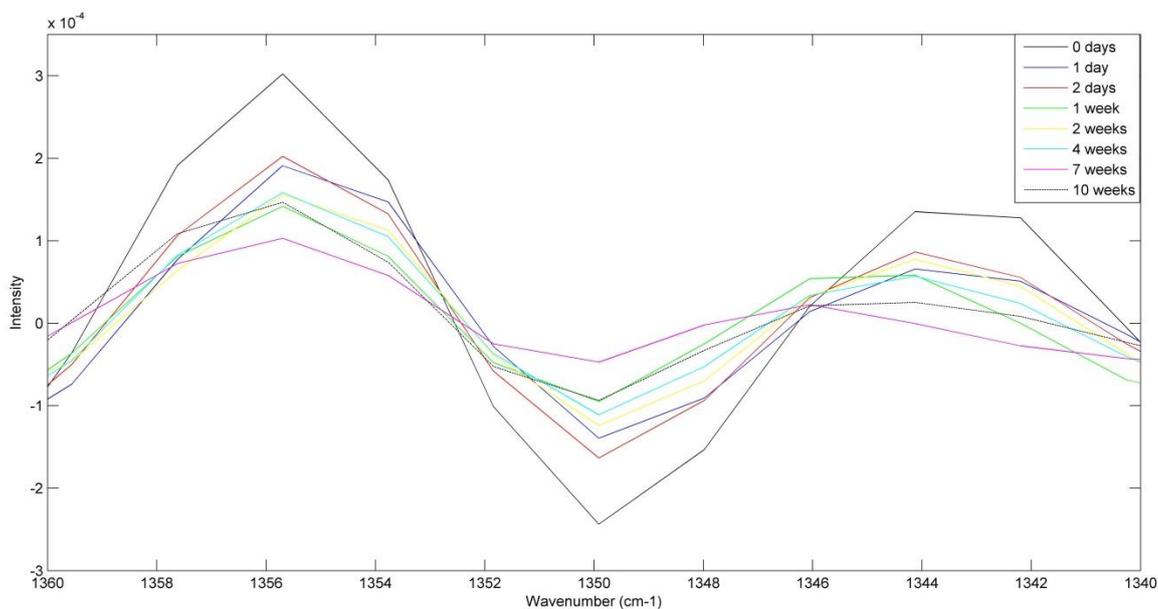
(b)

Figure 20. (a) Spectra of the Uni-ball Signo red ink aging over a wavenumber range of 922 cm^{-1} to 942 cm^{-1} . (b) Spectra of the Uni-ball Signo red ink aging over a wavenumber range of 1340 cm^{-1} to 1358 cm^{-1} .

Figure 21 contains the spectra of a Uni-ball Signo green ink sample over time at some of the most highly discriminating points of the spectrum. Figure 21a shows the spectrum over a wavenumber range of 922 cm^{-1} to 938 cm^{-1} . For the spectra between 0 and 2 days the gradient of the spectra before the point at 929.51 cm^{-1} becomes shallower as the time increases, and increases after the point at 929.51 cm^{-1} . At the later time periods, after 7 weeks, the spectra has greatly changed shape, with the gradient of the spectra now increasing up to the point at 929.51 cm^{-1} , before decreasing in gradient after this wavenumber. Figure 21b shows the spectrum over a wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} . For the peaks at day 0 and day 1 the spectrum is flat before the point. The gradient of the spectrum at the wavenumber of 1348 cm^{-1} increases as the time develops from 2 days until 4 weeks. After the age of the ink reaches 7 weeks the gradient of the spectrum decreases and flattens out. After this point the spectrum decreases sharply at times with newer inks, but these gradient decreases, before becoming flat and then increasing in gradient. The intensity of the point is also generally higher in older pens.



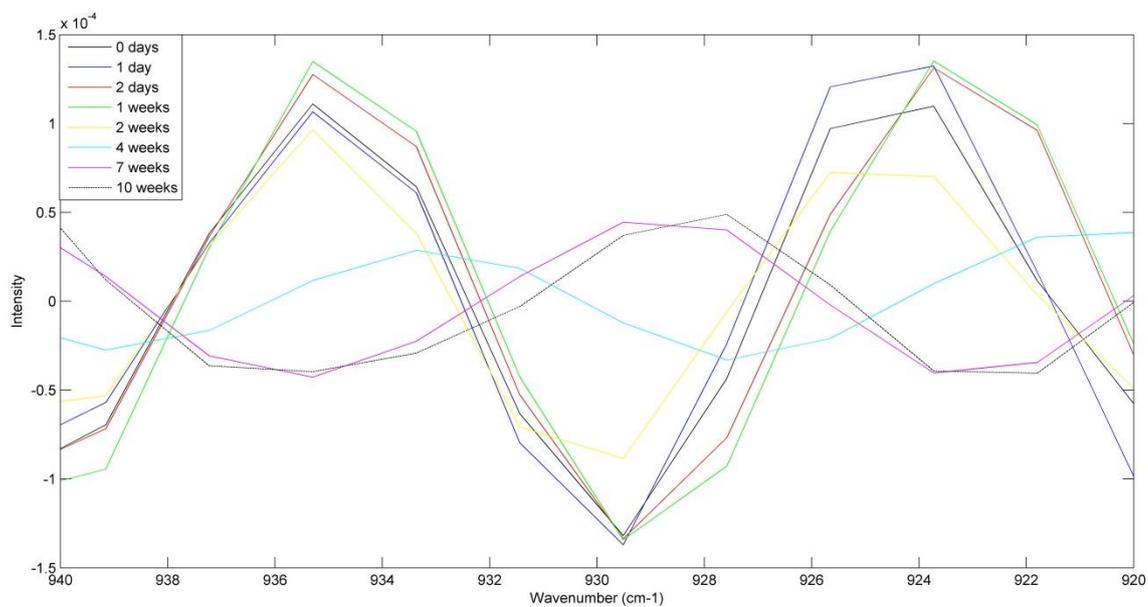
(a)



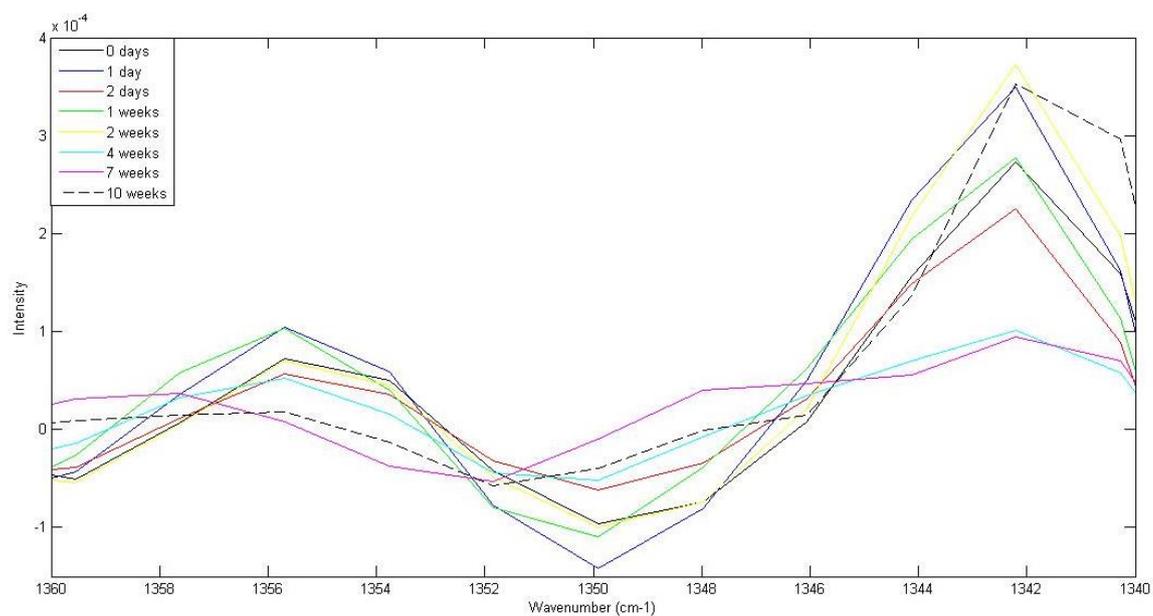
(b)

Figure 21. (a) Spectrum of the Uni-ball Signo green ink aging over the wavenumber range of 922cm^{-1} to 938 cm^{-1} . (b) Spectrum of the Uni-ball Signo green ink aging over the wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} .

Figure 22 contains the spectra of a Uni-ball Signo light blue ink sample over time at some of the most highly discriminating points of the spectrum. Figure 22a show the spectra over the wavenumber range 920 cm^{-1} to 940 cm^{-1} . It can be observed that the spectra from 0 days to 1 week all converge at very similar intensities to one another. In these spectra the gradient of the spectra at 0 days and 1 day is greater than the spectra at 2 days and 1 week. The spectrum for 2 weeks also has the same shape, but the intensity of the peak is less than that of the peaks before this time. The 4 weeks spectrum has a smoother shape, with a less sharp peak and a lower intensity. The spectra for the 7 weeks and 10 weeks is a contrast to the peaks for 4 weeks and less as the peaks have a positive gradient up to the wavenumber at 929.51 cm^{-1} . Figure 22b shows the spectra over the wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} . From this spectrum there is no observable evidence showing that the age of a gel pen ink can be determined from this spectrum.



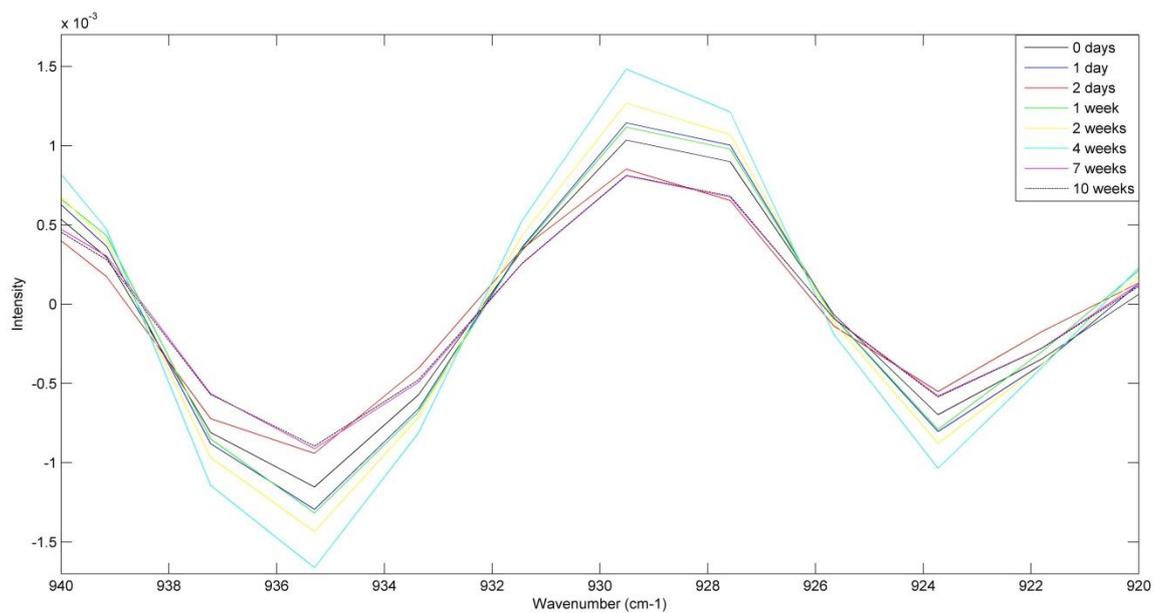
(a)



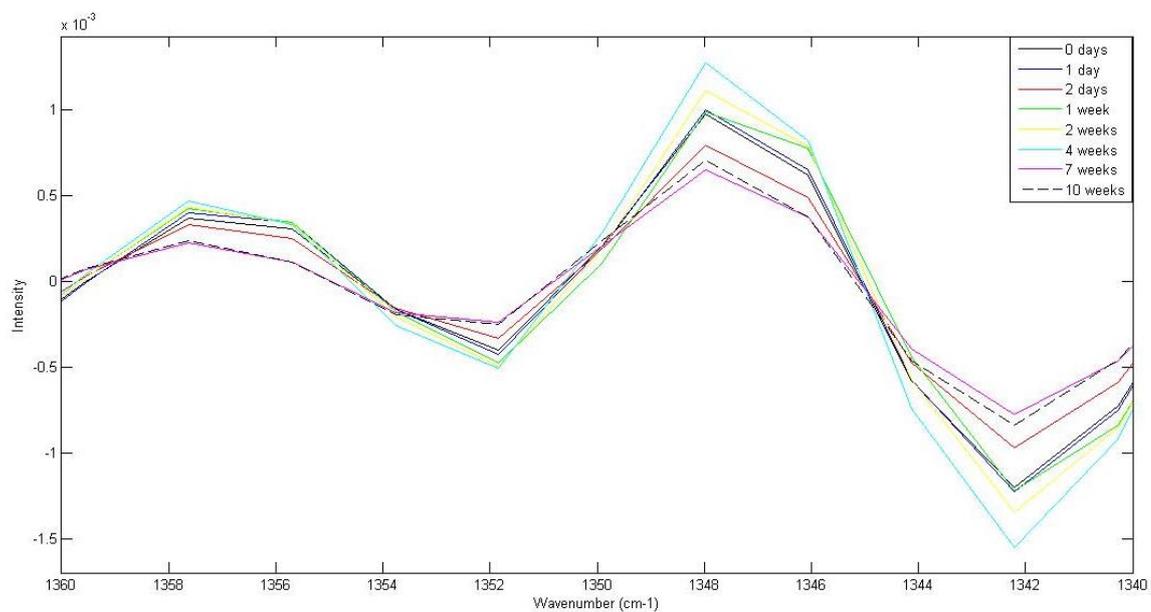
(b)

Figure 22. (a) Spectra of the Uni-ball Signo light blue ink aging over the wavenumber range of 920 cm^{-1} to 940 cm^{-1} . (b) Spectra of the Uni-ball Signo light blue ink aging over a wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} .

Figure 23 contains the spectra of a Uni-ball Signo purple ink sample over time at some of the most highly discriminating points of the spectrum. From analysing both spectra over the wavenumber ranges between 922 cm^{-1} to 940 cm^{-1} and 1340 cm^{-1} to 1360 cm^{-1} there is no detectable evidence to suggest that the age of a Uni-ball Signo gel pen ink can be determined. This is due to the spectra at all of the different time periods having the same shape to the spectra and the peaks at these wavenumbers. There is also no direct correlation.



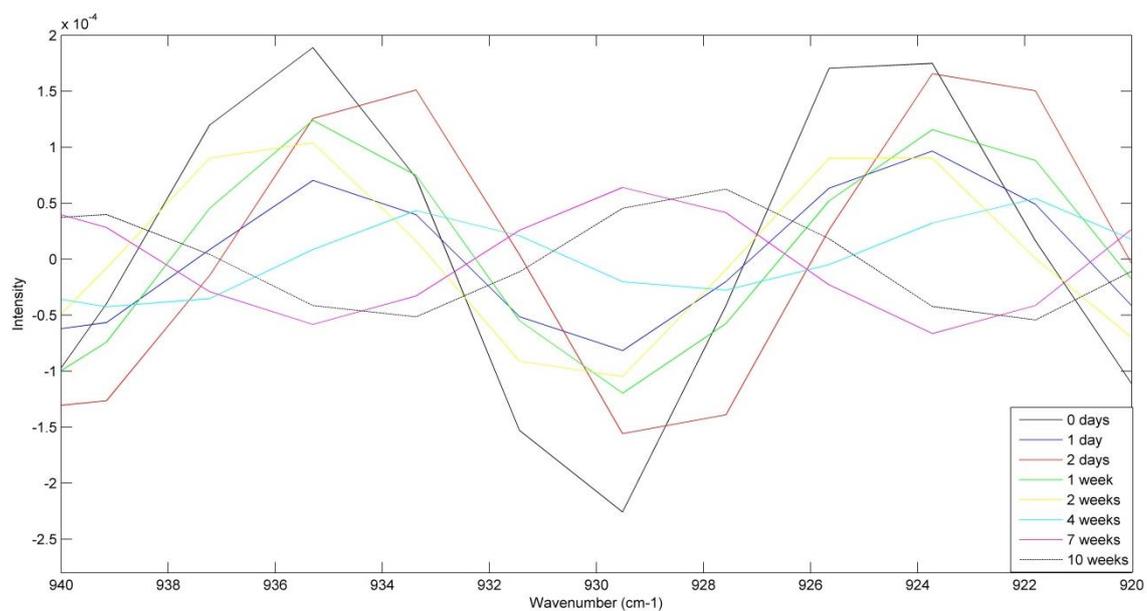
(a)



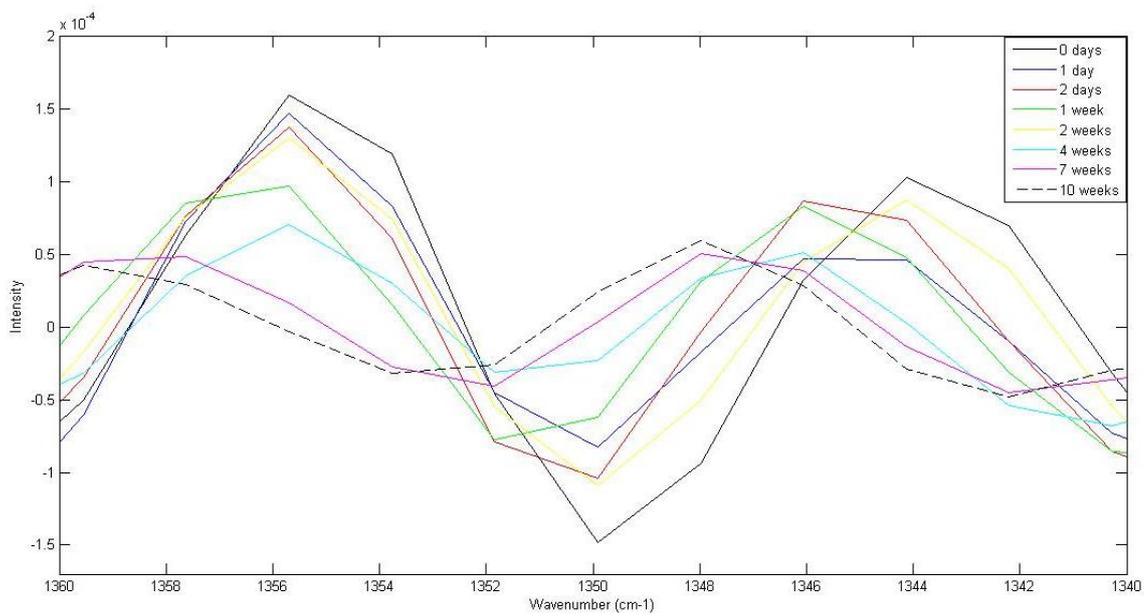
(b)

Figure 23. (a) Spectra of the Uni-ball Signo purple ink aging over the wavenumber range of 922 cm^{-1} to 940 cm^{-1} . (b) Spectra of the Uni-ball Signo purple ink aging over the wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} .

Figure 24 contains the spectra of a Uni-ball Signo pink ink sample over time at some of the most highly discriminating points of the spectrum. Figure 24a shows the spectra over a wavenumber range of 922 cm^{-1} and 940 cm^{-1} . The shapes of the spectra between 0 days to 4 weeks vary largely and due to this it is not possible to use the spectral shape as an indicator for the age of an ink sample. The spectra for the time periods of 7 weeks and 10 weeks contains shapes which are contrasting to the shape of the other spectra, as the spectra have a negative intensity peak, which is different to the positive intensity peak which is seen in the spectra with a time period of 4 weeks and less. Figure 24b shows the spectra over a wavenumber range of 1340 cm^{-1} and 1360 cm^{-1} . In a similar way to the spectra between 922 cm^{-1} and 940 cm^{-1} there is an observable correlation between the ink spectra and the time period, with one spectrum not fitting this trend. There is a linear correlation at the wavenumber of 1348 cm^{-1} with the exception of the spectrum at 2 weeks, which has a higher intensity compared to the spectra at 1 day, 2 days and 1 week. With the exception of this peak all of the other time periods show a linear correlation with the higher intensity of the spectrum at the wavenumber 1348 cm^{-1} corresponding to a spectrum for an ink which has aged for less time.



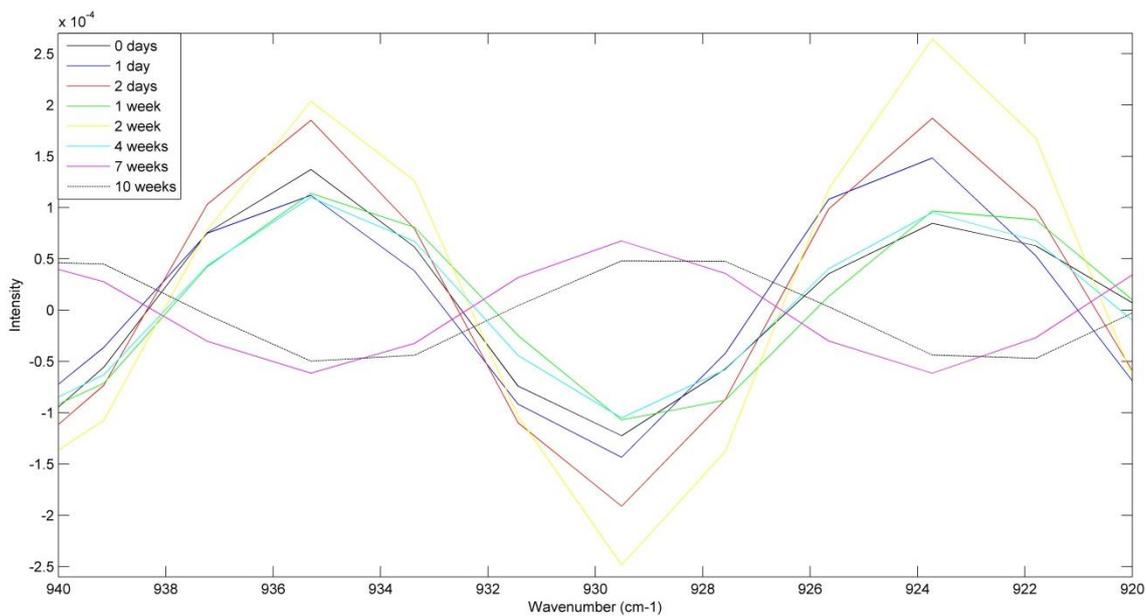
(a)



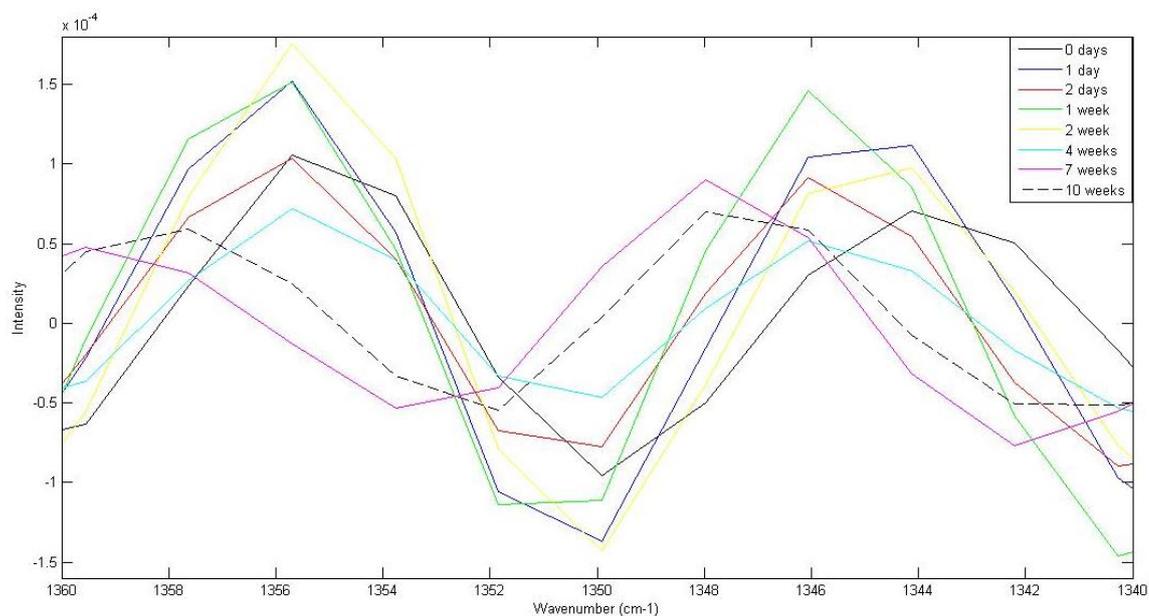
(b)

Figure 24. (a) Spectra of the Uni-ball Signo pink ink aging over the wavenumber range of 922 cm^{-1} to 940 cm^{-1} . (b) Spectra of the Uni-ball Signo pink ink aging over the wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} .

Figure 25 contains the spectra of a Uni-ball Signo orange ink sample over time at some of the most highly discriminating points of the spectrum. Figure 25a show the spectrum over the wavenumber range of 922 cm^{-1} to 942 cm^{-1} . From the spectrum no correlation can be observed between the intensity of the spectrum and the age of the ink sample. Each of the ink spectra between 0 days and 4 weeks show a positive intensity however the spectra which have the highest intensity are the spectra at 2 weeks and 2 days. The order of the intensity of the peaks at 929.51 cm^{-1} does not show a linear correlation. Figure 25b show the spectrum over the wavenumber range of 1340 cm^{-1} and 1360 cm^{-1} . From analysing the spectrum there is no evidence suggesting the aging of Uni-ball Signo orange gel pen ink at this wavenumber range. The order in which the intensity of the individual spectrum can be seen does not correspond to the order or the age of the ink samples.



(a)



(b)

Figure 25. (a) Spectra of the Uni-ball Signo orange ink aging over the wavenumber range 922 cm^{-1} to 942 cm^{-1} . (b) Spectra of the Uni-ball Signo orange ink aging over the wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} .

From looking at the spectra in Figures 18-25, containing each of the different coloured inks for a single manufacture, it can be observed that a correlation is detectable between the spectra and the age of the ink. This correlation is not a linear, and is not present in the entire collection of ink samples, however a generic trend can be observed between the spectra of gel pen inks which have only aged for a shorter length of time and the ink which have aged for a longer time length. In the majority of the ink samples a large alteration is detectable between the spectra of the group of time period of 4 weeks and shorter and the group of time period 7 weeks and longer. This leads to suggest that between the time periods of 4 weeks and 7 weeks is when the most alterations in gel pen inks occur. For some of the inks there was also an observable difference between the time periods of 2 days and 1 week which is another time period where major aging of the ink occurs. The change in when the alterations occur is likely to be as a result of the degradation of the dyes in the ink, as demonstrated by Andrasko. This shows the degradation of the dye does not occur over a linear time frame as the aging occurs at a faster rate between certain time periods.

Each of the inks compared during the aging study were analysed at the wavenumber ranges surrounding the wavenumbers at 929.51 cm^{-1} and 1348 cm^{-1} due to these wavenumbers being the areas of the spectra which were in the top 30 variable ranking for the highest number of inks. These wavenumbers were not present as a highly discriminative wavenumber in some of the ink sample. For this reason, not all of the ink samples will show aging at these specific points which have been demonstrated for some of the Uni-ball Signo inks, for example the purple ink. However these wavenumbers were chosen as a section to compare between all inks instead of comparison between the most discriminative wavenumbers for each individual ink,

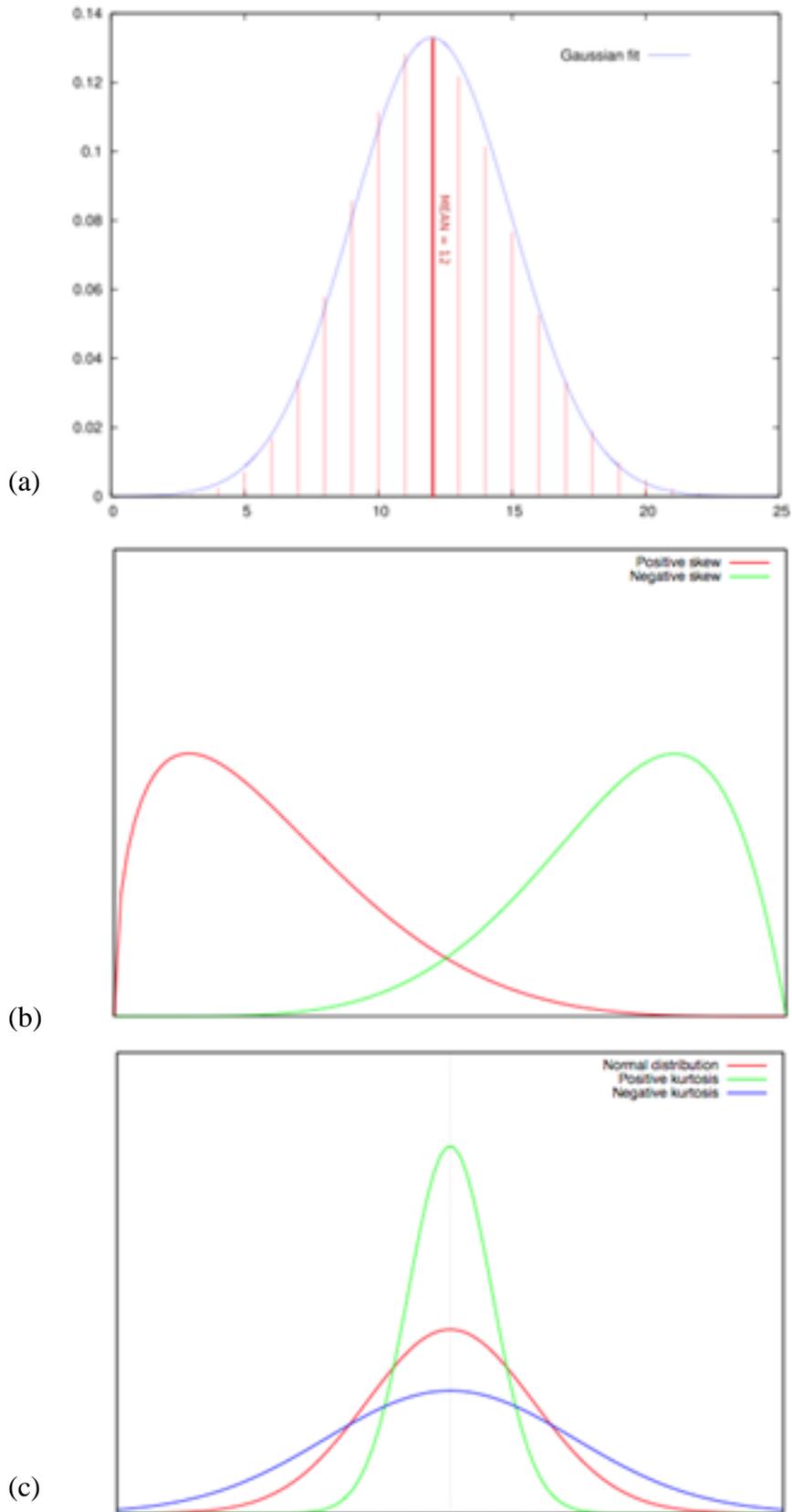
which would result in different areas of each spectrum being used for the analytical process.

The following aging trends which have been explained are specific to Uni-ball Signo inks. Whilst some of these trends are consistent between all 51 inks which were analysed, there are some trends which can only be seen in a small sample of the inks. For some of the ink samples a completely linear relation between the time periods can be seen, whereas for other spectra it is difficult to see a full correlation between all of the time periods. Appendix E contains a library of spectra for the other ink manufactures which were analysed at wavenumber ranges around the wavenumbers of 929.5 cm^{-1} and 1348 cm^{-1} to allow looking at trends which may or may not be observable between the ink samples.

4.3 Feature extraction

There are four types of spectral moment which are examined by feature extraction and group scatter plot for the ink aging study. These are peak centroid, peak skew, peak kurtosis and root mean squared (RMS) energy. The peak centroid is the central part of the peak. The peak skew is where a peak is slanted toward either side. If the peak is skewed so the top of the peak is towards the lower frequency, this is known as a positive skew, whereas if the top of the peak is towards the higher frequency, this is known as negative skew. Peak kurtosis is the steepness of the peak. If a peak is steeper than the peak will have positive kurtosis, whereas if the peak is at a lower intensity and is shallower, then the peak has a negative kurtosis. The RMS energy of a peak is a statistical measure for the magnitude of the energy of the peaks. This is calculated by

the square root of the average of the square of the energy for each peak. Figure 26 shows images representing each of these types of spectral moment.



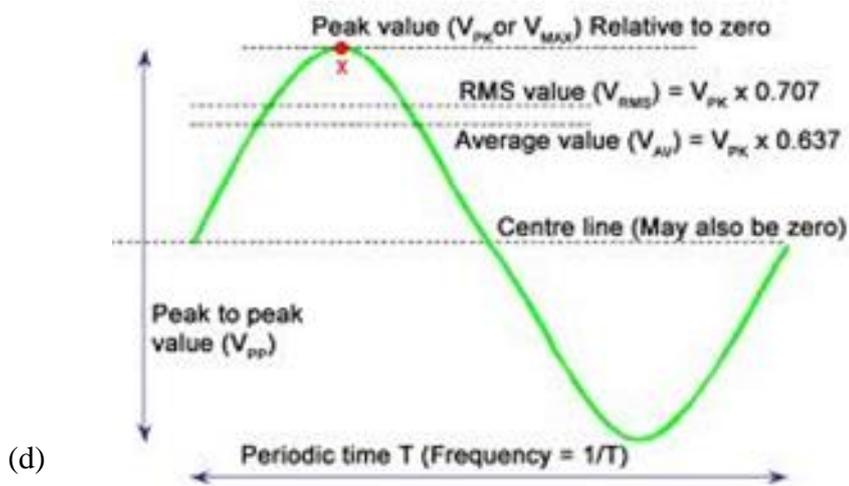


Figure 26. (a) Spectrum showing a peak centroid. (b) Spectrum showing a peak skew. (c) Spectrum showing a peak kurtosis. (d) Spectrum showing Root Mean Squared energy. Adapted from [78].

Table 6 shows the features of the second derivatised spectrum for each of the inks analysed with the highest discrimination. The table also shows the type and wavenumber of each feature on the X-axis and Y-axis of the group scatter plot for each of the ink sample.

Table 6. Wavenumber of the peaks compared using group scatter plots

Ink	X-axis wavenumber (cm⁻¹)	Y-axis wavenumber (cm⁻¹)
Club black	Skew 1323-1342	Skew 1296-1325 v skew 1047-1070
Club blue	Skew 945-951 v skew 1338- 1344	RMSN 939-945
Club red	Skew 1325-1333 v skew 1290- 1296	Skew 1290-1296
Club green	Centroid 999-1009 v centroid 1009-1018	RMSN 999-1009 v RMSN 1009-1018
Papermate black	Centroid 999-1006 v centroid 1325-1332	Centroid 1325-1332
Papermate blue	RMSN 1439-1444 v RMSN 1352-1363	RMSN 1446-1456 v RMSN 1352- 1363
Papermate red	Skew 924-937	Skew 1446-1458 v skew 924-937
Papermate green	Skew 1444-1458	RMSN 1282-1290 v RMSN 1352- 1360
Uni-ball black	Skew 920-928 v skew 1277- 1284	RMSN 1236-1248 v RMSN 920-928
Uni-ball blue	RMSN 945-951	RMSN 939-945 v RMSN 1136-1146
Uni-ball red	RMSN 1381-1387 v RMSN 1431-1437	RMSN 1227-1236 v RMSN 920-931

Uni-ball green	Centroid 1267-1275	RMSN 1340-1350
Uni-ball light blue	Centroid 1267-1273 v centroid 1000-1007	RMSN 922-928 v RMSN 1000-1007
Uni-ball violet	Kurtosis 937-947	Skew 937-947 v skew 1282-1292
Uni-ball orange	RMSN 1252-1259 v RMSN 931-937	RMSN 1252-1259 v RMSN 922-928
Uni-ball pink	Skew 1272-1279	Skew 1271-1279 v skew 920-931
Wilko green	RMSN 903-910 v RMSN 920- 931	RMSN 920-931
Wilko orange	Skew 906-914	RMSN 1072-1082 v RMSN 920-928
Wilko pink	RMSN 1267-1275 v RMSN 928-935	RMSN 1267-1275 v RMSN 906-916
Wilko purple	Skew 943-951 v skew 912-920	Skew 933-939 v skew 912-920
Wilko yellow	RMSN 1252-1259 v RMSN 922-928	Skew 1022-1028 v skew 1352-1360
WHSmith black	RMSN 899-908 v RMSN 908- 918	Skew 899-908
WHSmith blue	Skew 1340-1354	Skew 1352-1363 v skew 933-947

WHSmith light blue	RMSN 1348-1356	RMSN 885-895 v RMSN 1338-1348
WHSmith green	RMSN 1340-1352	Kurtosis 1340-1352 v kurtosis 1225-1230
WHSmith lime	RMSN 1228-1236 v RMSN 931-939	Kurtosis 1346-1356 v kurtosis 991-1002
WHSmith orange	RMSN 883-897	RMSN 937-947 v RMSN 1360-1367
WHSmith peach	RMSN 1348-1354 v RMSN 1227-1236	RMSN 1389-1398 v RMSN 1227-1236
WHSmith purple	RMSN 1225-1234 v RMSN 1377-1387	RMSN 1225-1234 v RMSN 1340-1352
WHSmith violet	Kurtosis 274-278 v kurtosis 294-298	Kurtosis 274-278 v kurtosis 41-46
WHSmith pink	Centroid 1180-1186 v centroid 1271-1279	Centroid 1271-1279
WHSmith yellow	RMSN 1315-1323 v RMSN 1333-1342	RMSN 1315-1323 v RMSN 1342-1348
WHSmith gold	RMSN 1344-1352	Skew 1344-1352 v skew 885-891
WHSmith silver	RMSN 1340-1348 v RMSN 1427-1435	RMSN 1340-1348
WHSmith brown	Centroid 1367-1375 v centroid 1298-1306	Centroid 1298-1306

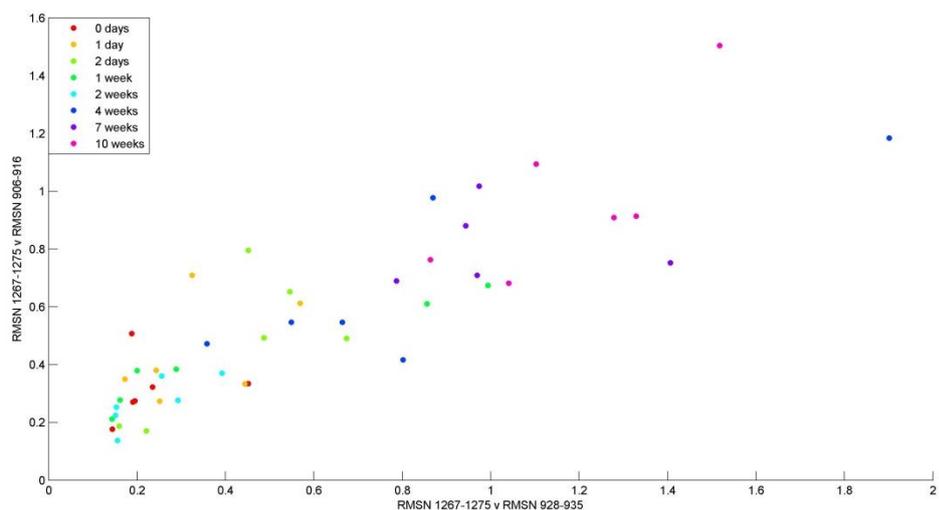
WHSmith mauve	RMSN 1265-1271 v RMSN 1348-1354	Skew 1271-1279 v skew 1444-1448
WHSmith glitter black	Skew 219-223 v skew 956-965	Skew 1277-1279
WHSmith glitter blue	RMSN 1350-1354 v RMSN 1342-1348	Kurtosis 1342-1348 v kurtosis 1255- 1259
WHSmith glitter red	RMSN 1336-1342	RMSN 1344-1350
WHSmith glitter green	RMSN 1439-1446 v RMSN 1452-1460	Centroid 1446-1452
WHSmith glitter light blue	RMSN 1340-1346 v RMSN 1265-1275	Skew 1016-1024
WHSmith glitter orange	Skew 910-916 v skew 1286- 1292	RMSN 903-910 v RMSN 910-916
WHSmith glitter pink	RMSN 1340-1346 v RMSN 920-924	Skew 1082-1088 v skew 920-924
WHSmith glitter purple	RMSN 1340-1350 v RMSN 1373-1381	RMSN 914-922 v RMSN 900-910
WHSmith glitter gold	RMSN 1365-1373 v RMSN 941-949	RMSN 903-912 v RMSN 941-949
WHSmith glitter silver	RMSN 1340-1348	RMSN 1348-1354

From Table 6 above it can be seen that the majority of the features in the scatter plots are present in the following ranges: 912-950 cm^{-1} , 1230-1290 cm^{-1} and 1340-1360 cm^{-1} . The wavenumber range between 912-950 cm^{-1} corresponds to the range around the terminal epoxy peak at 929.5 cm^{-1} . The wavenumber range between 1230-1290 cm^{-1} corresponds to the range around the aromatic (Ar-O) peak at 1248 cm^{-1} . The wavenumber range between 1340-1360 cm^{-1} corresponds to the triarylmethane peak at 1348 cm^{-1} .

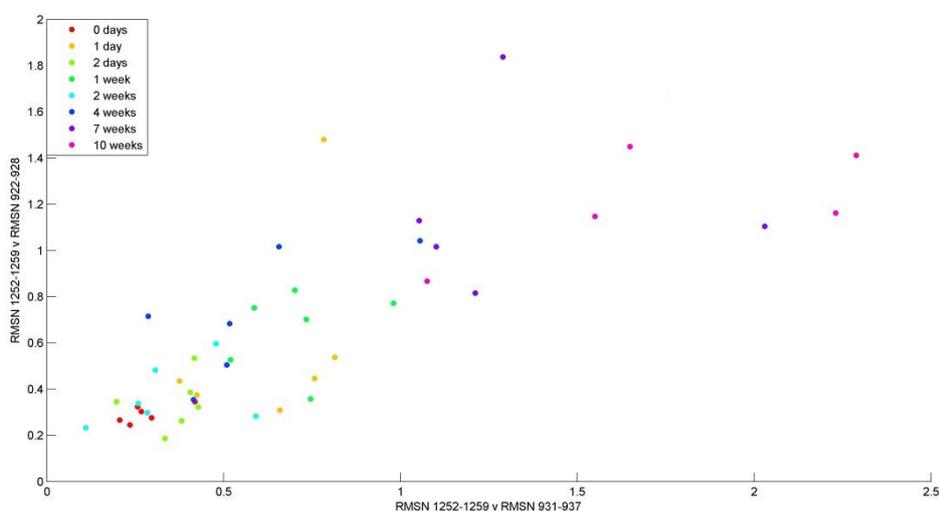
4.4 Group scatter plots

Group scatter plots of the data were produced to further enhance the analysis stage for the aging of the inks. Group scatter plots for each ink are used to compare the differences between the two peaks which were the most discriminating after feature extraction was completed. The position of the point on the spectrum is linked to the relationship between two peaks and how much they differ. A correlation between two sets of peaks will show a linear progression across the diagonal of the group scatter plot. A correlation between the groups of spectral points showing the earliest time points situated in one corner of the plot and the latest time points situated in the opposite corner of the plot shows evidence for aging of the gel pen inks. In these spectra each time period of the study is represented by a different colour.

An example of a group scatter plots for two different inks can be seen in Figure 27. Both of these plots contain the ratio between the RMS of two peaks on the X-axis and Y-axis.



(a)



(b)

Figure 27. (a) Group scatter plot for blue Wilko ink. (b) Group scatter plot for pink Uni-ball Signo ink.

Figure 27 shows strong evidence to suggest the aging of gel pen inks can be observed by the use of ATR-FTIR spectroscopy. The red and yellow points on the spectra correspond to the earliest time periods of 0 day and 1 day. All of the red points and the majority of the yellow points are all situated towards the lower left corner of the spectra, where the score space of the spectrum is at its lowest. The purple and pink points on the spectra corresponding to the latest time periods of 7 weeks and 10 weeks, which in contrast to the red and yellow points are situated towards to upper right corner

of the spectrum where the score spaces of the spectral axes are at their greatest. The other points representing time periods between 2 days and 4 weeks are situated in the area in the middle of the spectra between the points representing the earliest and latest time periods. There is some overlap between these points and the lowest points with some of the green, cyan and blue points in the area which contains the red and yellow points. On the other hand none of these points overlap with the purple and pink points. Overall there is evidence suggesting that the aging of gel pen inks can be detected and linked to a range of time periods, however it is not possible to say exactly how much time has passed since an ink sample had been written. There is not a direct linear correlation that can be observed between the different periods of time, however it is clear to see that there is an observable difference between the time periods before and after 7 weeks.

Appendix F contains a collection of the spectra which were produced from the group scatter plots showing the aging of the inks. Comparisons between the inks show a general trend with inks at an early time periods being situated in one of the corners of the spectrum, moving on a diagonal towards the other corner of the spectrum. The earliest points of the spectra don't always start from the same corner of the spectra but does generally go towards the opposite diagonal. In certain spectra this trend is not so clear and the spectral points move more in a horizontal or vertical direction, for example in figure 21, as well as some figures where no clear correlation is detectable, for example in figure 30.

The aging study has demonstrated that ATR-FTIR can be used as a technique for the aging of gel pen inks. The correlation between the ages of the inks is not linear,

however a strong difference is observable between the inks before 4 weeks and after 7 weeks.

Chapter 5

Conclusions

Throughout the experimentation of the project it has been proven that ATR-FTIR can be used to determine the age of a gel pen ink over a range of time. Overall, analysis on data obtained from the ATR-FTIR has shown aging can be demonstrated by looking at two important peaks of the spectrum. These peaks correspond to the terminal epoxy at 929.51 cm^{-1} and triarylmethane at 1348 cm^{-1} .

Results which have been obtained have proven that all of the sheets of paper in a ream are the same as each other. After analysis was conducted on 300 paper spectra it was observed that there were no major differences that could be observed. Analysis of the mean and standard deviation of the samples provided results with all of the spectra containing the same peaks and a maximum standard derivation of 0.036.

Results have shown that a $1\text{ }\mu\text{l}$ pure sample of a gel pen ink takes 10 minutes to dry. This can be seen from a spectrum of the ink in which alterations in the intensity of the spectrum occurs until after 10 minutes. These alterations are either increases or decreases depending on the wavenumber of the peak which is being observed.

After data processing consisting of noise reduction, second derivatisation and vector normalisation was carried out on the data for the aging study analysis could be observed to show aging can be seen from the second derivatised data. Analysis shows that aging of the ink can be observed, with differences observable between the different time periods. The clearest difference can be observed between the spectra before and after the 7 week time period.

The final part of the data processing involved carrying out feature extraction, and variable ranking on the data which had been derivatised, and plotting group scatter plots. This data showed evidence for aging of ink as the points for the earliest time periods were generally found to be in one corner of the spectrum, whereas the data for the latest time periods were generally found to be in the opposite corner of the spectrum to the earliest time points. This correlation of aging over time is not a linear relationship as there are overlaps present between certain time periods, however evidence can be seen suggesting ink aging can be determined by the use of infrared spectroscopy.

Overall, evidence has shown that ATR-FTIR can be used as a technique to calculate the age of a gel pen ink. A linear correlation between the different time periods analysed is not detectable however correlation is detectable between ranges of time, with strong results that show a detectable difference between ink before and after 7 weeks.

Chapter 6

Future Work

In order to develop and increase on the results which have been during the project an increase in the number of ink samples being analysed would allow a more thorough investigation would take into account a larger quantity of manufactures.

Further investigation would take place over a longer period of time. By increasing the total length of time between the first and last time period, and including more stages of analysis in between would allow more information to be gain and the potential to see more areas of time in which a large alteration occurs between the spectra of two time period, e.g. between 4 weeks and 7 weeks, as alterations like this one may occur again at another point in time. It would also allow more thorough analysis between this time period to determine the exact point between 4 weeks and 7 weeks where the change occurs.

Further work would consider storing ink in different environmental conditions to see how the inks would age in different conditions, as during this research all of the inks were stored in the same conditions. Different environmental conditions are likely to affect the aging in different ways. Altering the temperature, humidity and amount of light the inks are exposed to may cause the ink samples to alter in differently to the conditions used in this project.

Analysis of the paper in which the ink samples were written on could be analysed over the same time period as the ink to determine if any aging can be seen in the paper as this was not taken into consideration as a control and may be an aging

factor which was not considered. The ink samples could be written onto different types of paper and colour of paper to determine whether the surface in which an ink is written on affects the environmental aging of the ink.

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Appendices

Appendix A

Appendix A contains the abstract for the poster entitled “Using vibrational spectroscopy to analyse the composition and effect of environmental factors on gel pen ink” accepted by the SciX 2014 conference in Reno, United states and the poster which was presented.

Using vibrational spectroscopy to analyse the composition and effect of environmental factors on gel pen inks

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Document examination is an important area in combating fraud. Fraud is a major problem and the cost to the private and public sectors of the UK was £21.2 billion and £20.6 billion respectively in 2013 [1]. During the 1970s and 1980s the examination of writing inks had a greater impact on the investigation of fraudulent documents than any other field in forensic science [2], and with the increase in the use of writing instrumentation over recent decades has increased the number of ink formulations that have been produced from various countries [3].

Previous research in the field of ink aging has been carried out by a range of groups throughout the years, using a variety of techniques including Thin Layer Chromatography, Gas Chromatography – Mass Spectrometry, Fourier Transform Infrared Spectroscopy, and solvent extraction. The majority of this previously conducted research has looked into aging studies related to ball point pen inks, with research into pens of other types concentrated onto mainly black and blue pens due to their common use.

This paper will discuss using infrared spectroscopy as a method for ink age determination, of gel pen inks concentrating on a variety of colours as well as black and blue inks. The pens used for analysis represent a range of manufactures and colours. Analysis was carried out over a 10 week time period, with spectra being taken after the ink had aged for 1 day, 2 days, 1 week, 2 weeks, 4 weeks, 7 weeks and 10 weeks. Infrared is a rapid, easy to use technique that will enable identification of age of ink whilst keeping forensic operational tempo.

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Appendix B

Appendix B contains a collection of spectra for the drying study conducted on each of the ink samples. Each spectrum displays all of the spectra for each individual ink at each of the time periods where spectra were collected.

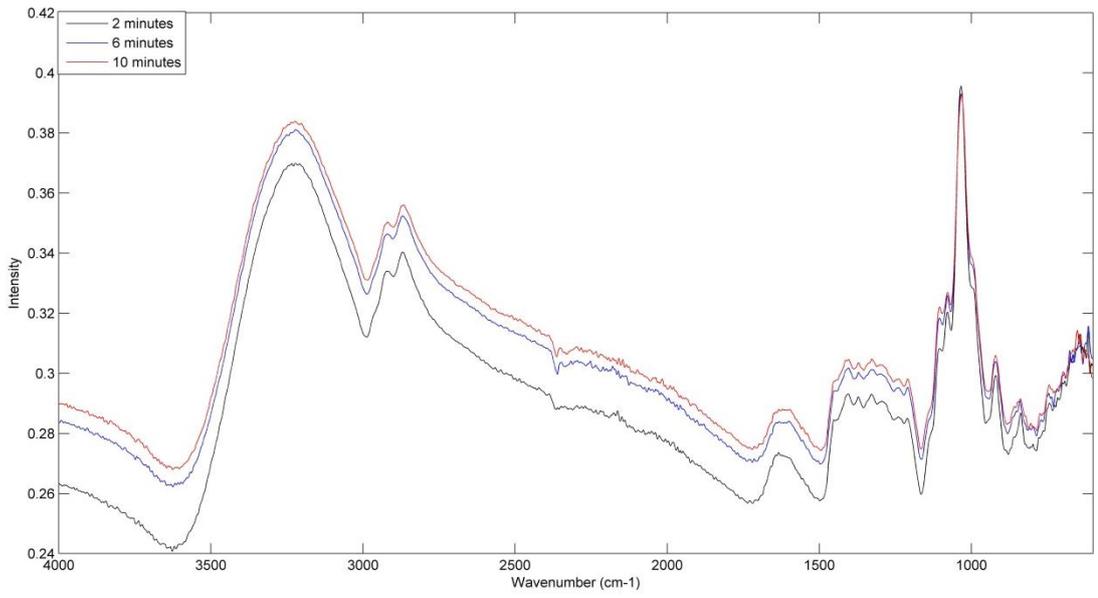


Figure 1: Drying study for Club black ink

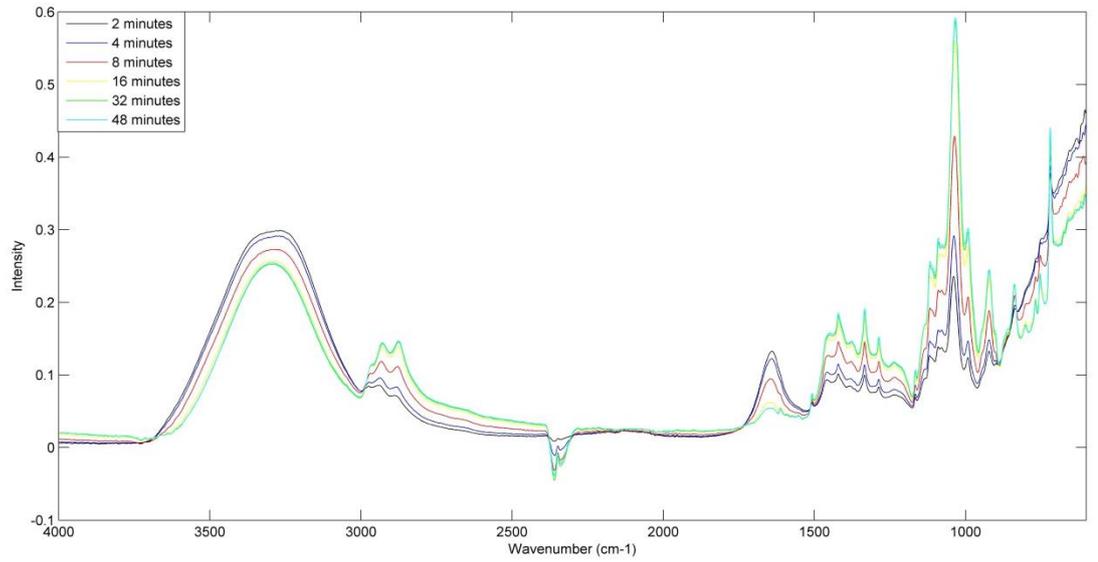


Figure 2: Drying study for Club blue ink

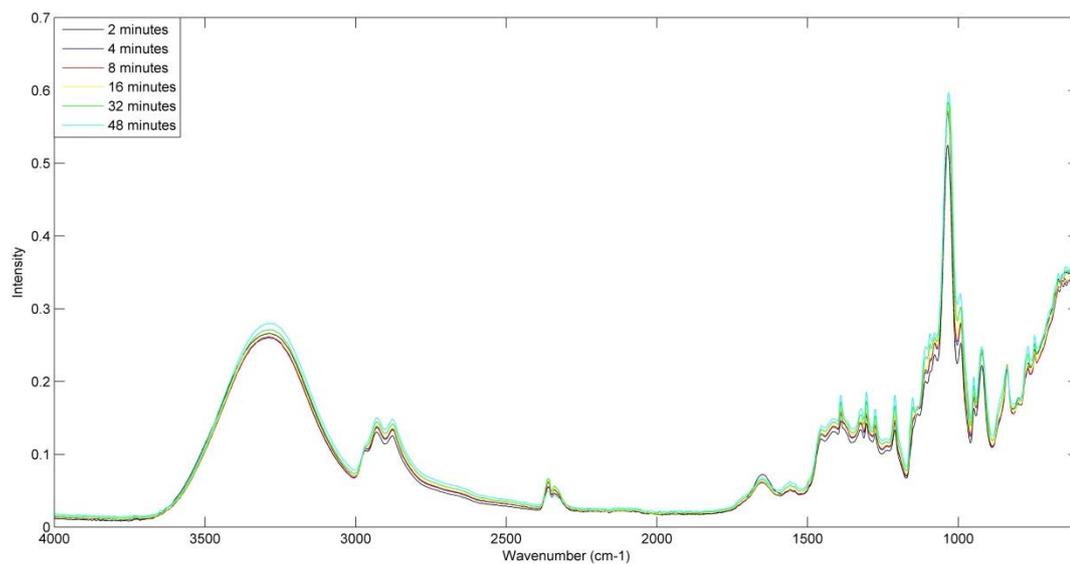


Figure 3: Drying study for Club green ink

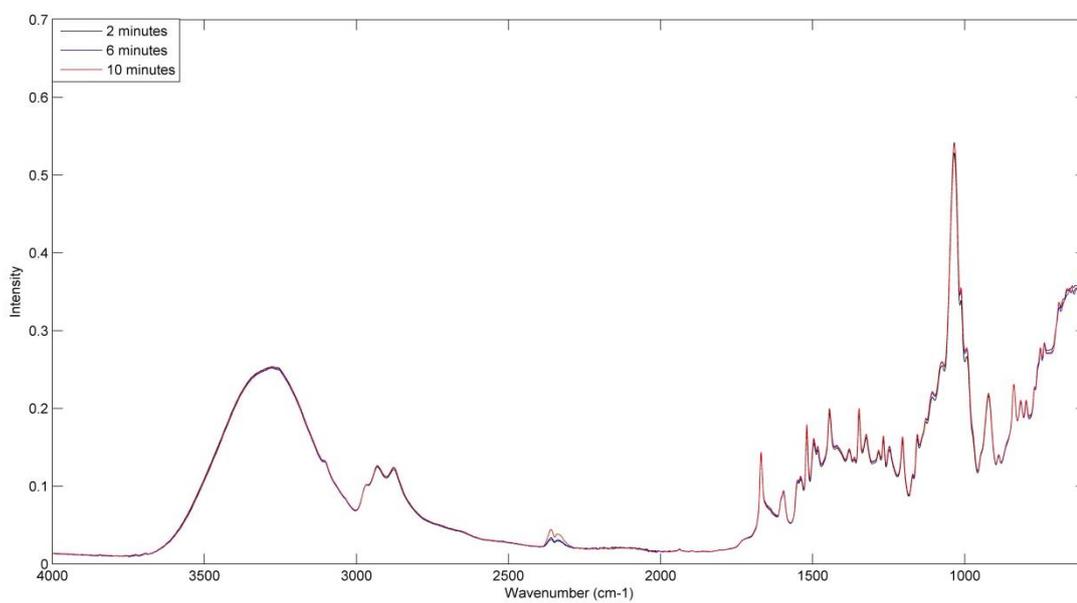


Figure 4: Drying study for Club red ink

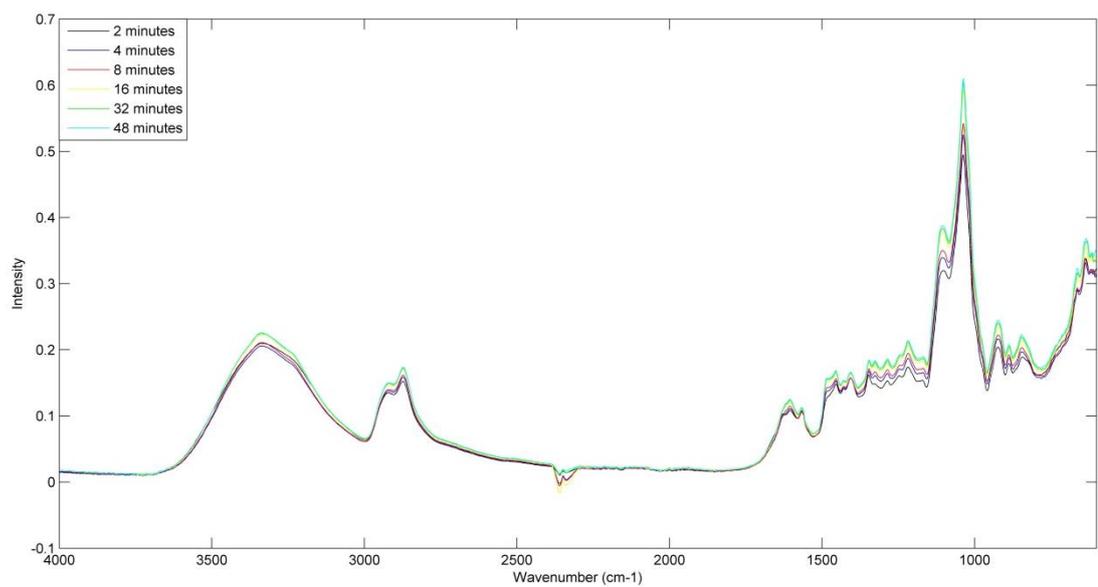


Figure 5: Drying study for Papermate black ink

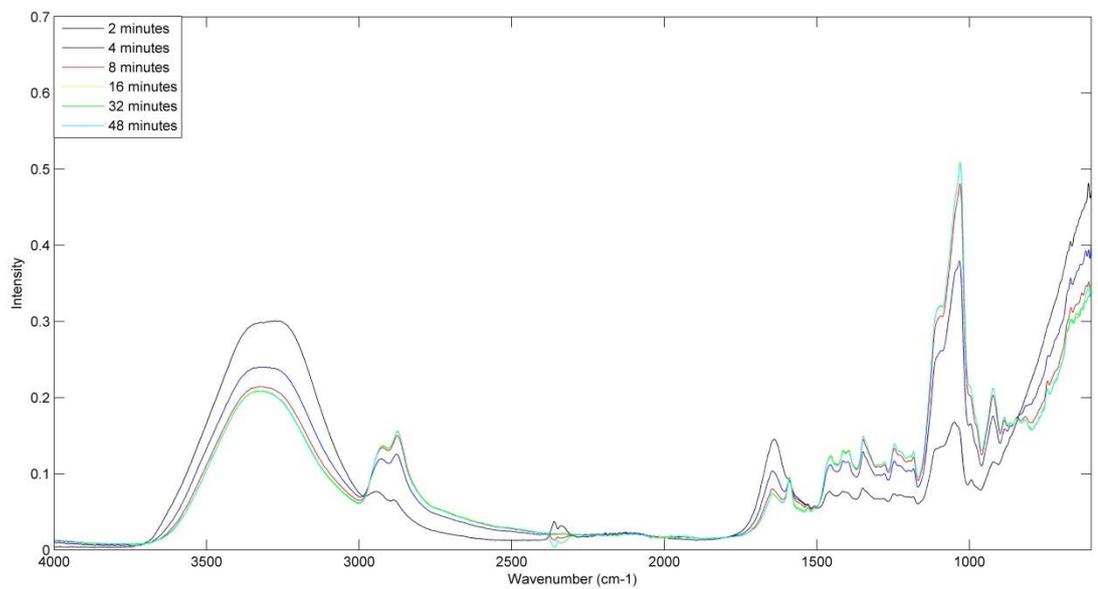


Figure 6: Drying study for Papermate blue ink

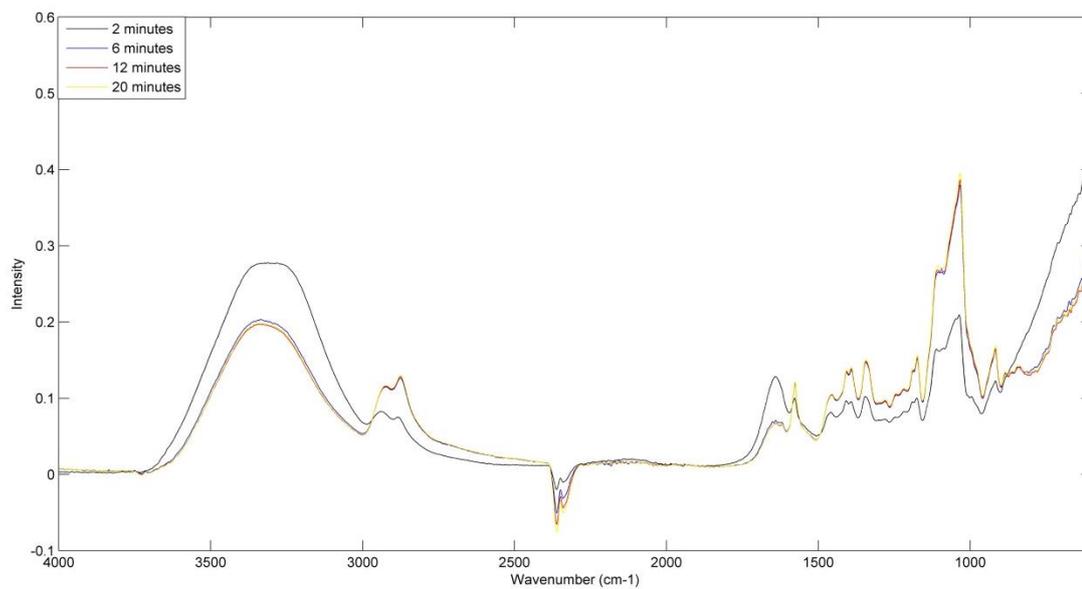


Figure 7: Drying study for Papermate green ink

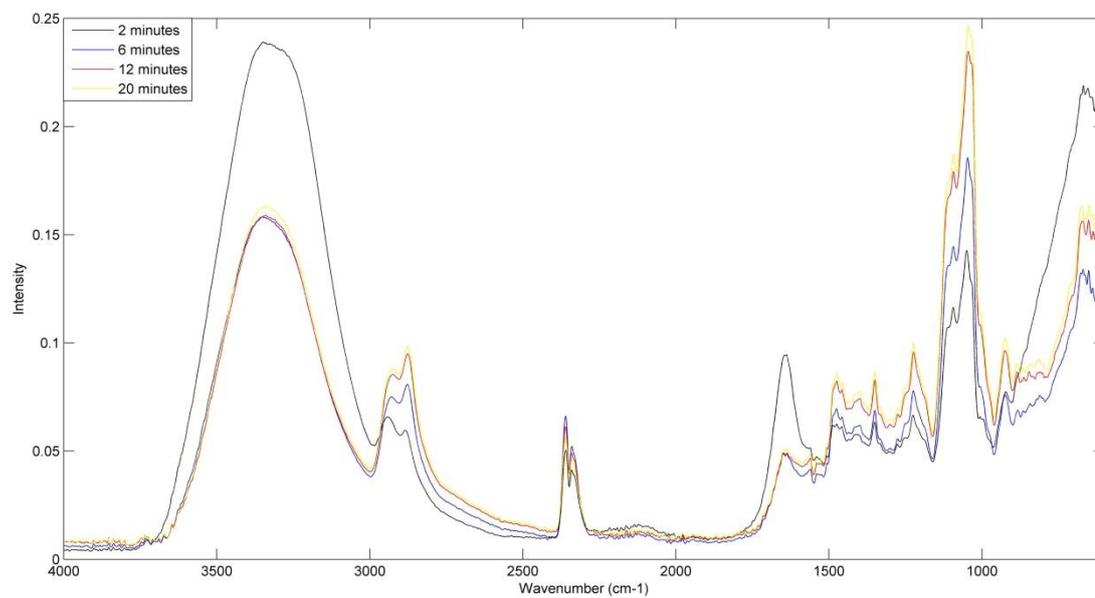


Figure 8: Drying study for Papermate red ink

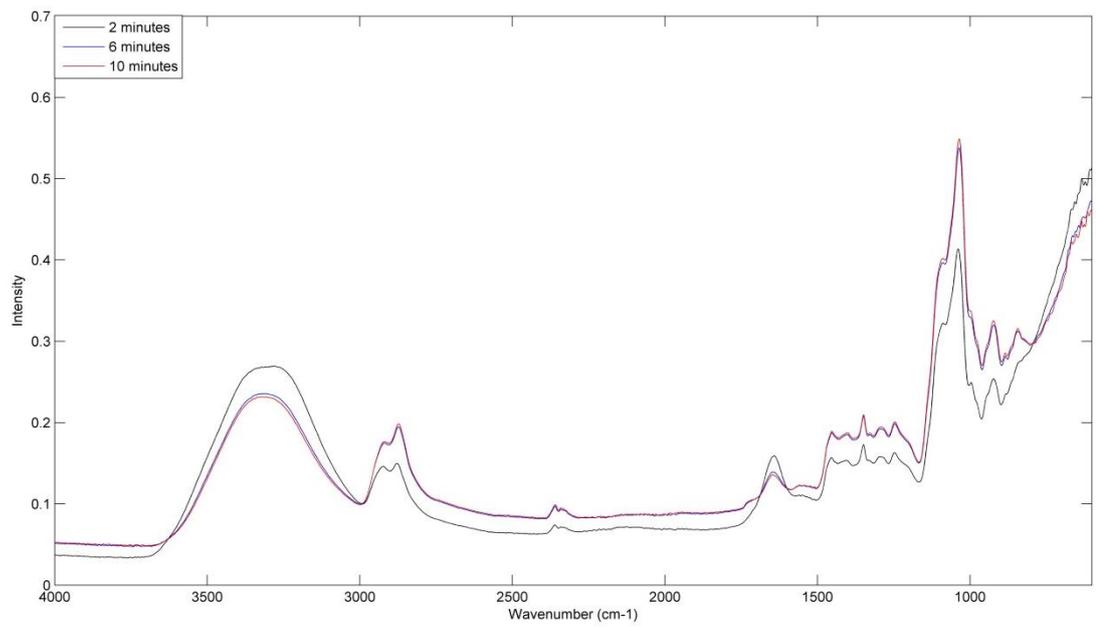


Figure 9: Drying study for WHSmith black ink

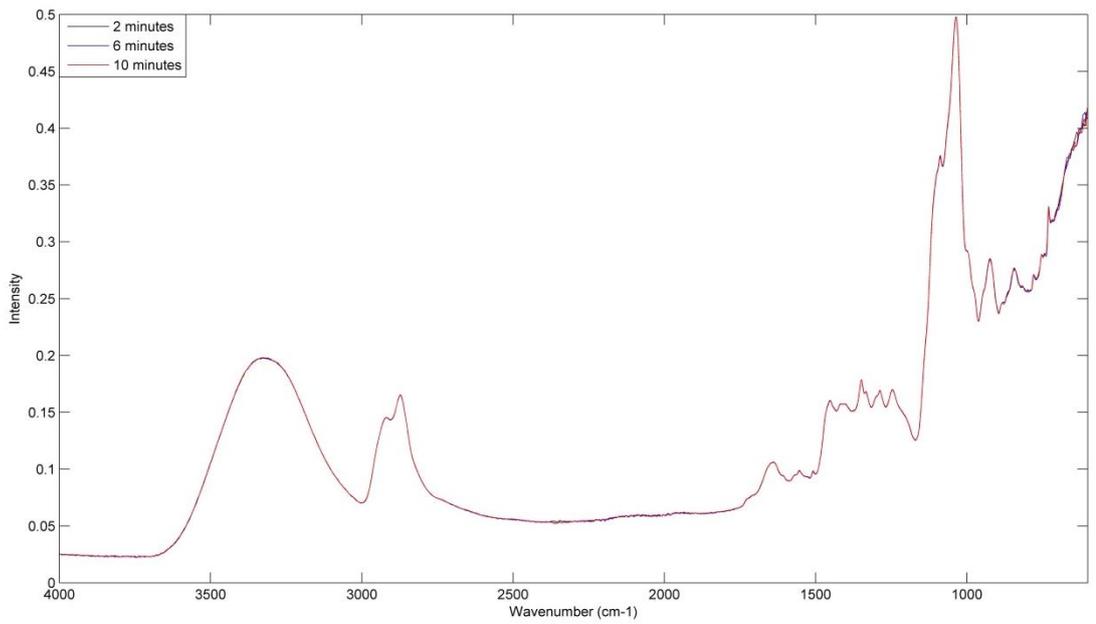


Figure 10: Drying study for WHSmith blue ink

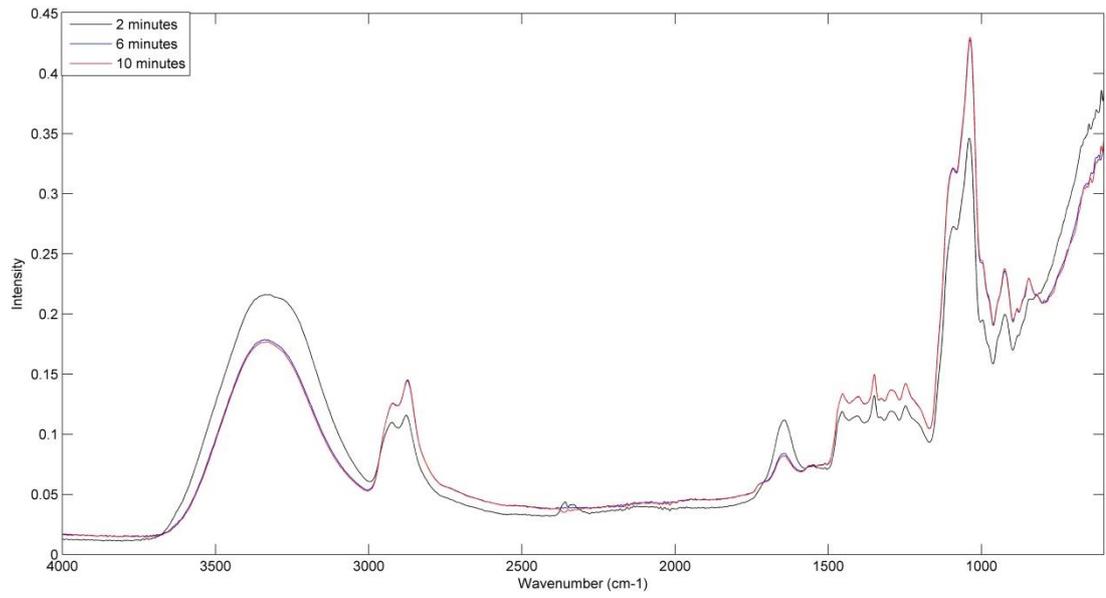


Figure 11: Drying study for WHSmith brown ink

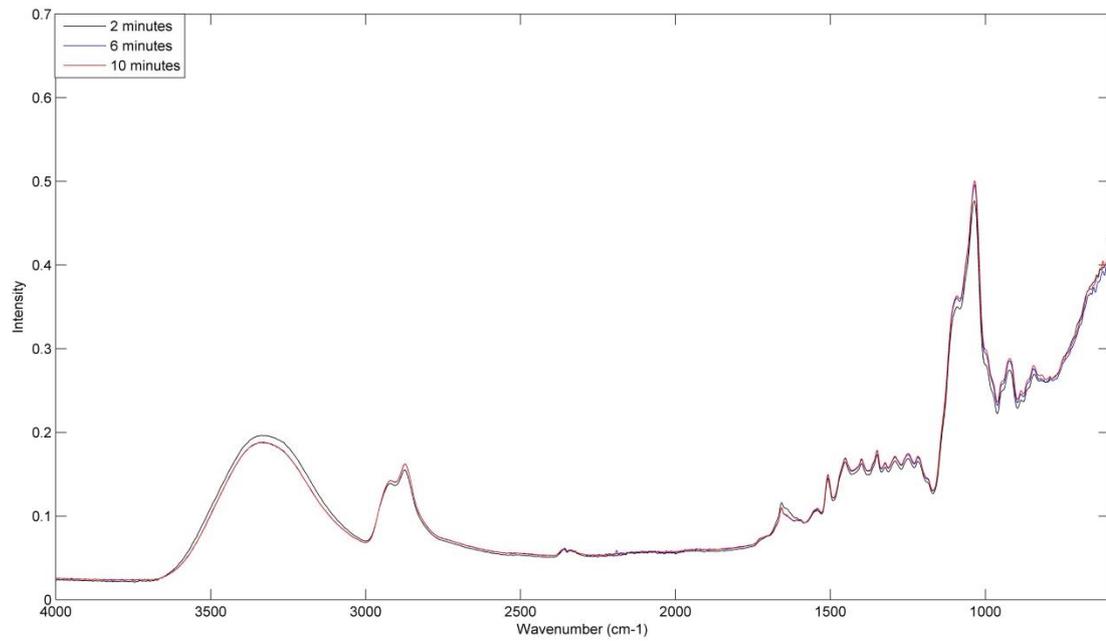


Figure 12: Drying study for WHSmith gold ink

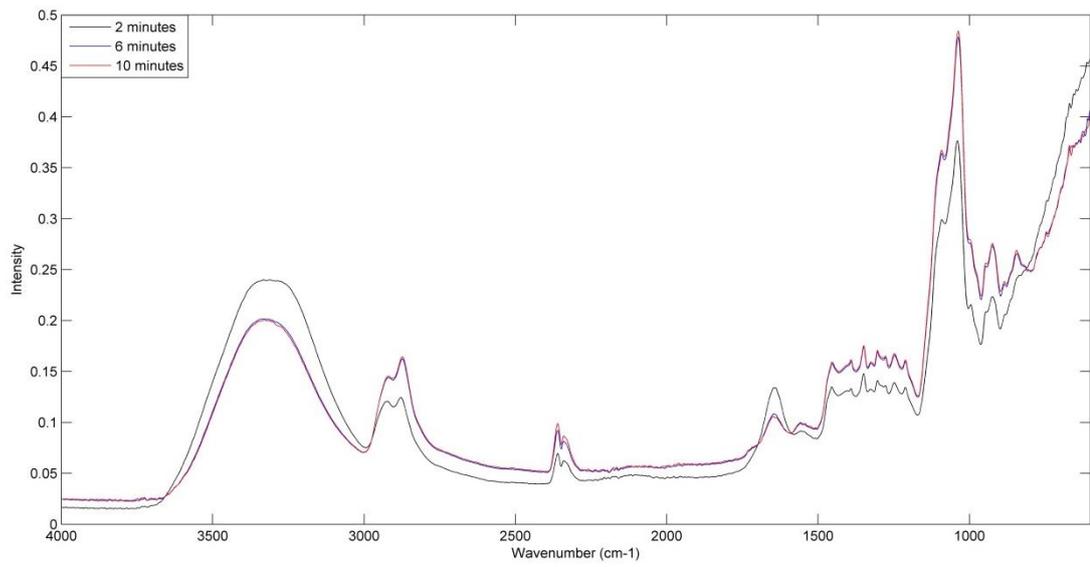


Figure 13: Drying study for WHSmith green ink

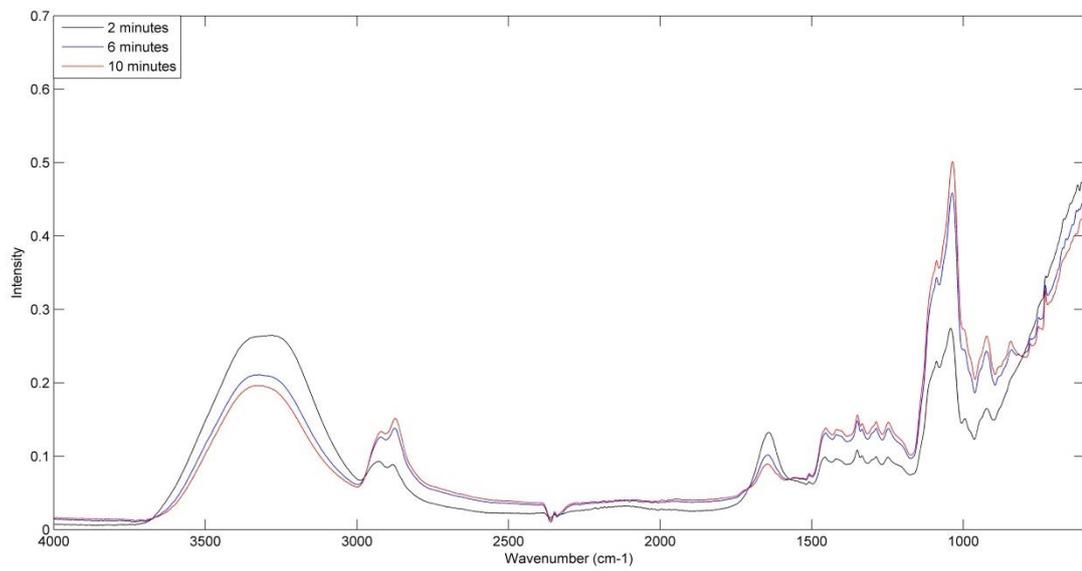


Figure 14: Drying study for WHSmith light blue ink

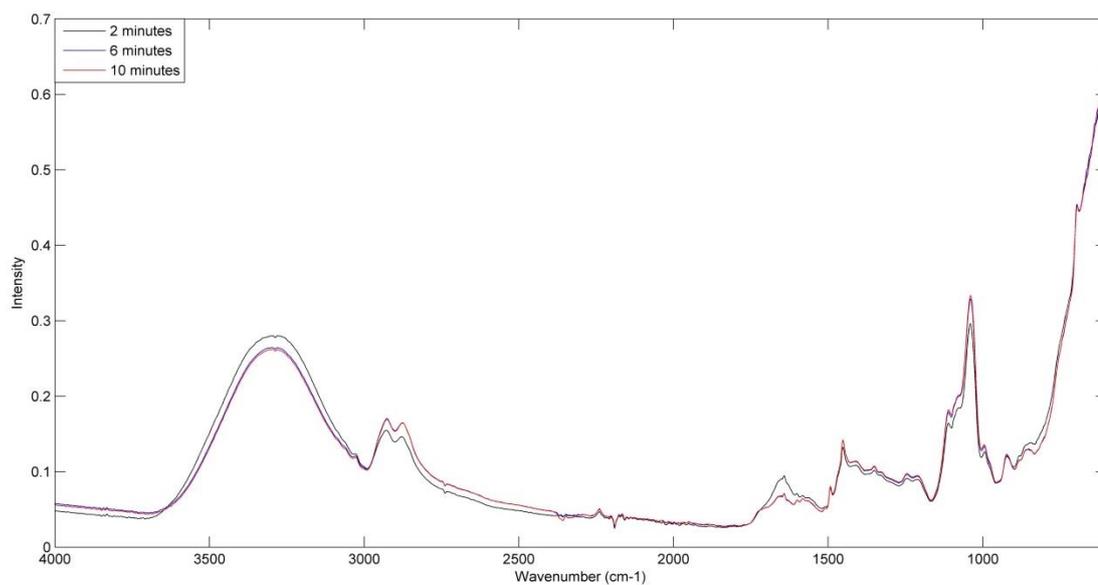


Figure 15: Drying study for WHSmith lime ink

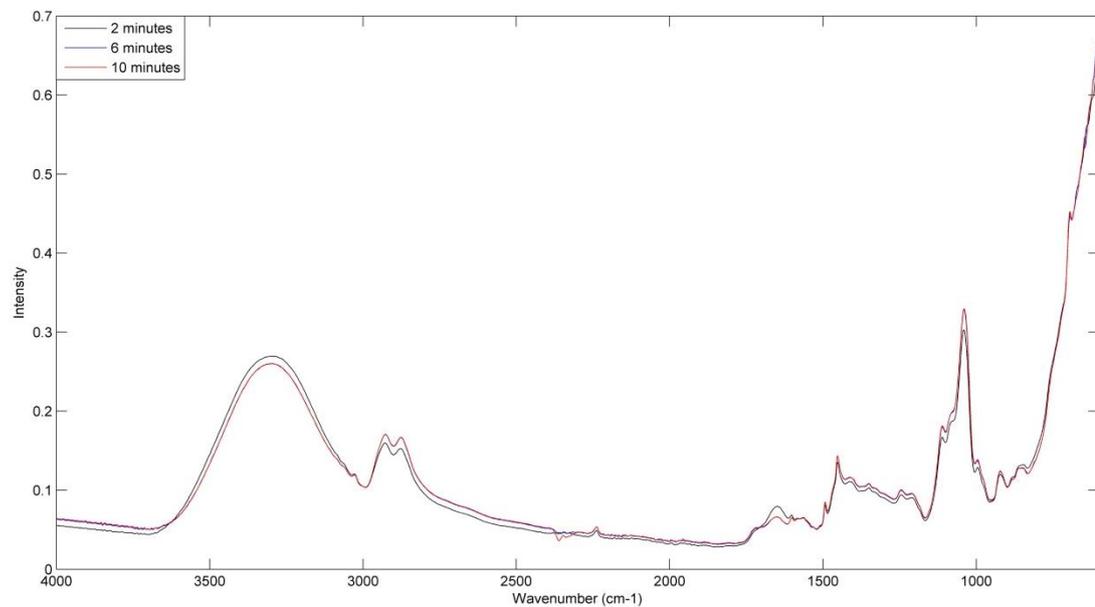


Figure 16: Drying study for WHSmith orange ink

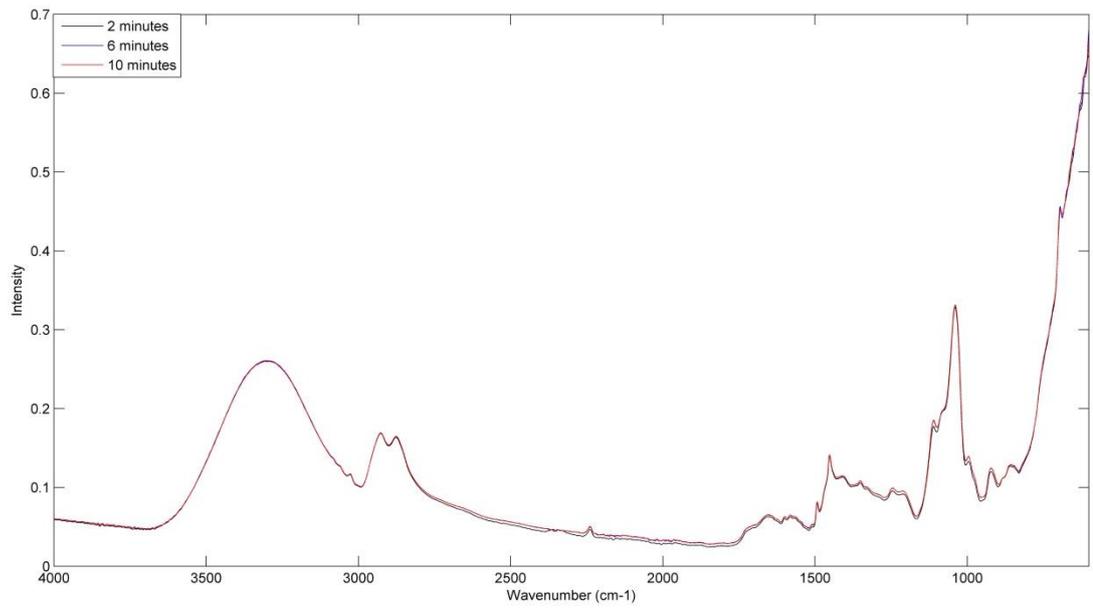


Figure 17: Drying study for WHSmith peach ink

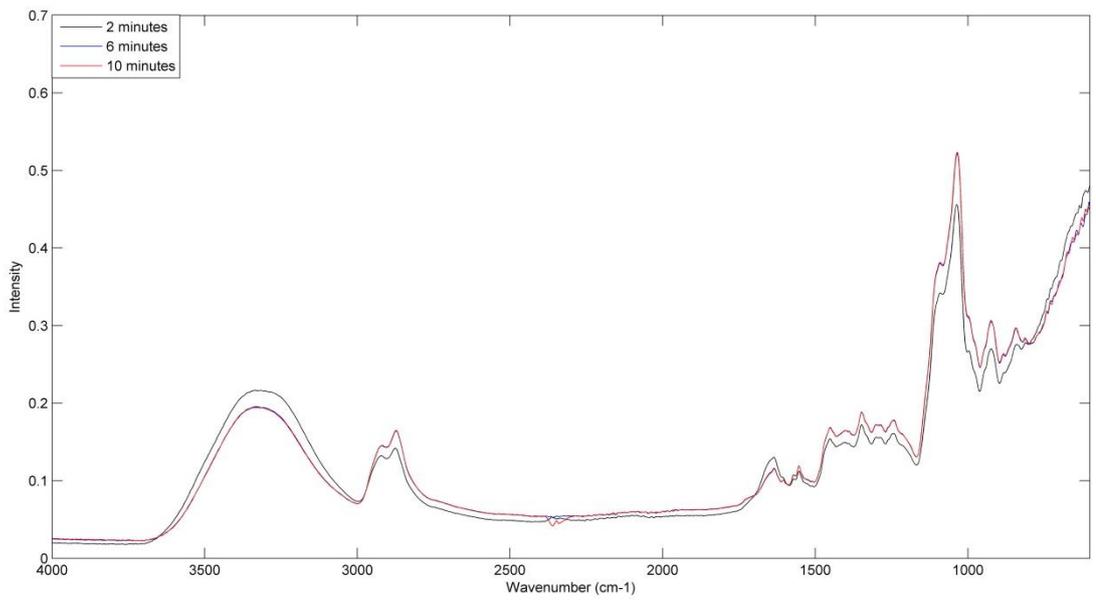


Figure 18: Drying study for WHSmith pink ink

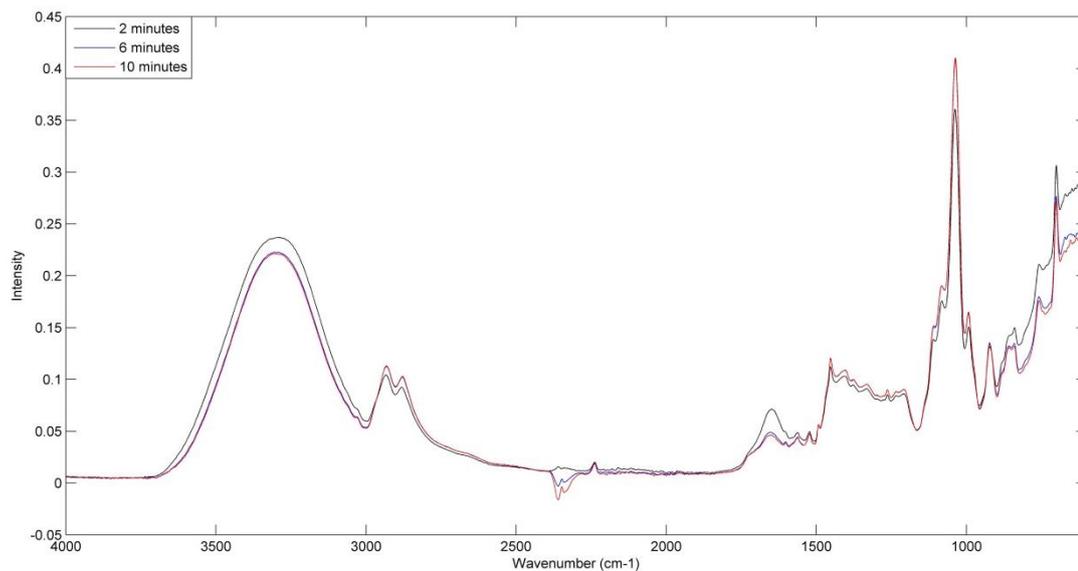


Figure 19: Drying study for WHSmith purple ink

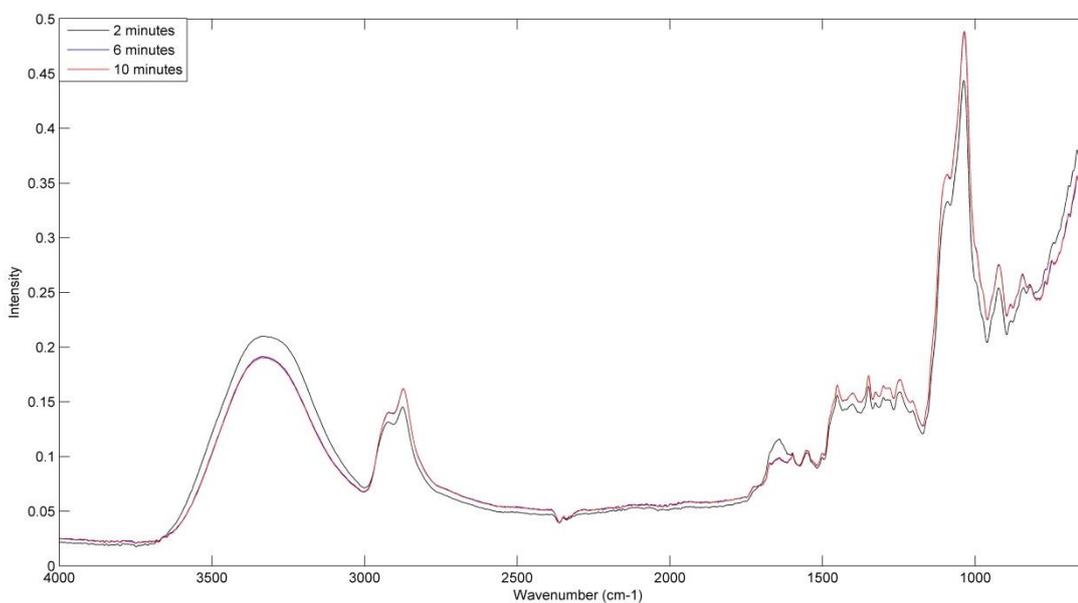


Figure 20: Drying study for WHSmith silver ink

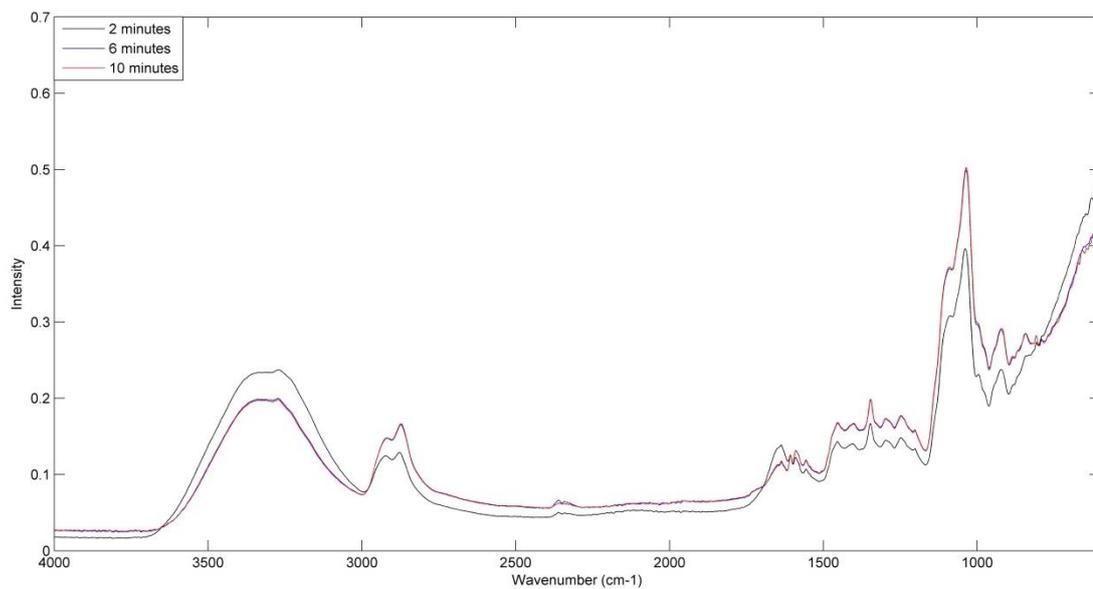


Figure 21: Drying study for WHSmith violet ink

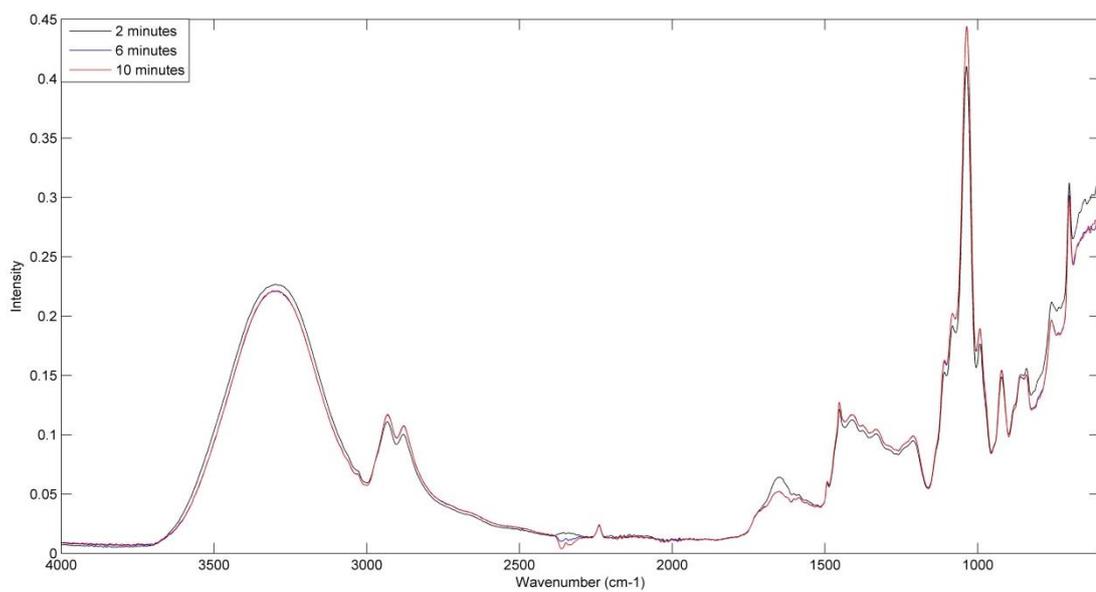


Figure 22: Drying study for WHSmith yellow ink

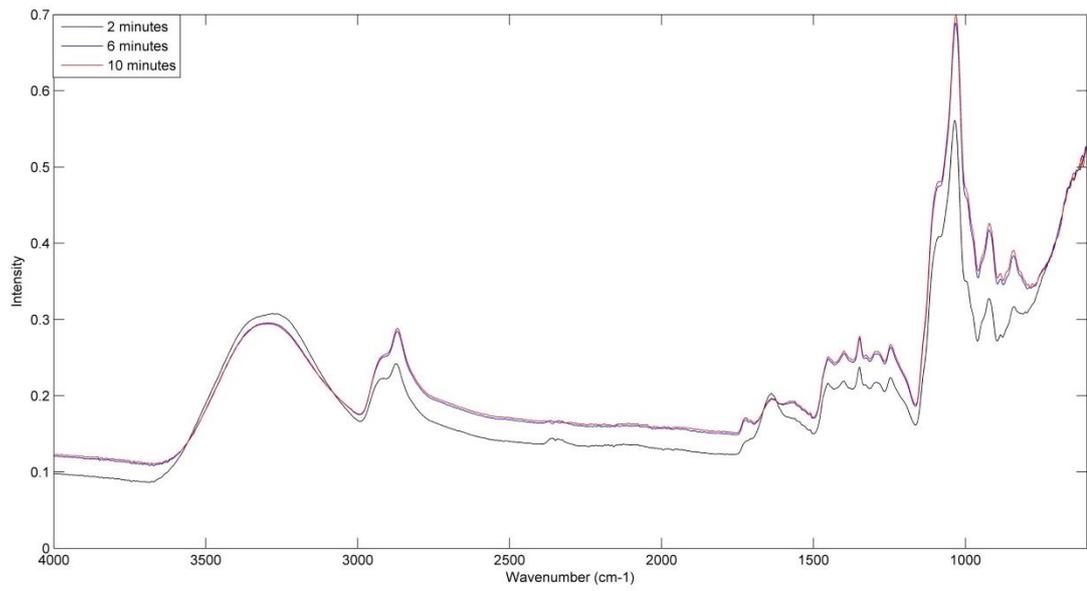


Figure 23: Drying study for WHSmith glitter black ink

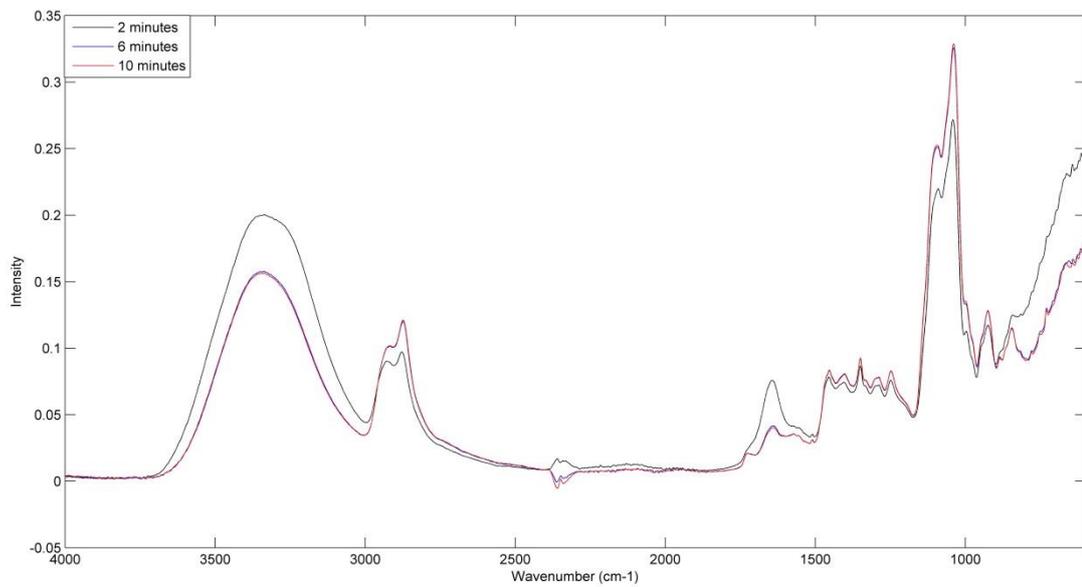


Figure 24: Drying study for WHSmith glitter blue ink

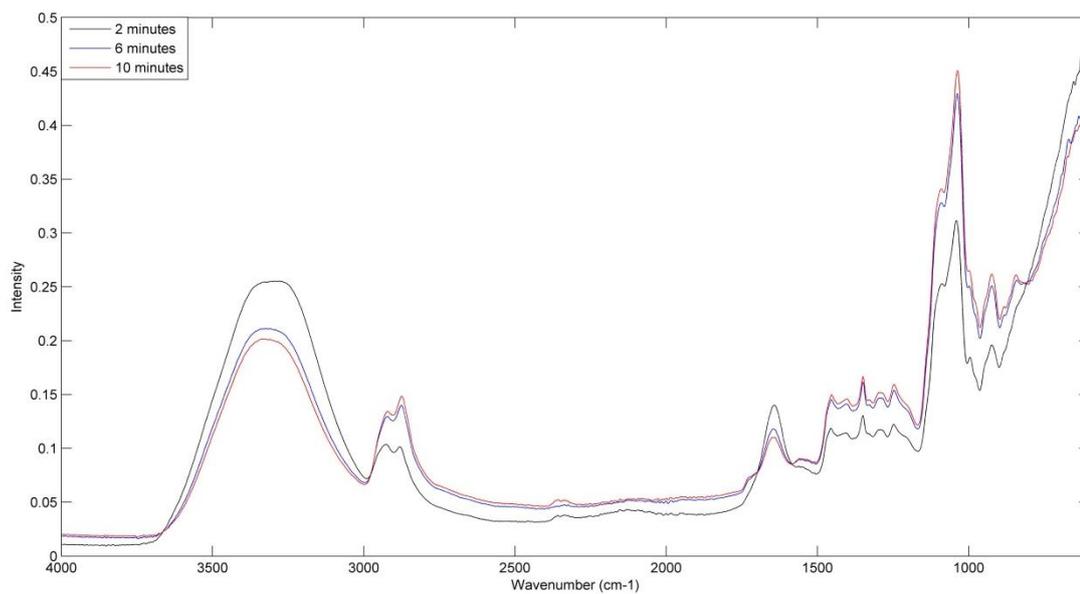


Figure 25: Drying study for WHSmith glitter gold ink

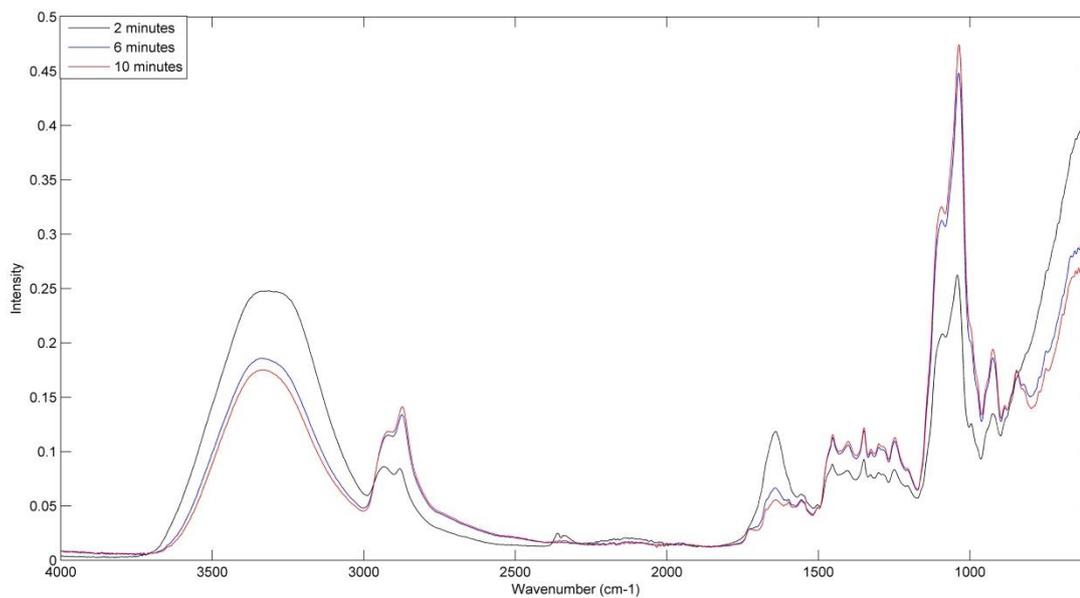


Figure 26: Drying study for WHSmith glitter green ink

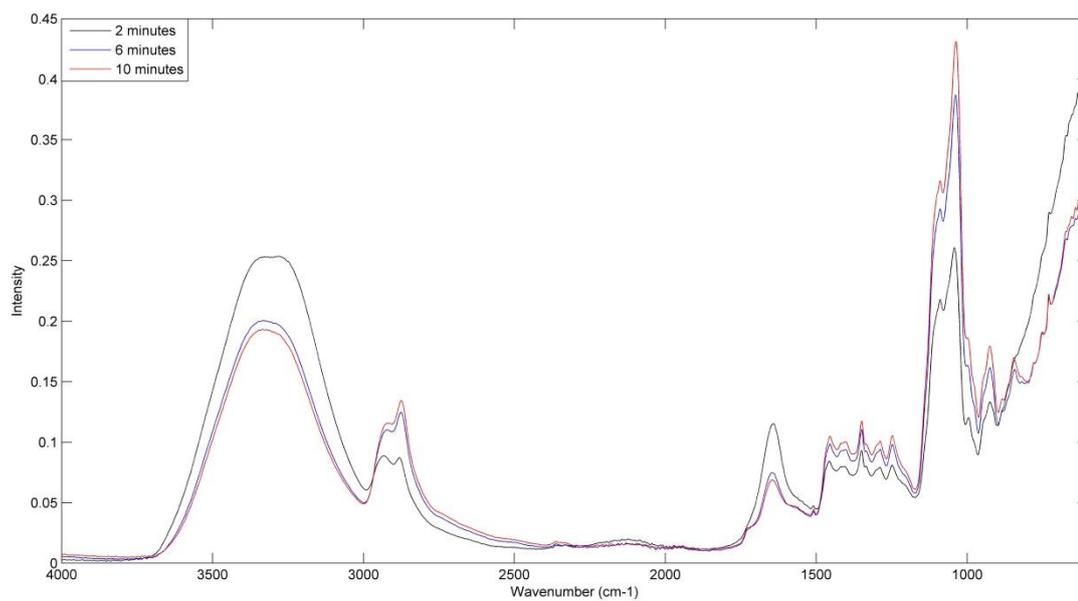


Figure 27: Drying study for WHSmith glitter light blue ink

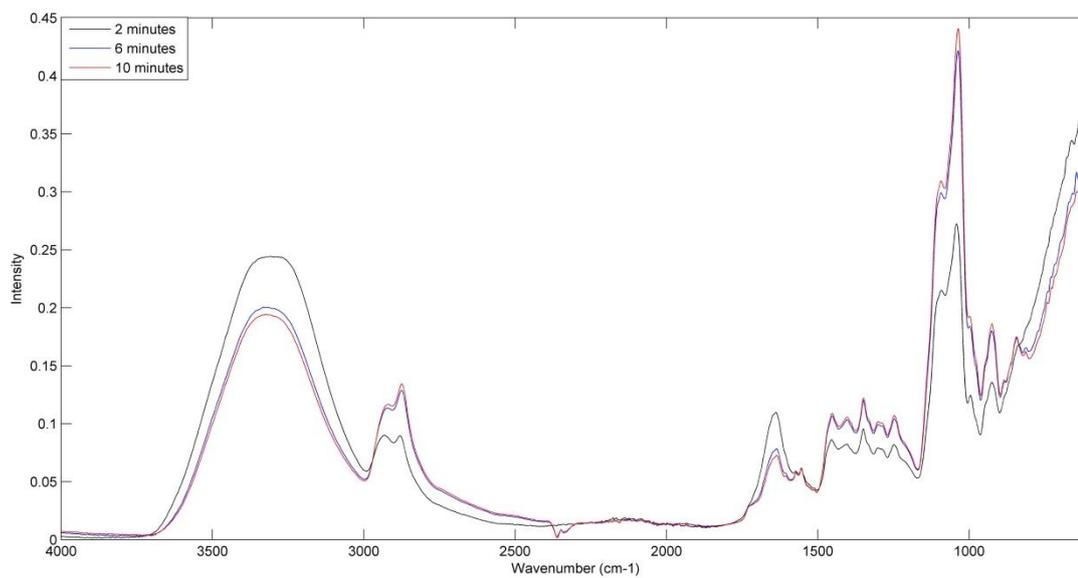


Figure 28: Drying study for WHSmith glitter orange ink

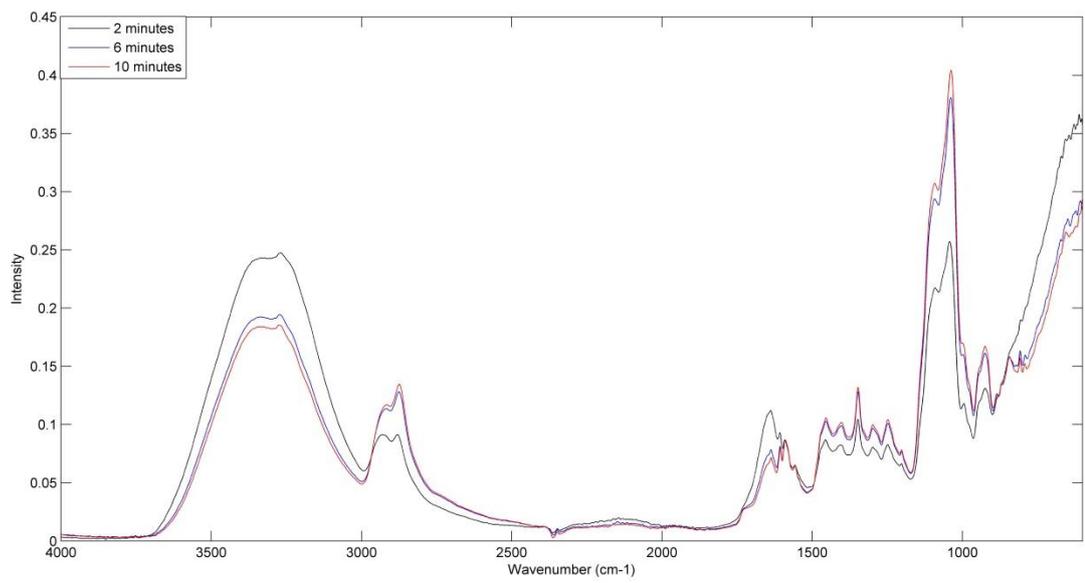


Figure 29: Drying study for WHSmith glitter pink ink

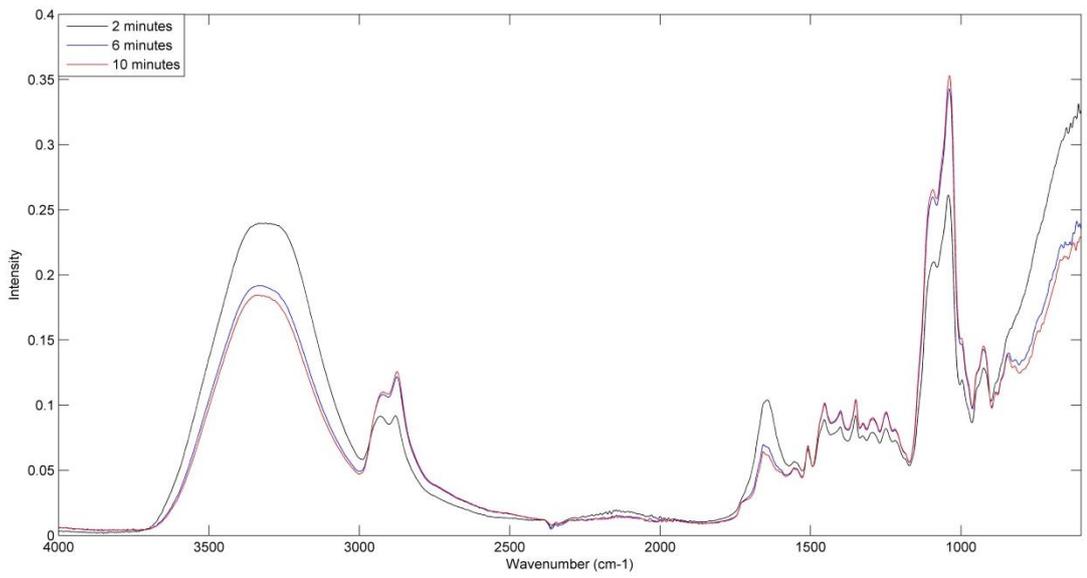


Figure 30: Drying study for WHSmith glitter purple ink

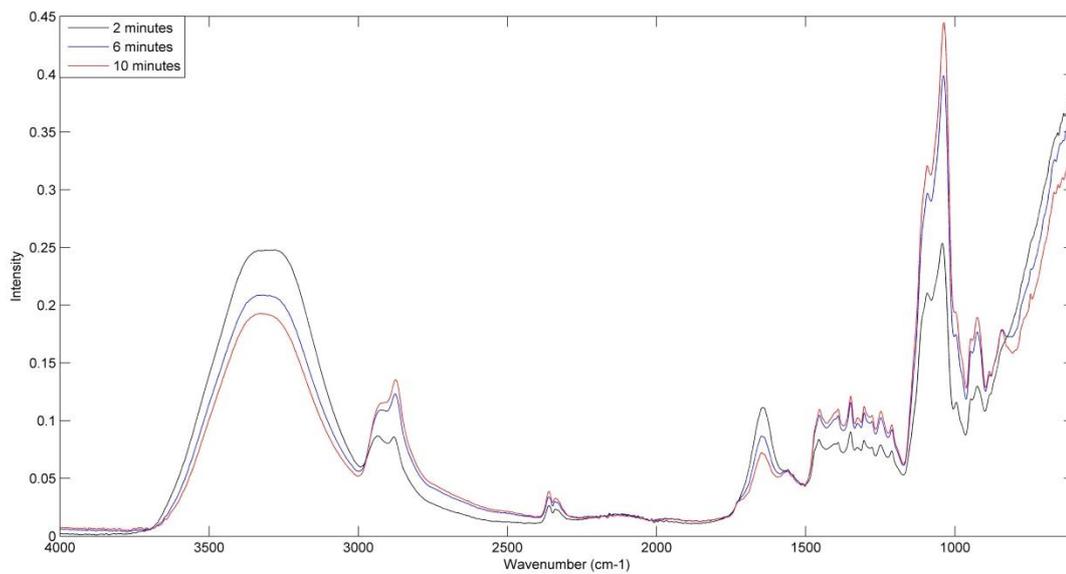


Figure 31: Drying study for WHSmith glitter red ink

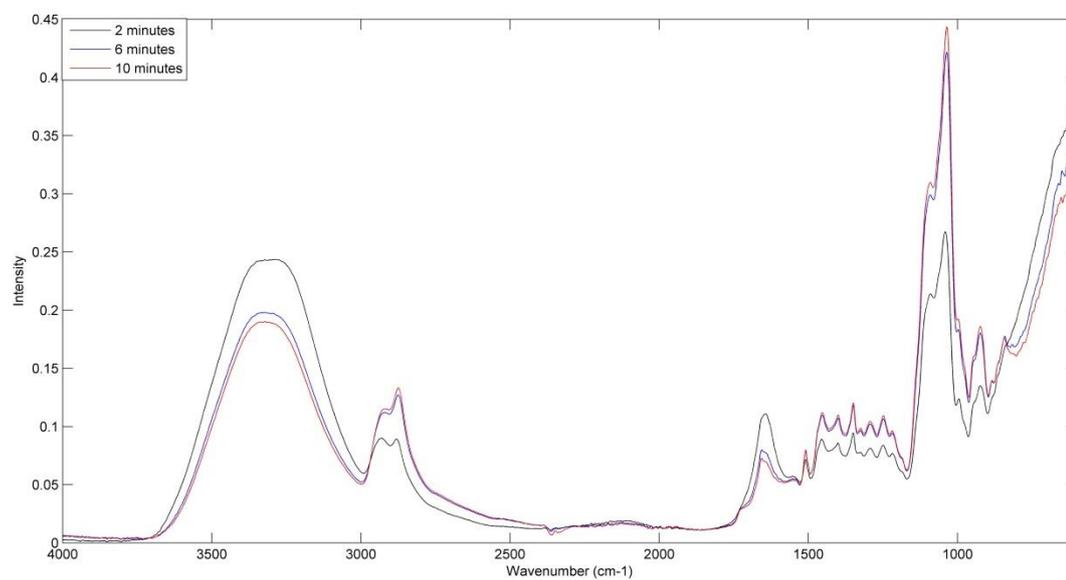


Figure 32: Drying study for WHSmith glitter silver ink

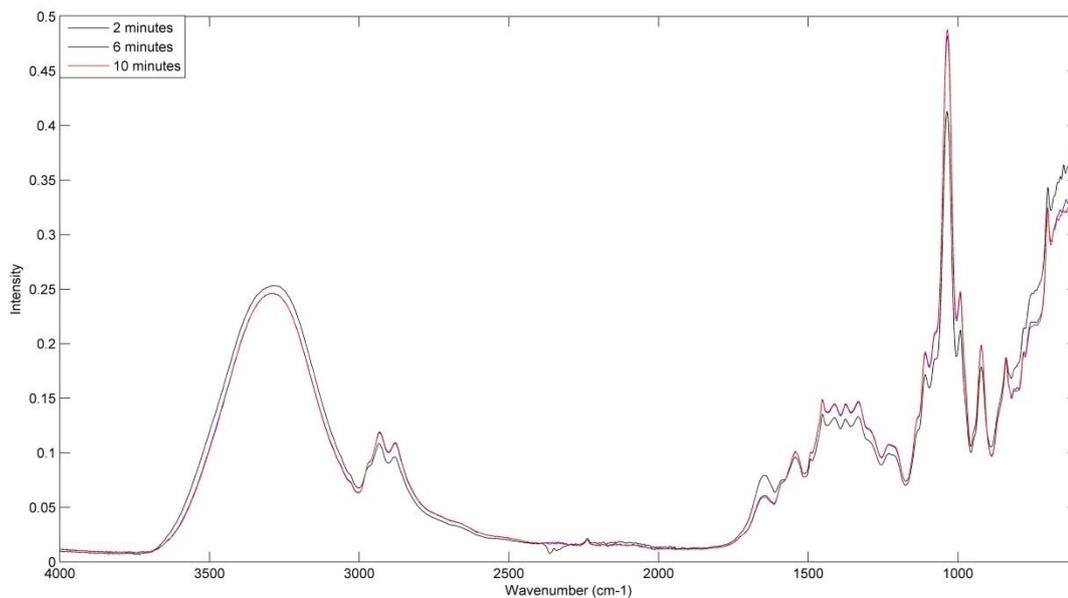


Figure 33: Drying study for Wilko green ink

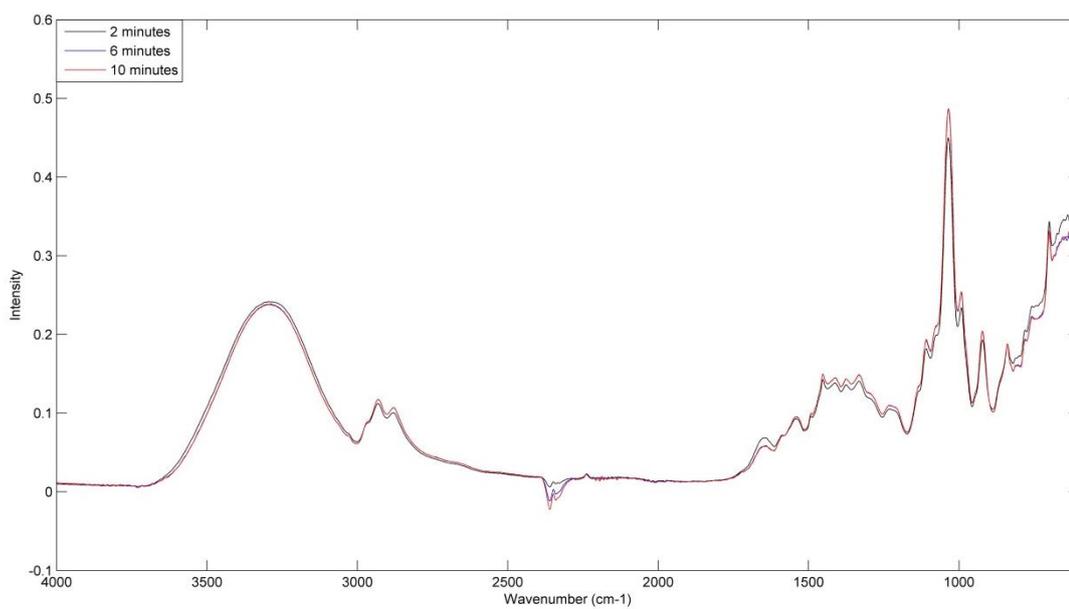


Figure 34: Drying study for Wilko orange ink

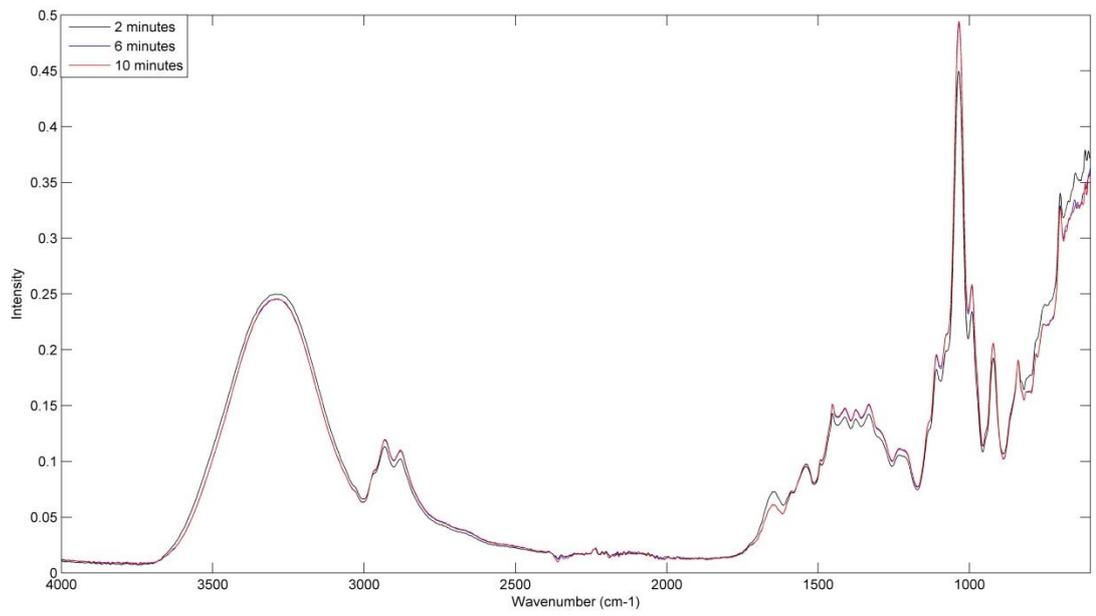


Figure 35: Drying study for Wilko pink ink

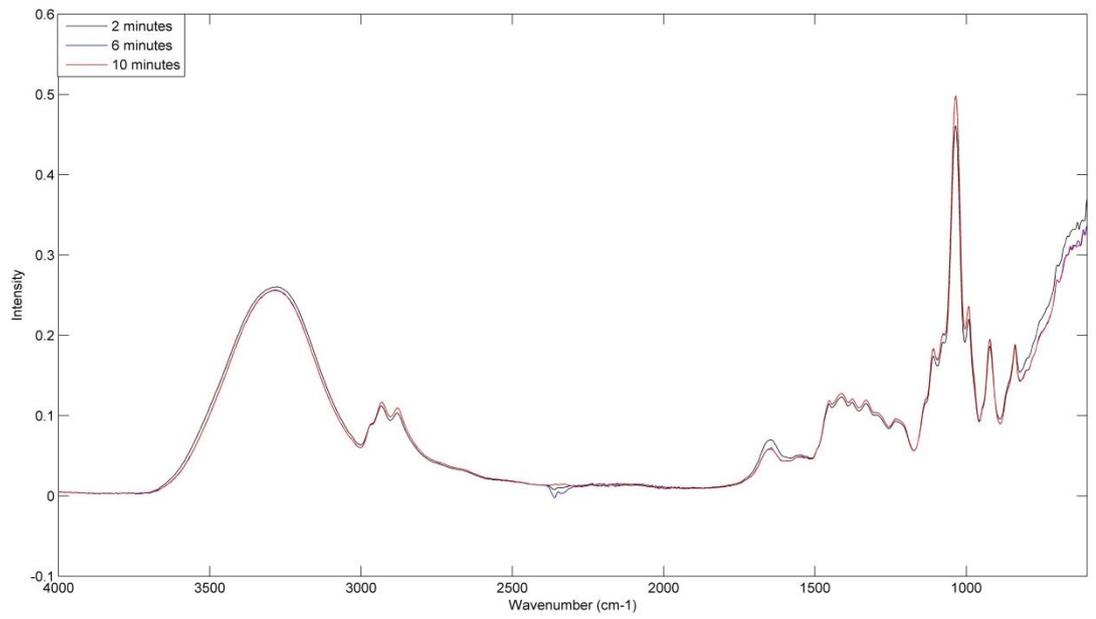


Figure 36: Drying study for Wilko purple ink

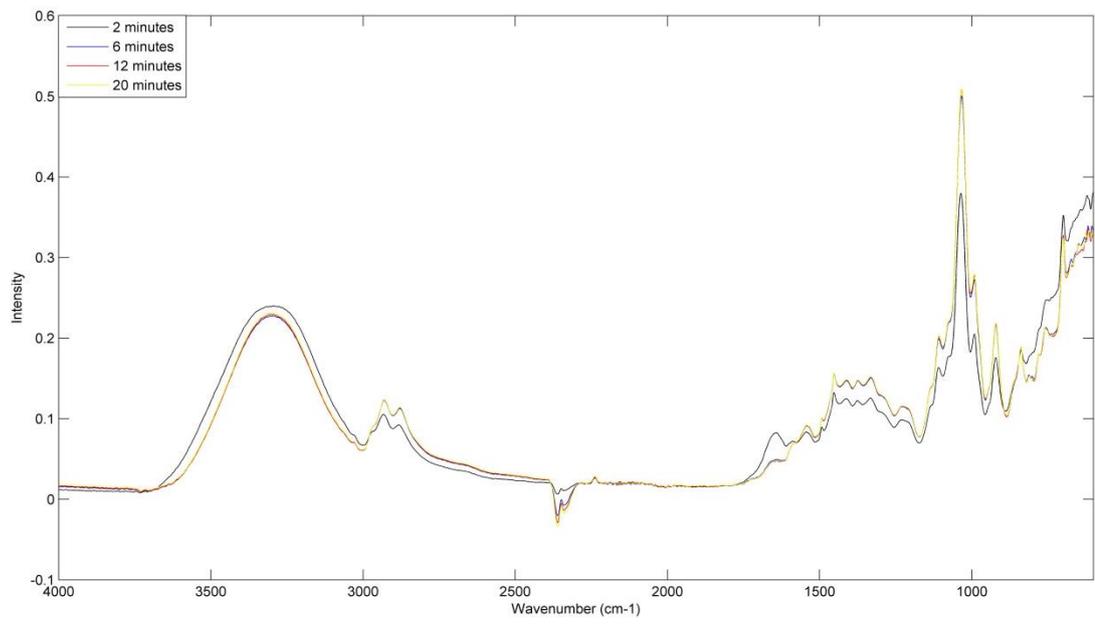


Figure 37: Drying study for Wilko yellow ink

Appendix C

Appendix C contains a collection of spectra showing each of the inks being analysed after the ink has been allowed to fully dry.

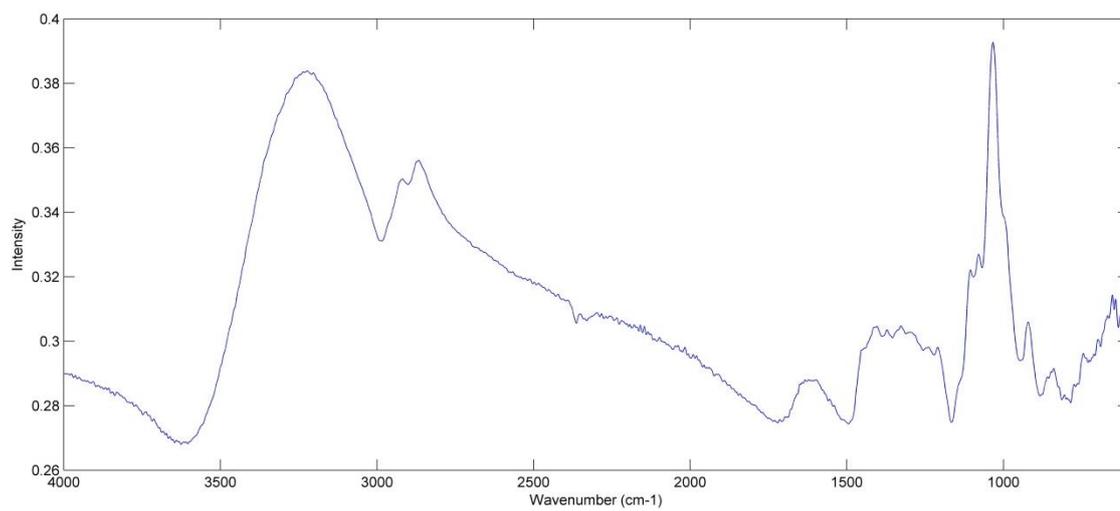


Figure 1: Dry Club black ink

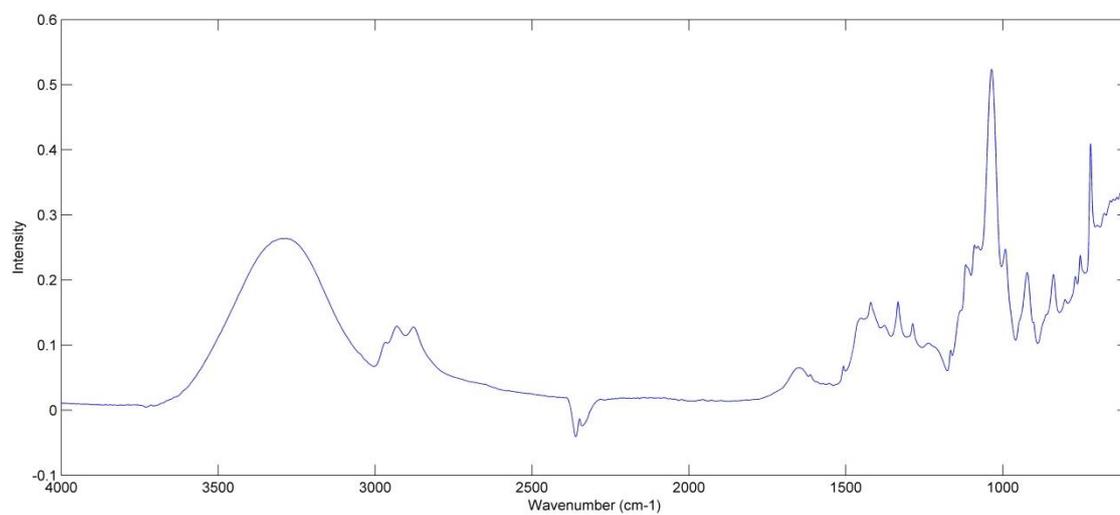


Figure 2: Dry Club blue ink

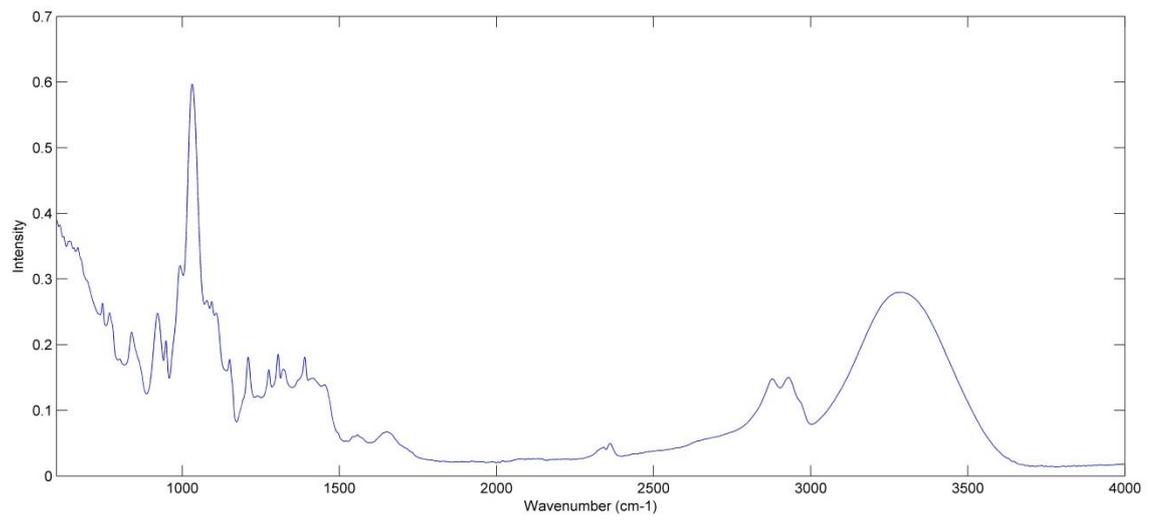


Figure 3: Dry Club green ink

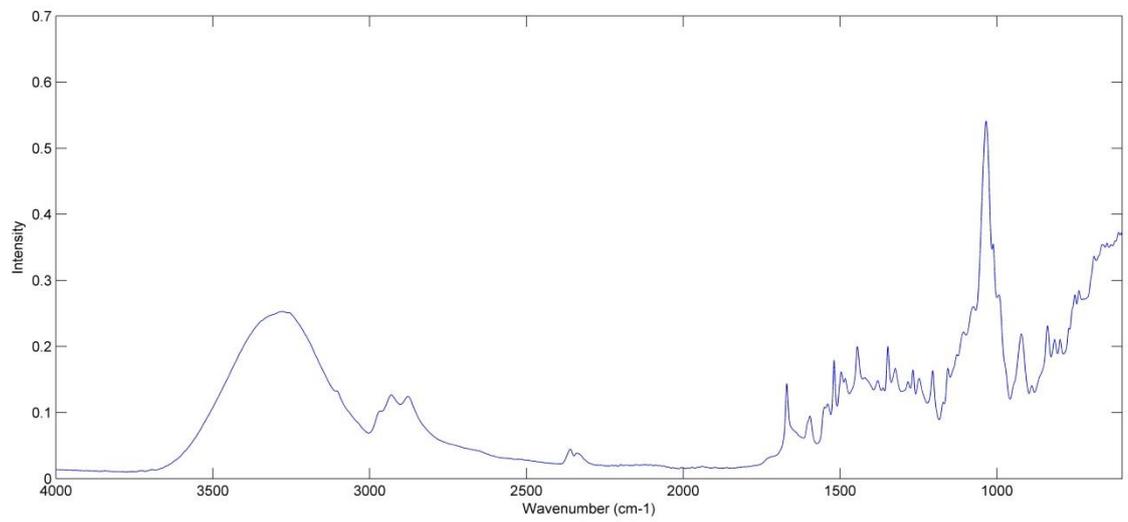


Figure 4: Dry Club red ink

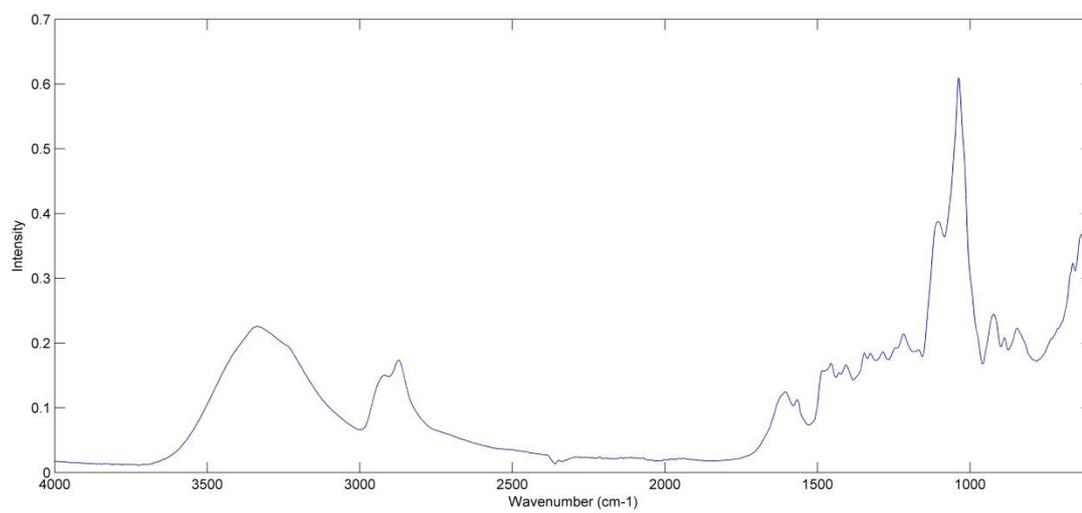


Figure 5: Dry Papermate black ink

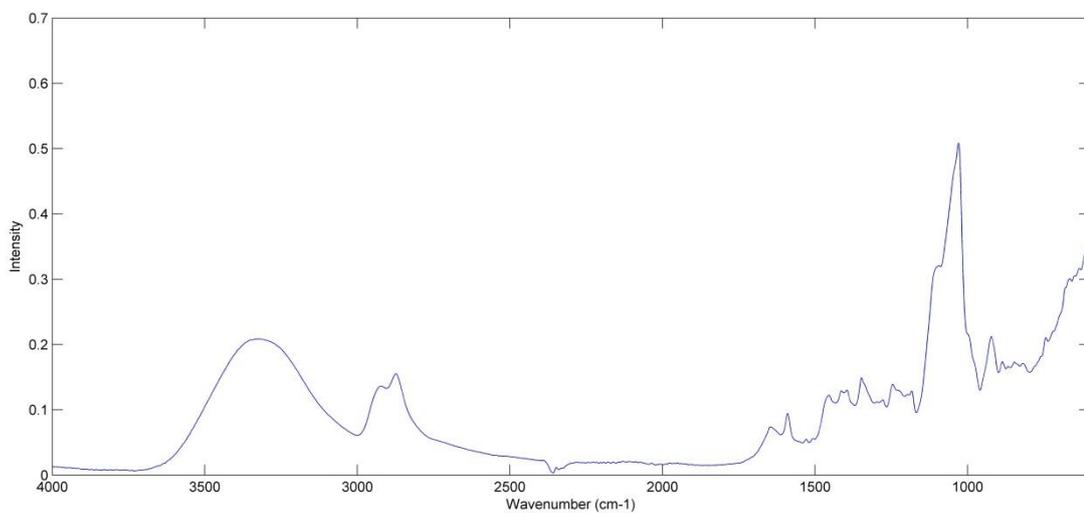


Figure 6: Dry Papermate blue ink

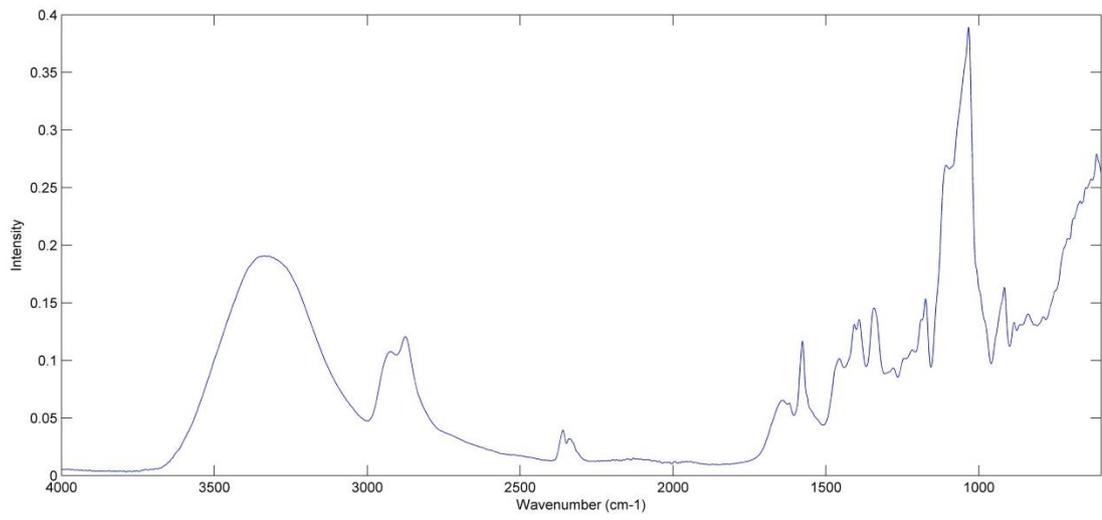


Figure 7: Dry papermate green ink

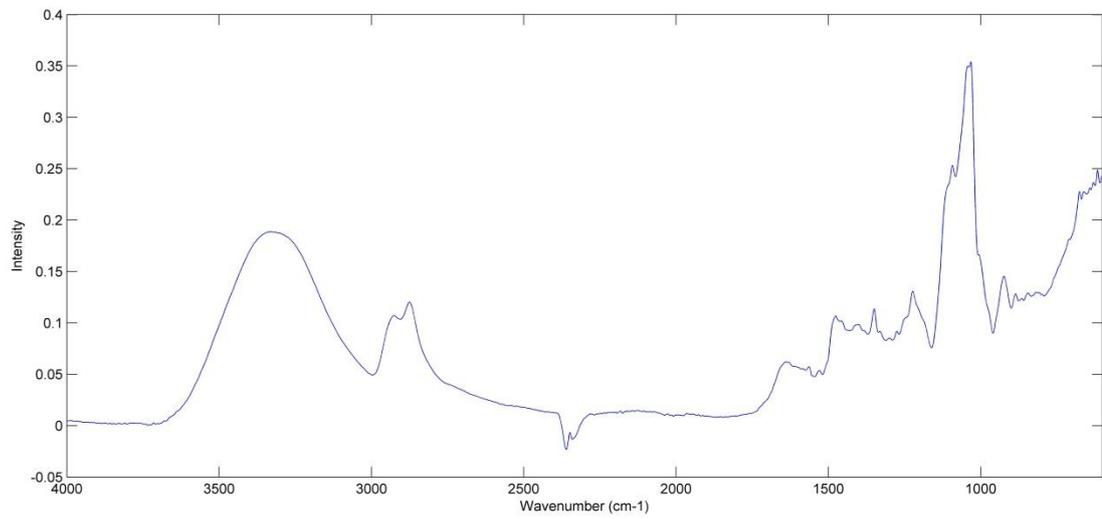


Figure 8: Dry Papermate red ink

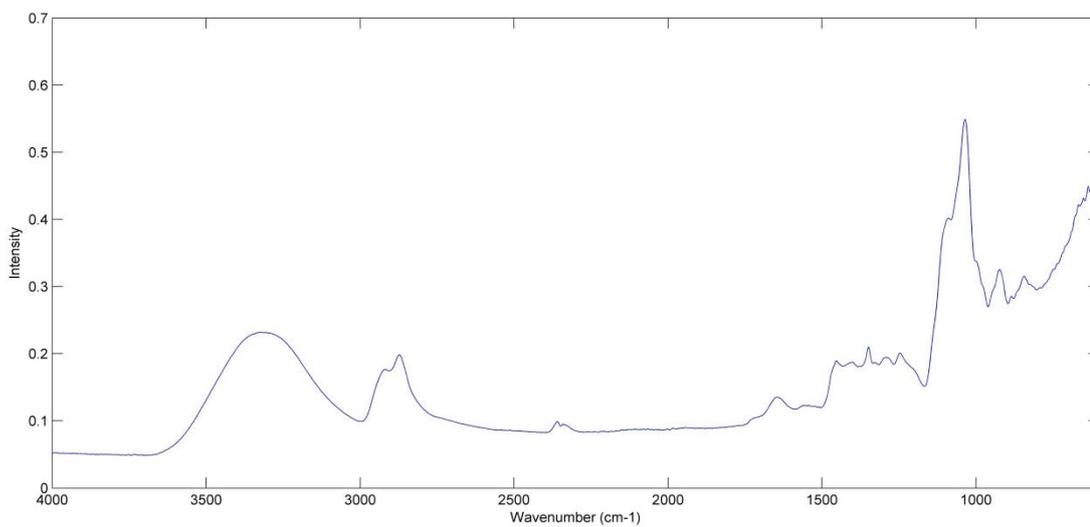


Figure 9: Dry WHSmith black ink

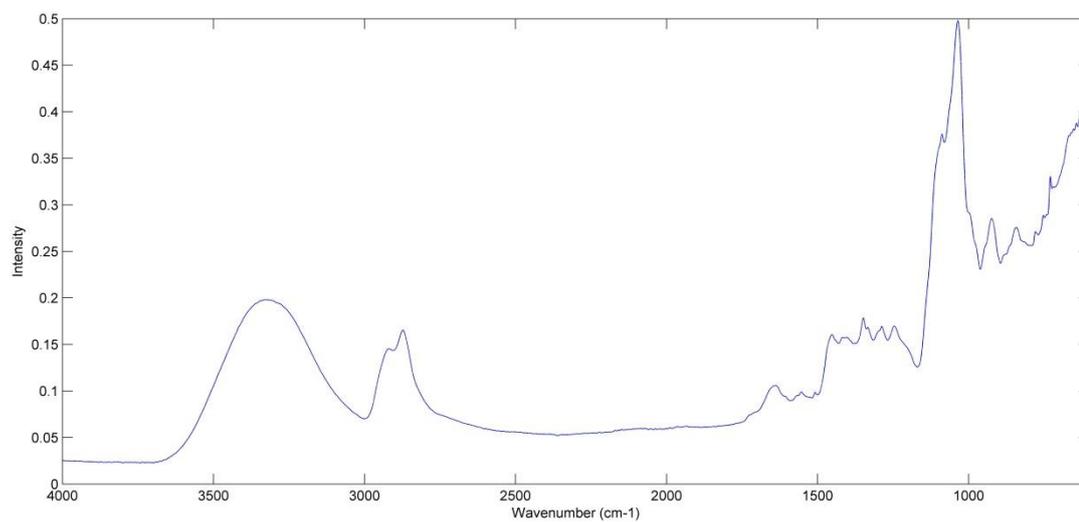


Figure 10: Dry WHSmith blue ink

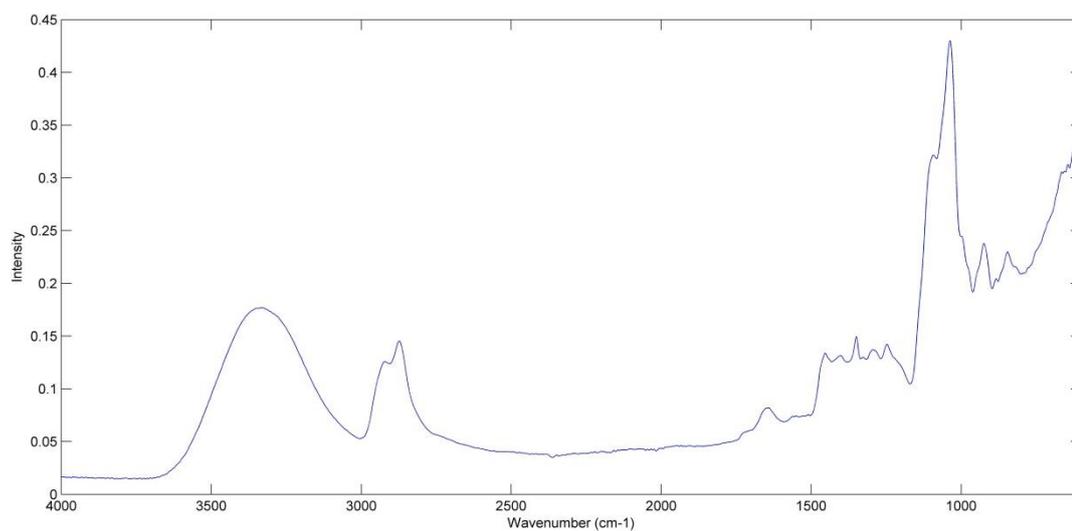


Figure 11: Dry WHSmith brown ink

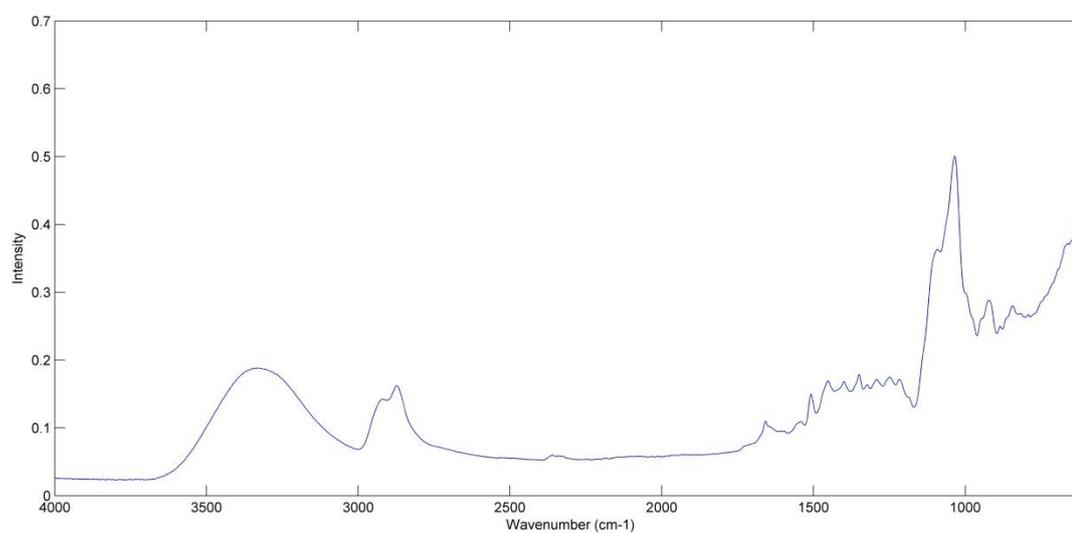


Figure 12: Dry WHSmith gold ink

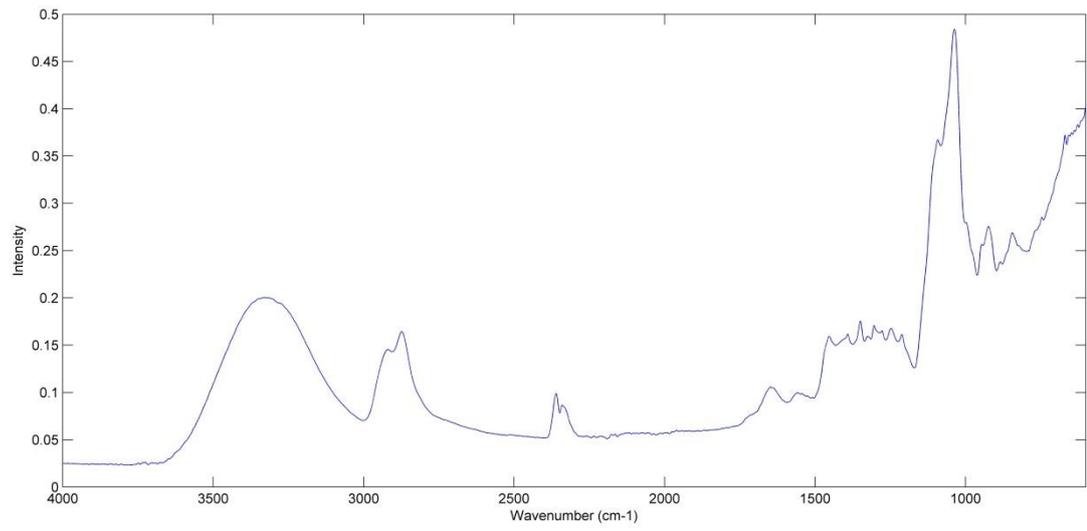


Figure 13: Dry WHSmith green ink

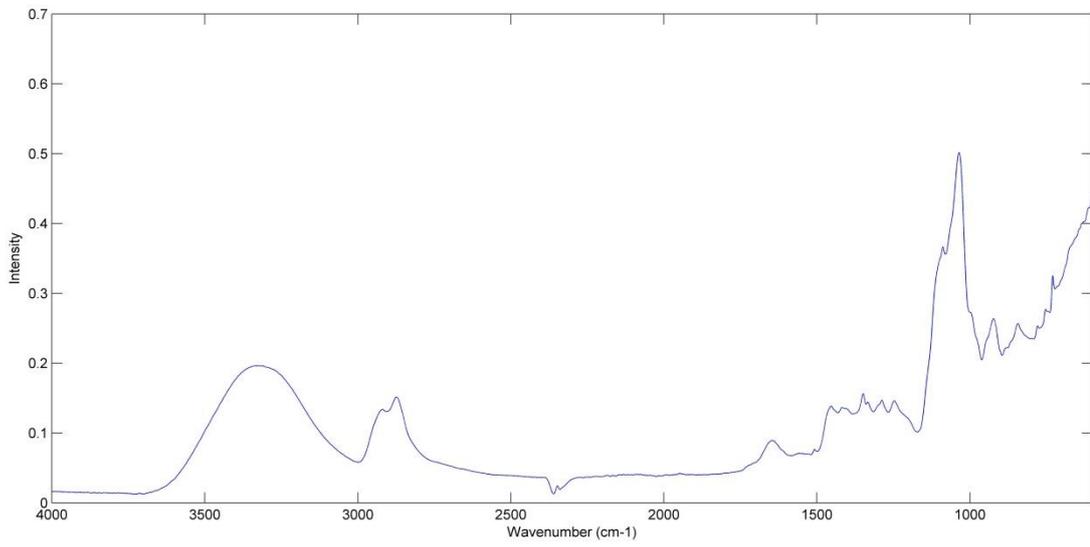


Figure 14: Dry WHSmith light blue ink

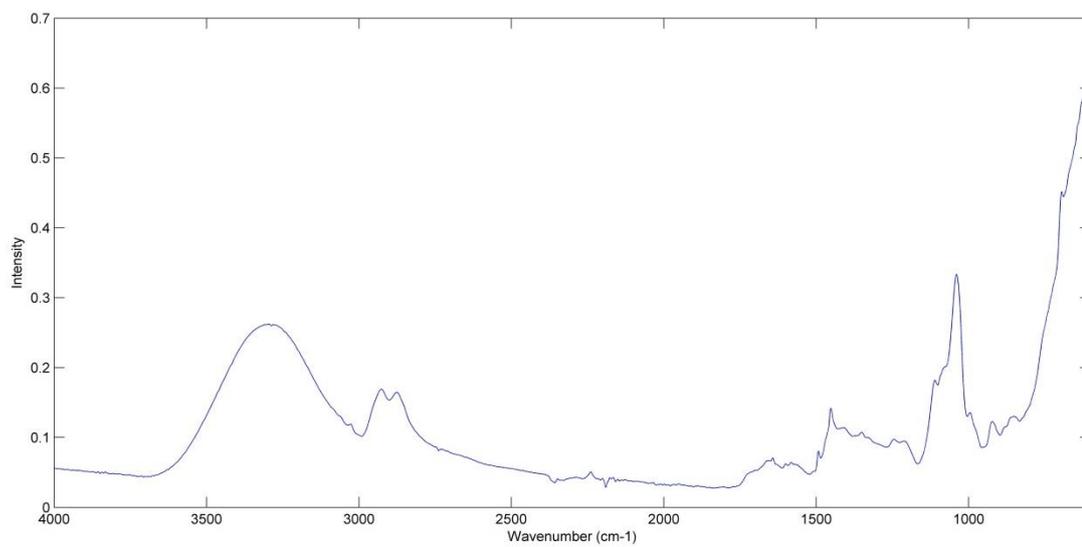


Figure 15: Dry WHSmith lime ink

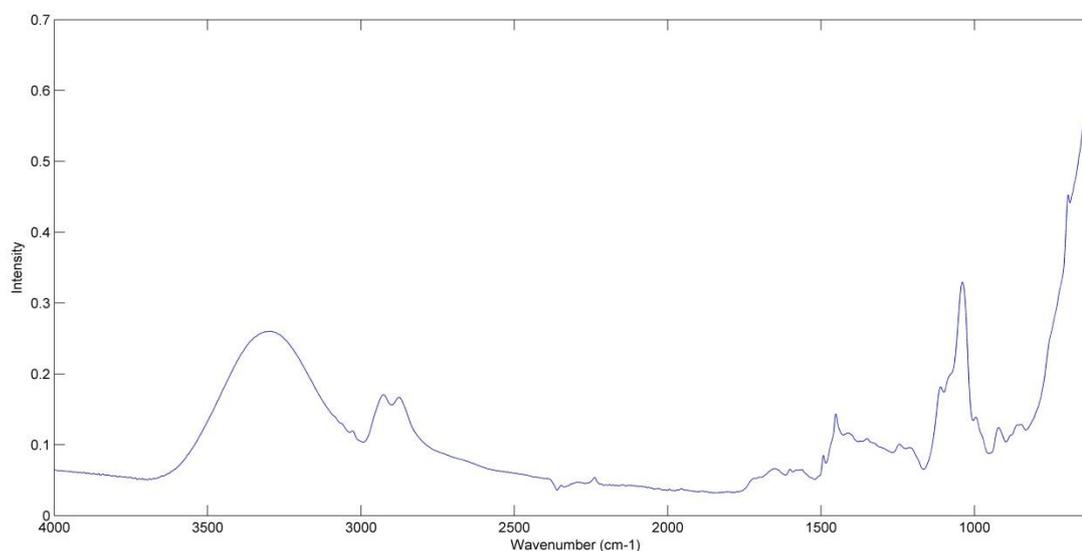


Figure 16: Dry WHSmith orange ink

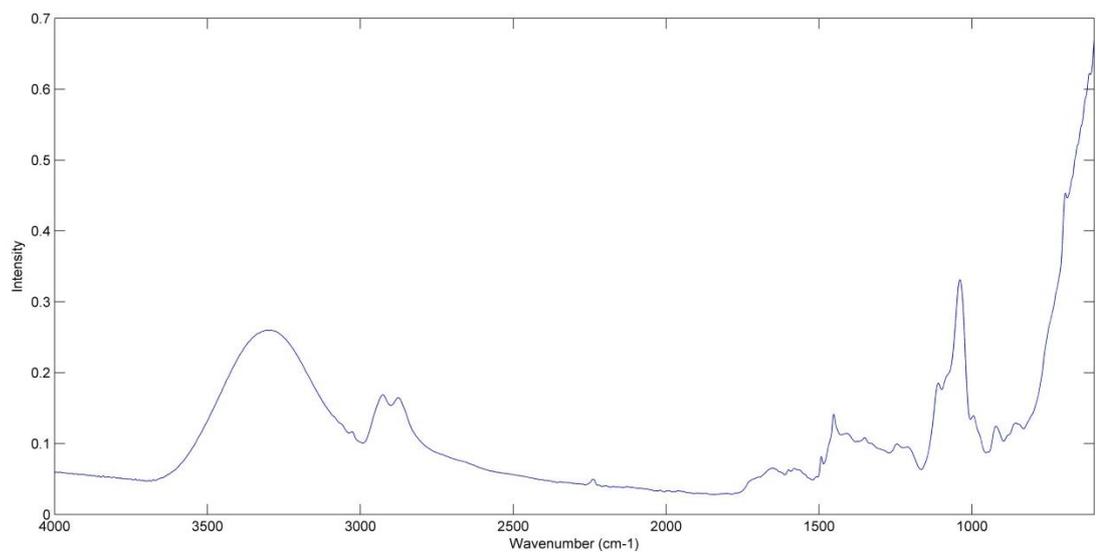


Figure 17: Dry WHSmith peach ink

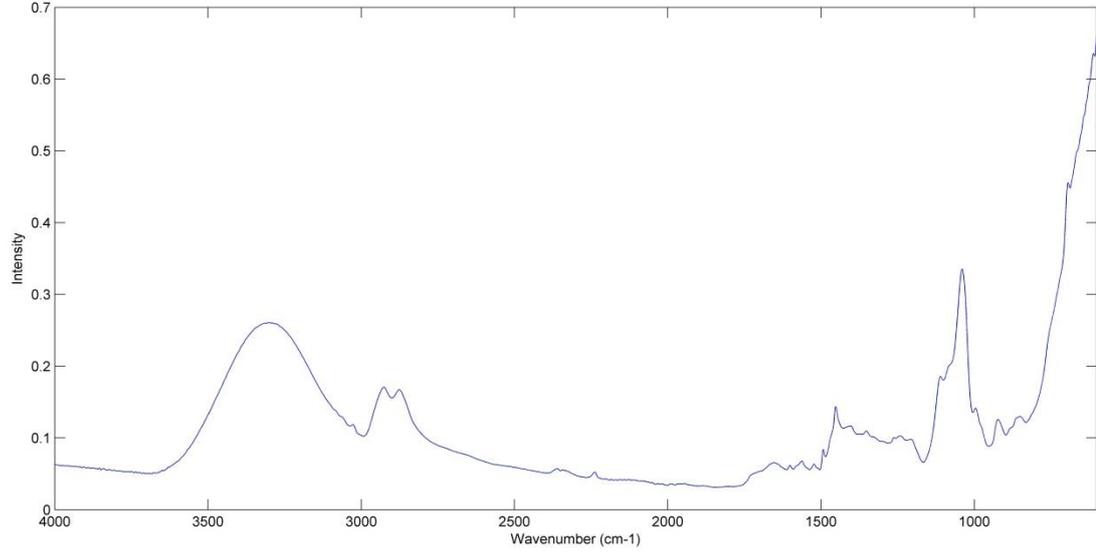


Figure 18: Dry WHSmith pink ink

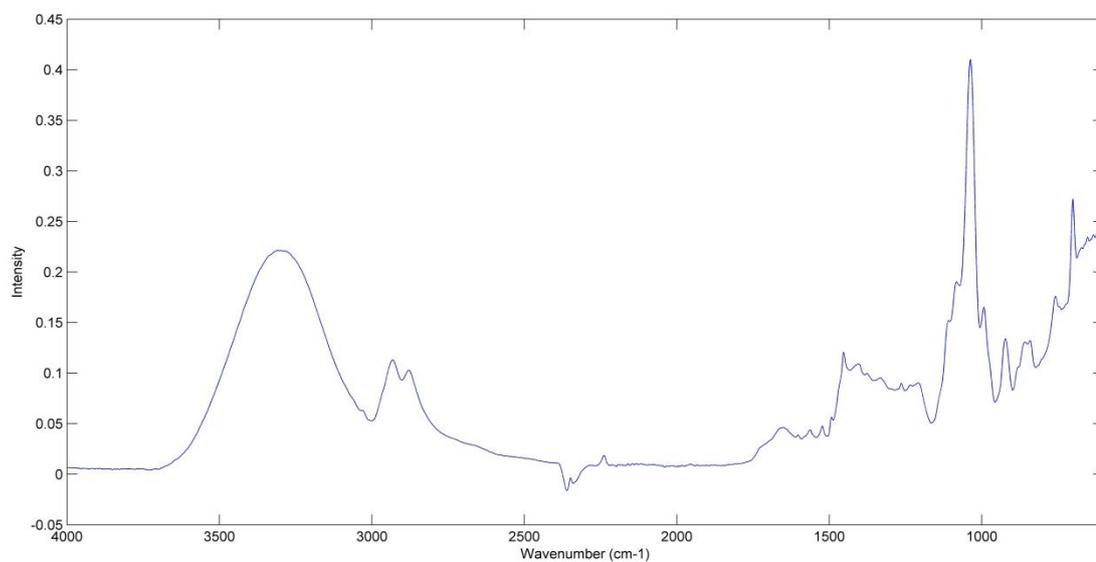


Figure 19: Dry WHSmith purple ink

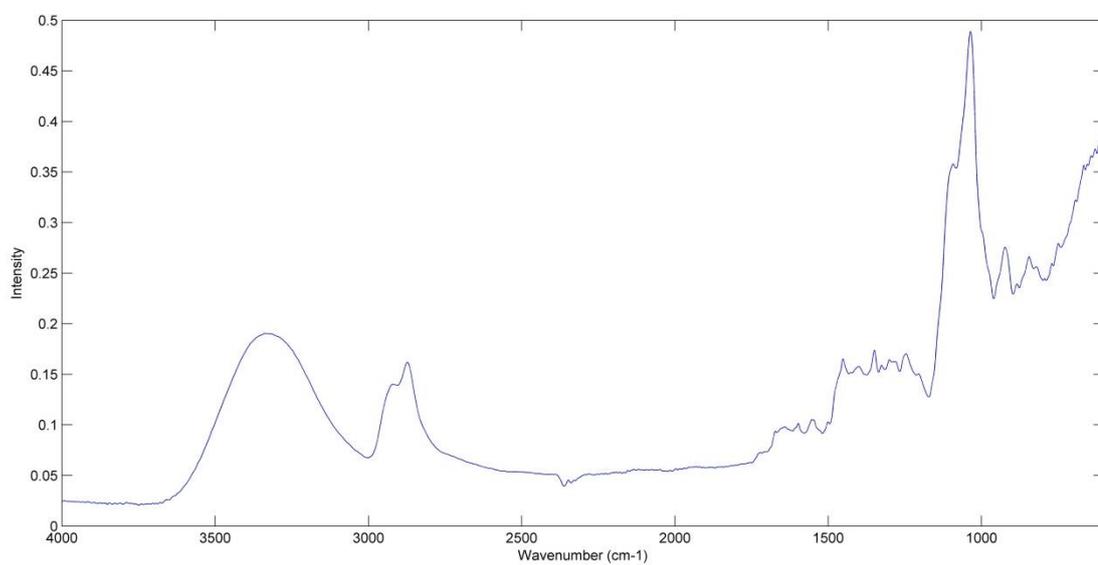


Figure 20: Dry WHSmith silver ink

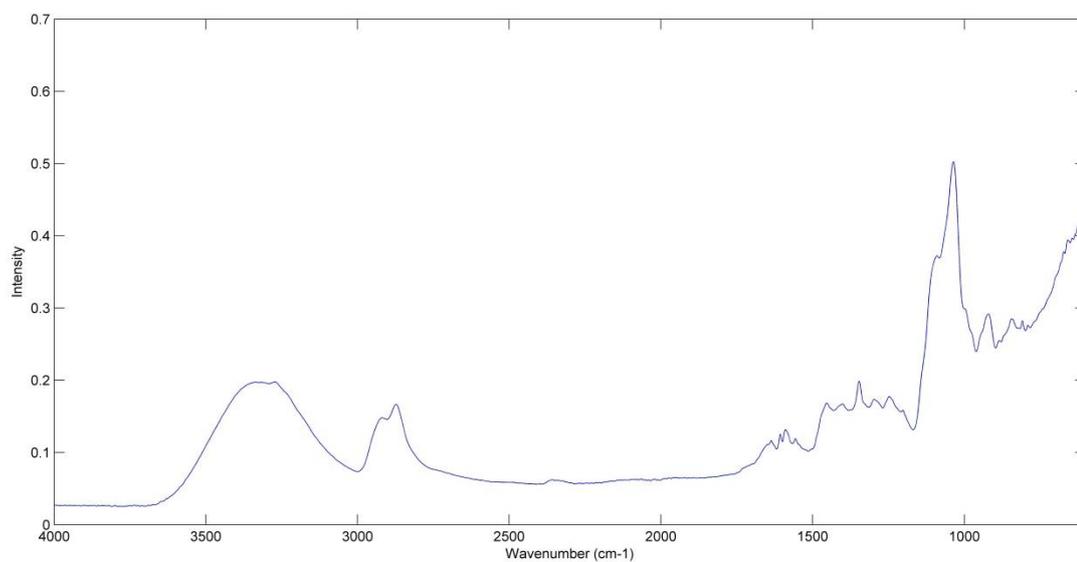


Figure 21: Dry WHSmith violet ink

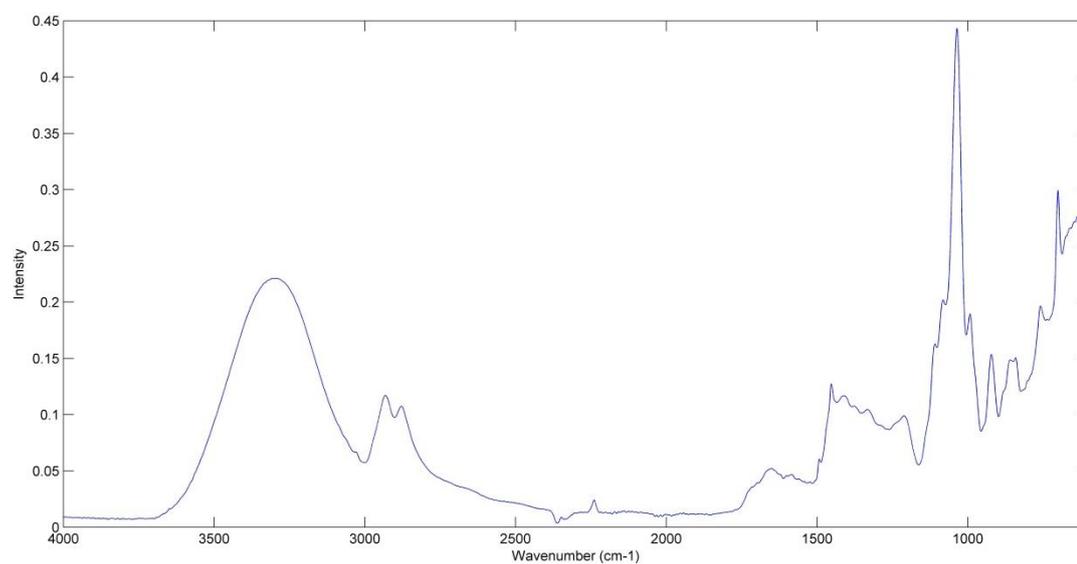


Figure 22: Dry WHSmith yellow ink

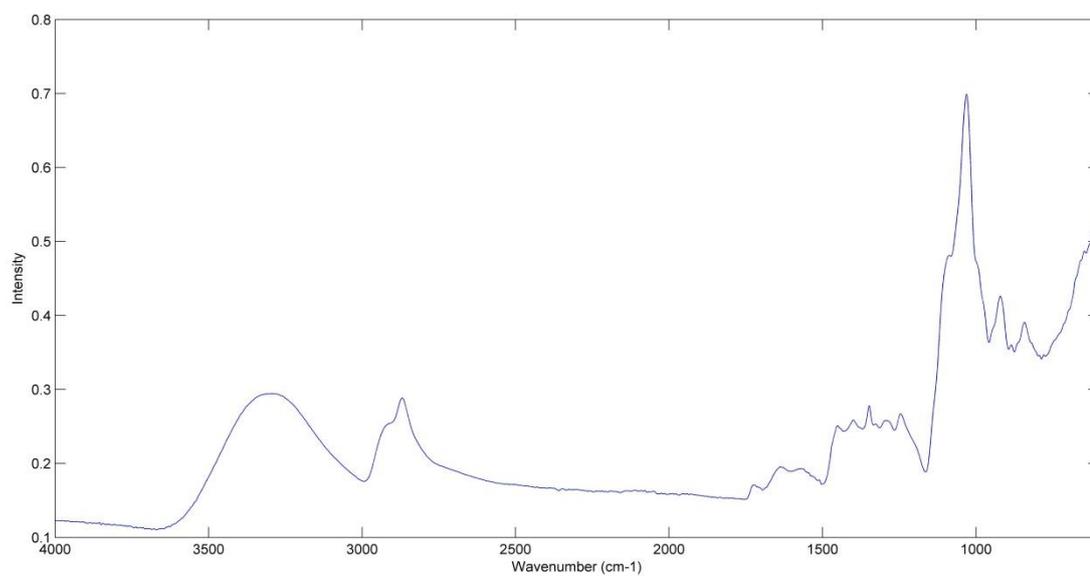


Figure 23: Dry WHSmith glitter black ink

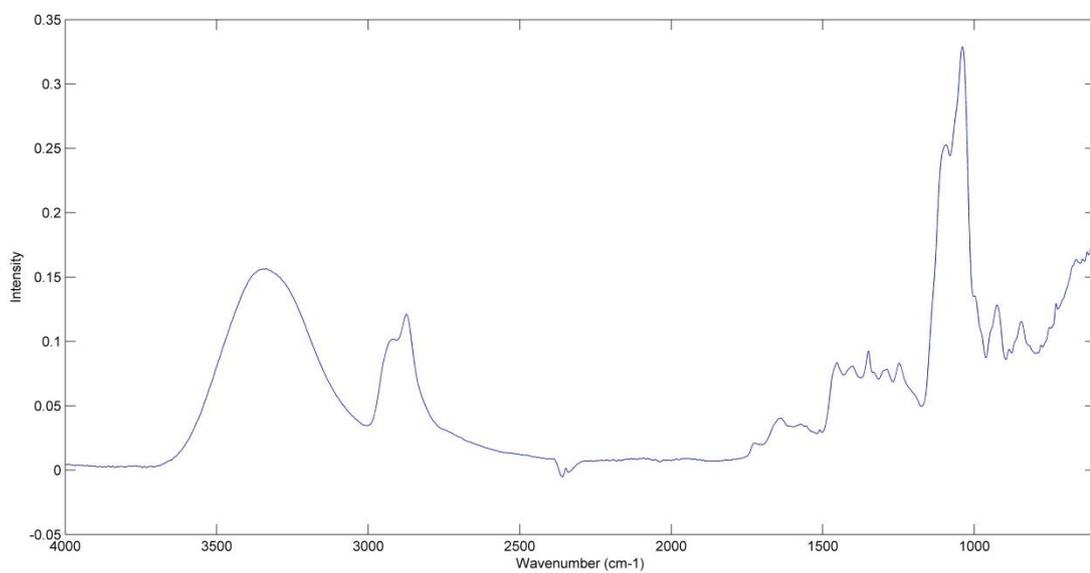


Figure 24: Dry WHSmith glitter blue ink

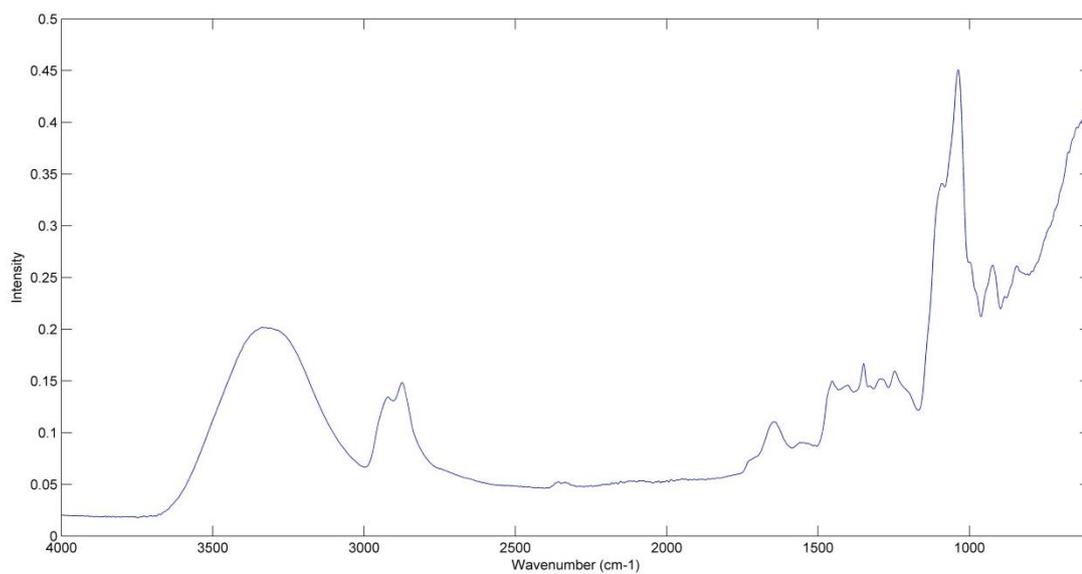


Figure 25: Dry WHSmith glitter gold ink

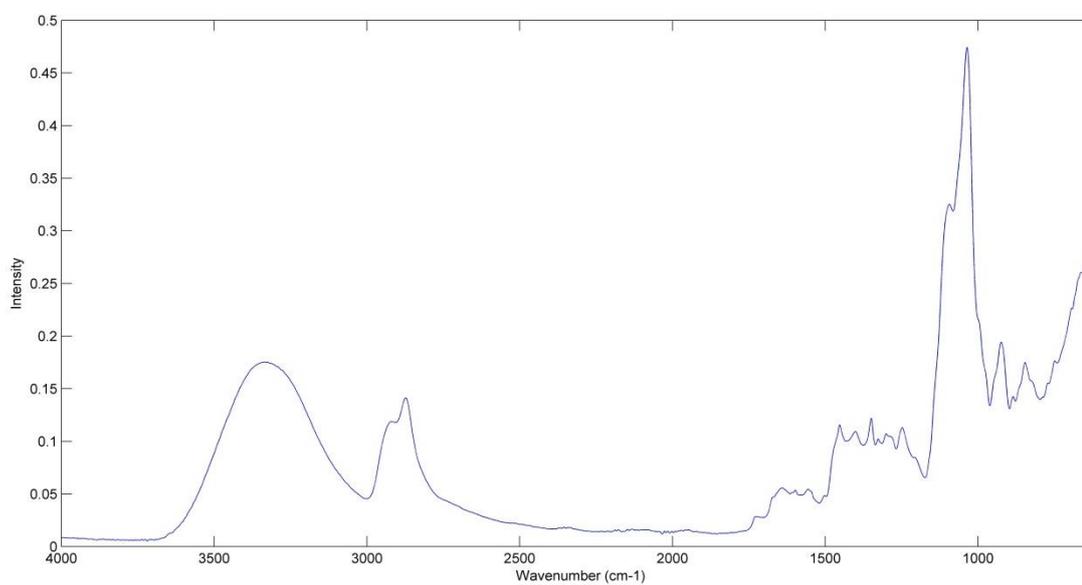


Figure 26: Dry WHSmith glitter green ink

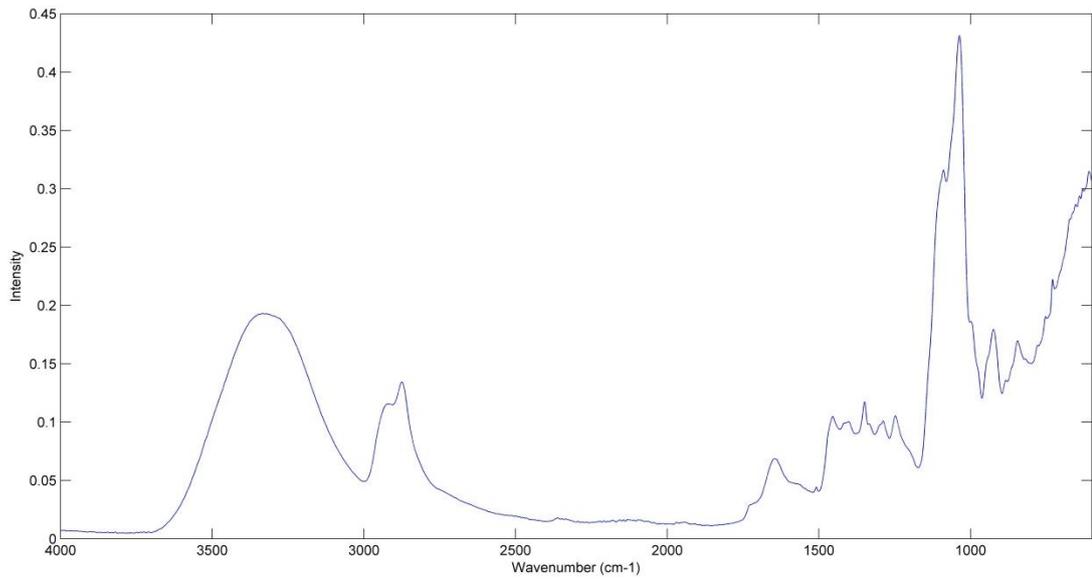


Figure 27: Dry WHSmith glitter light blue ink

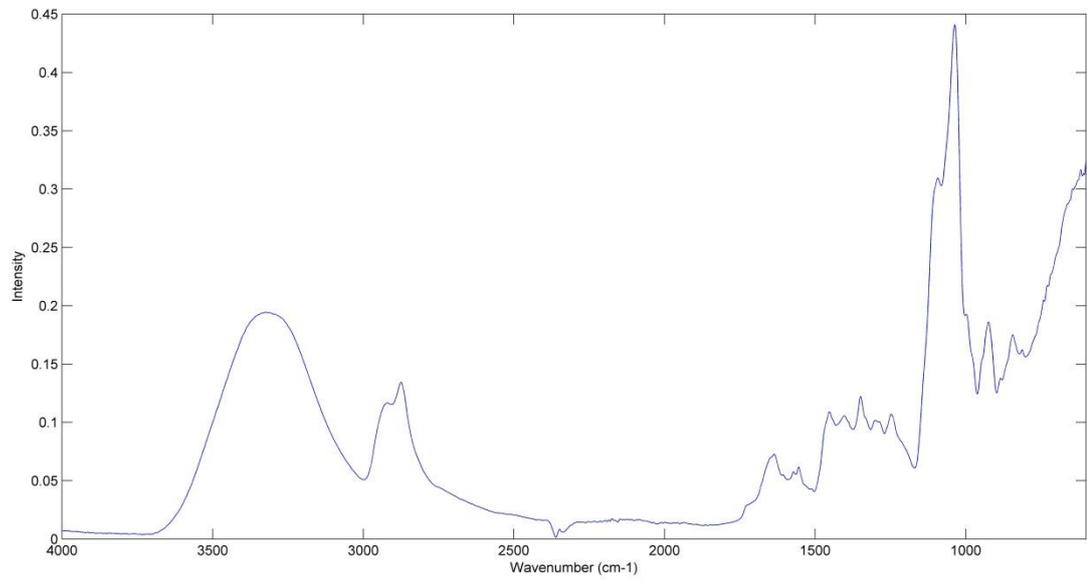


Figure 28: Dry WHSmith glitter orange ink

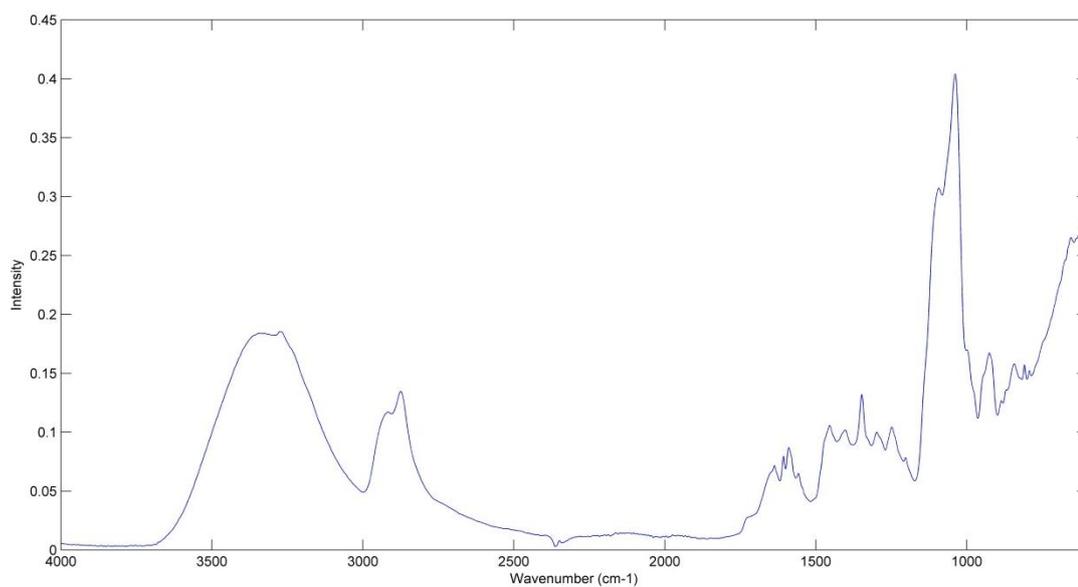


Figure 29: Dry WHSmith glitter pink ink

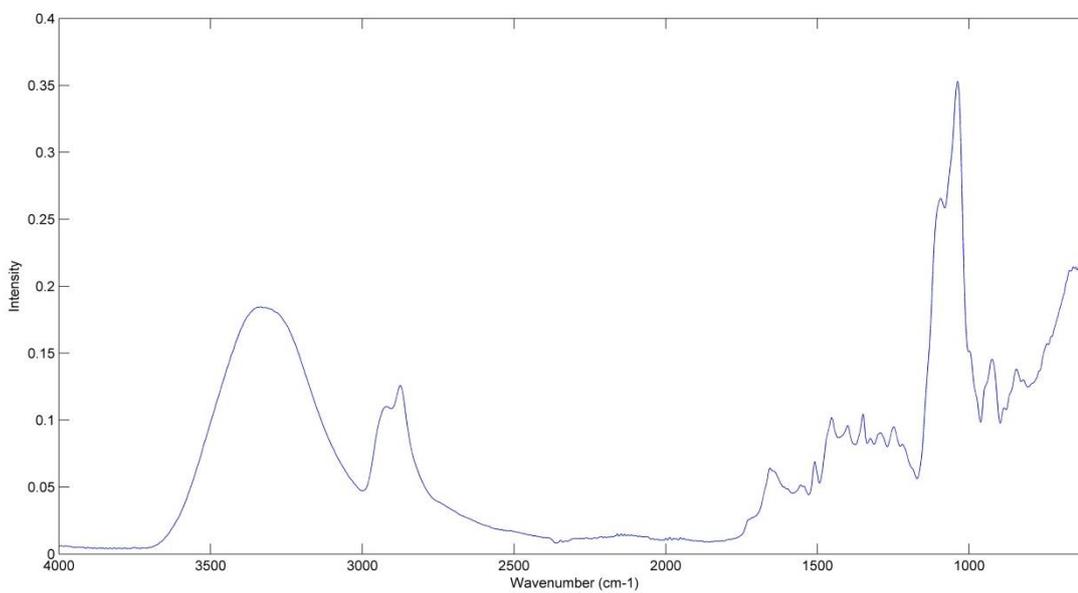


Figure 30: Dry WHSmith glitter purple ink

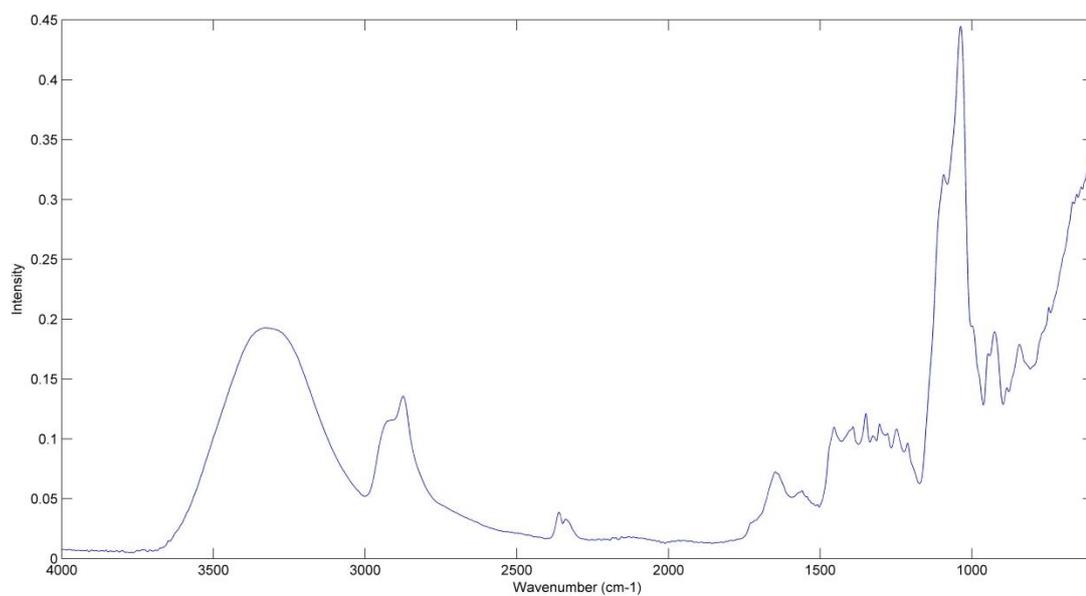


Figure 31: Dry WHSmith glitter red ink

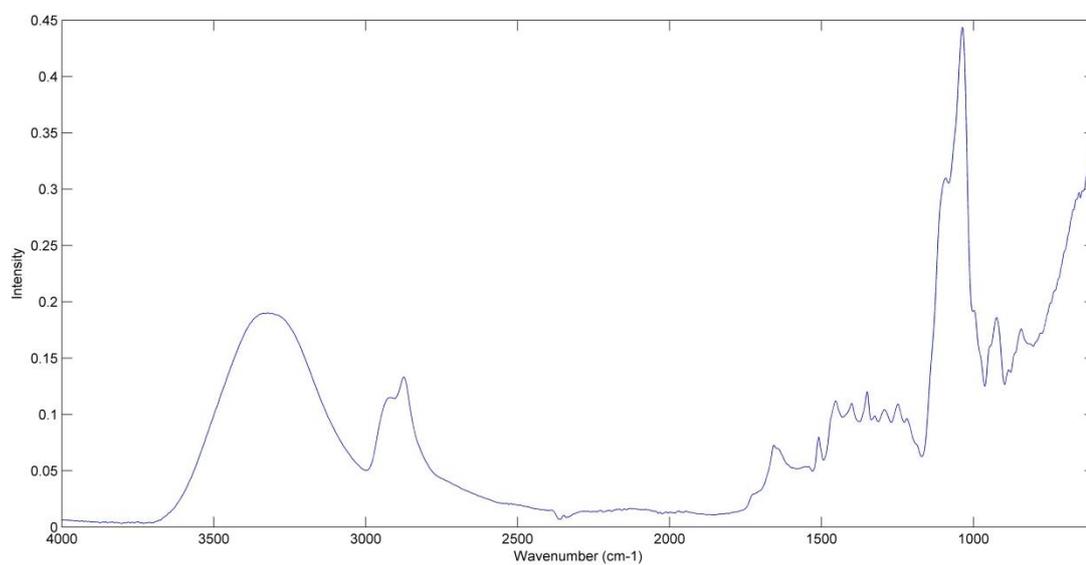


Figure 32: Dry WHSmith glitter silver ink

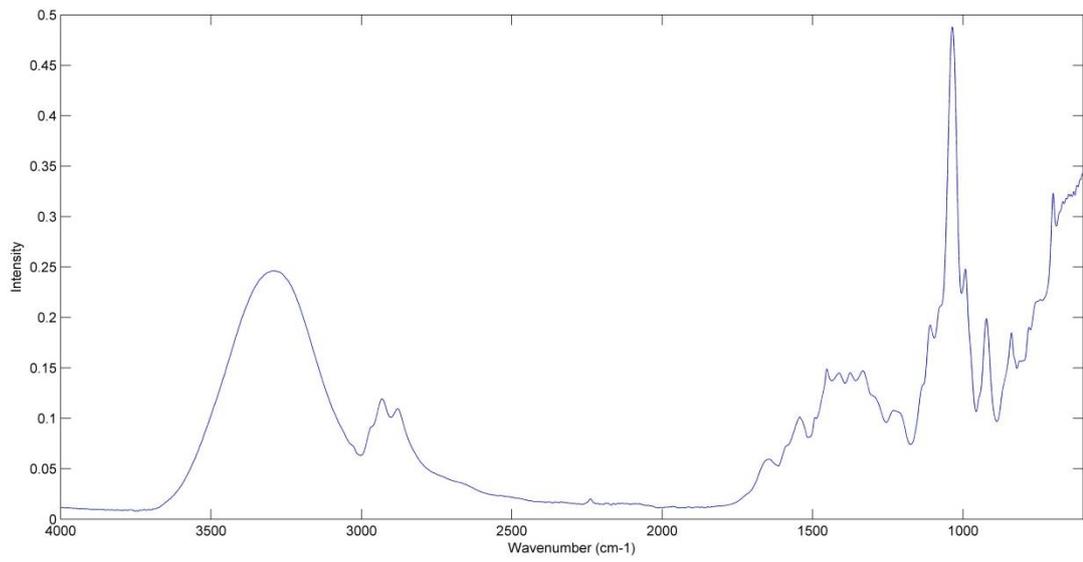


Figure 33: Dry Wilko green ink

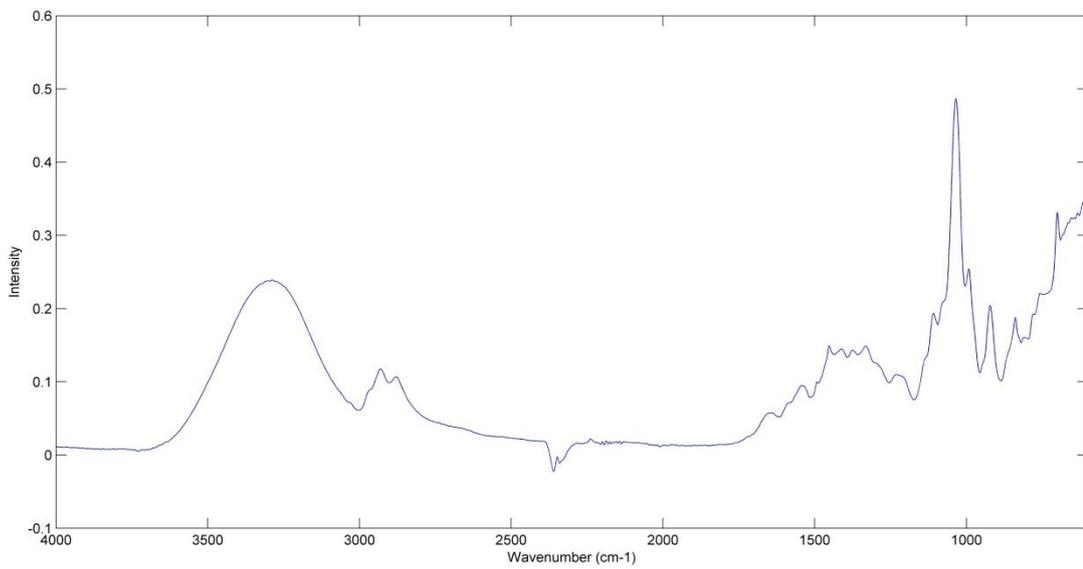


Figure 34: Dry Wilko orange ink

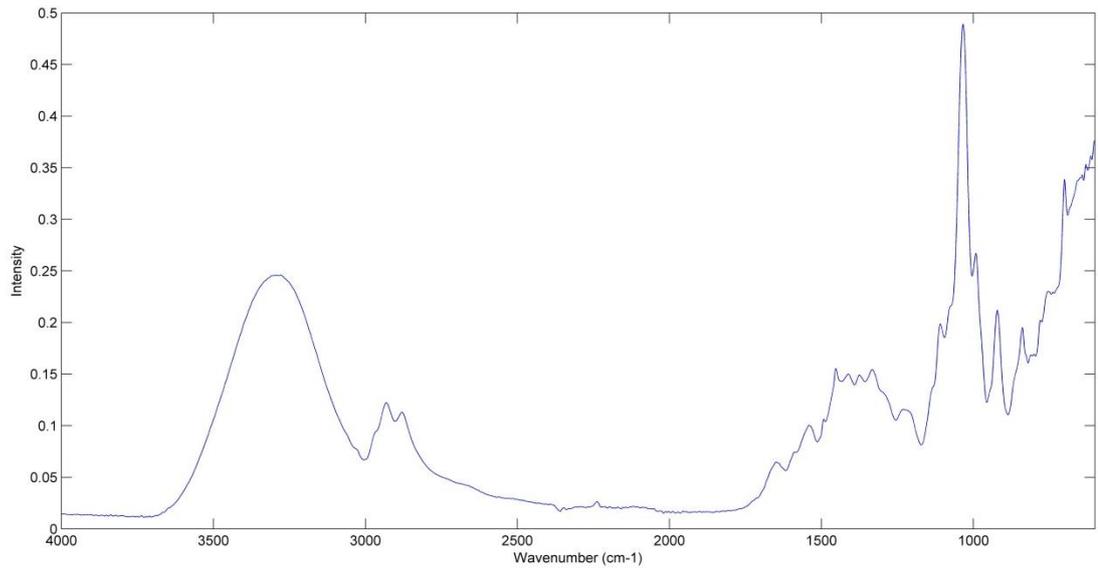


Figure 35: Dry wilko pink ink

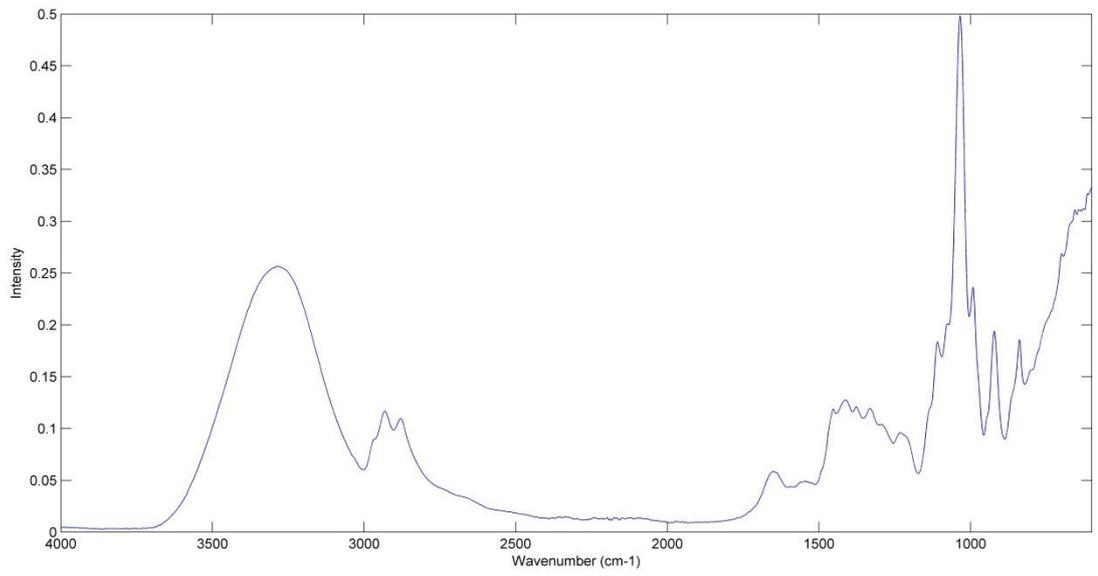


Figure 36: Dry Wilko purple ink

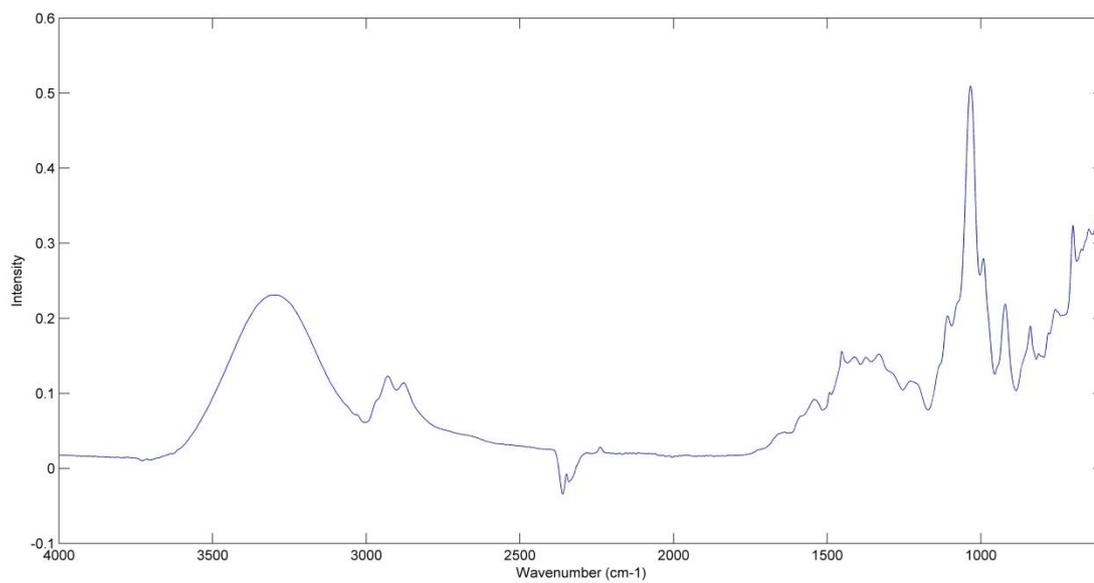


Figure 37: Dry Wilko yellow ink

Appendix D

Appendix D contains a collection of spectra comparing between the spectrum of paper, dried ink and ink written on paper for each of the inks.

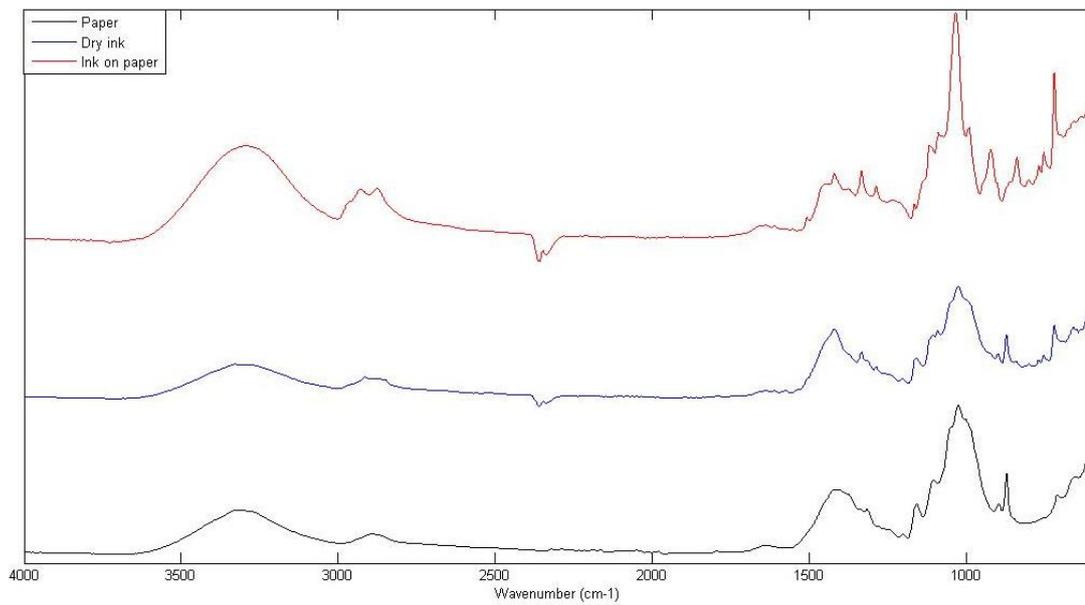


Figure 1: Comparison between paper, ink on paper and dry ink for Club blue ink

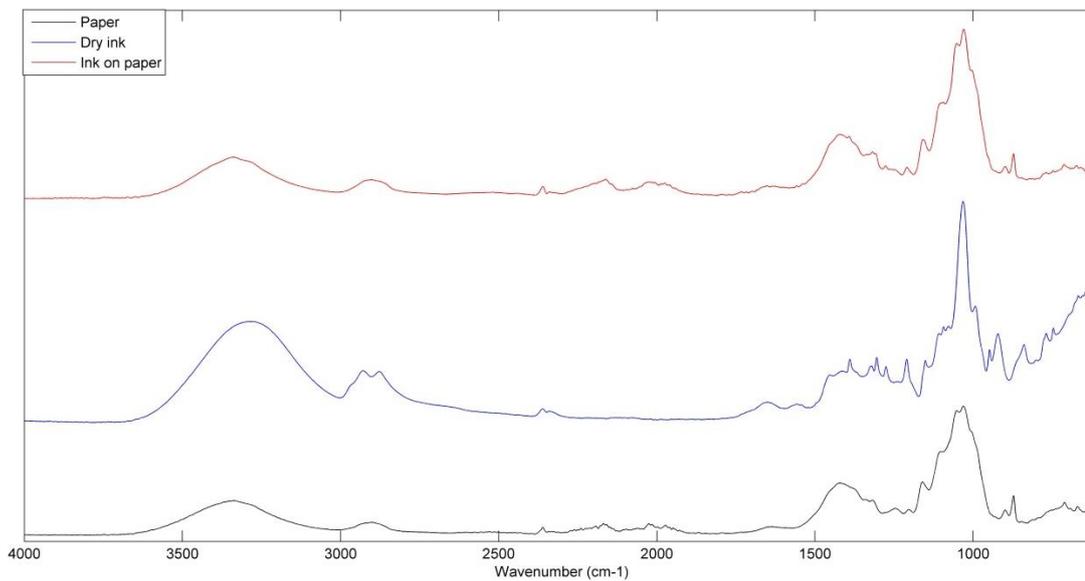


Figure 2: Comparison between paper, ink on paper and dry ink for Club green ink

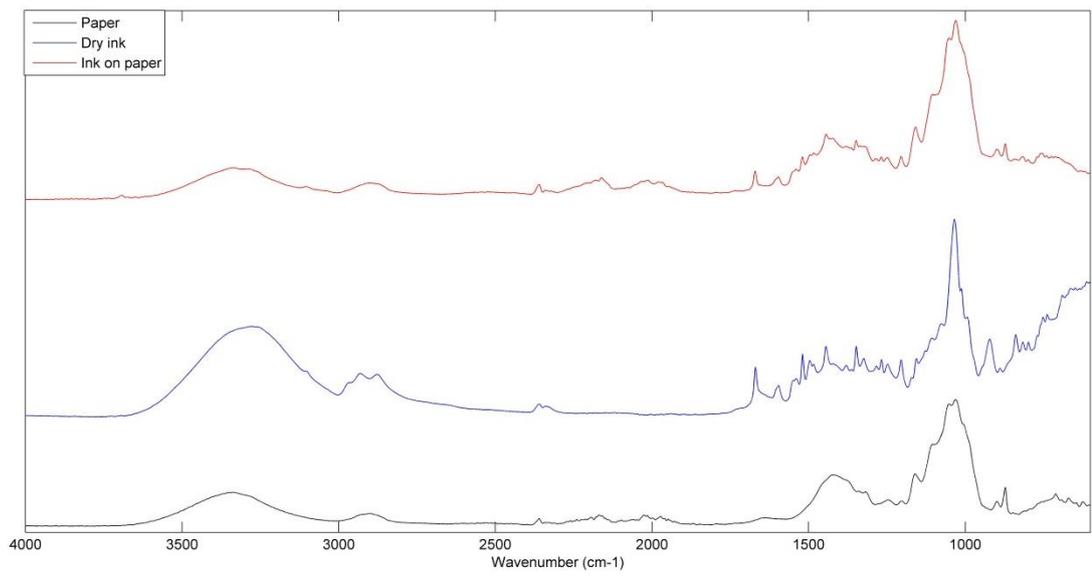


Figure 3: Comparison between paper, ink on paper and dry ink for Club red ink

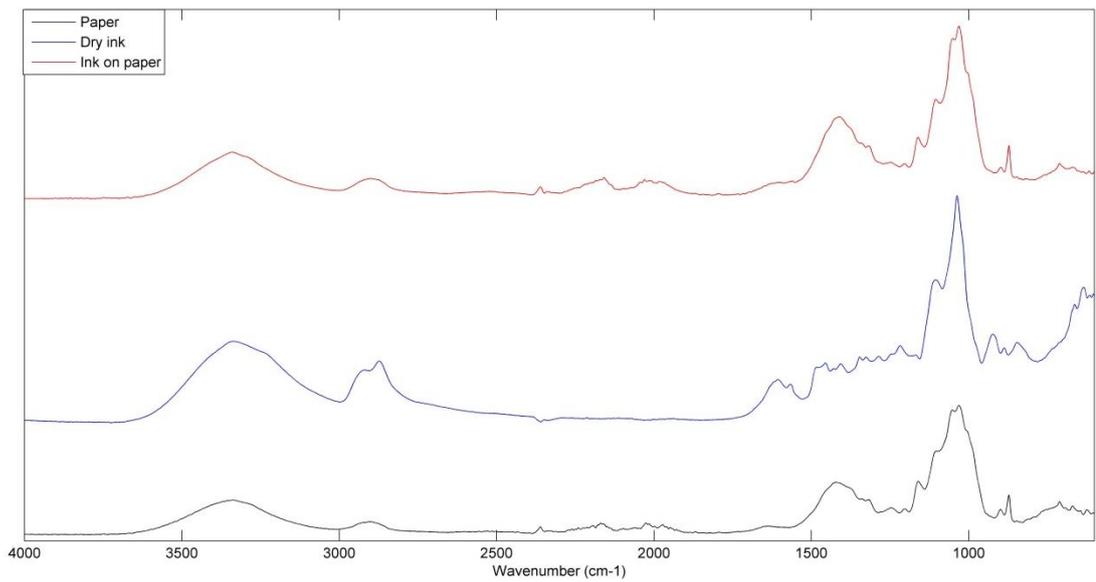


Figure 4: Comparison between paper, ink on paper and dry ink for Papermate black ink

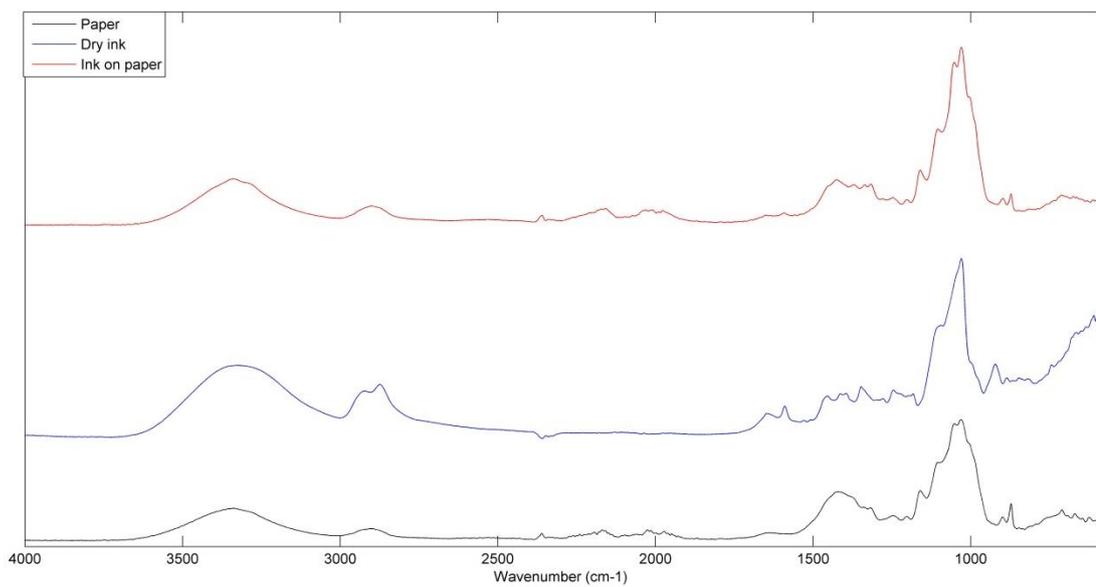


Figure 5: Comparison between paper, ink on paper and dry ink for Papermate blue ink

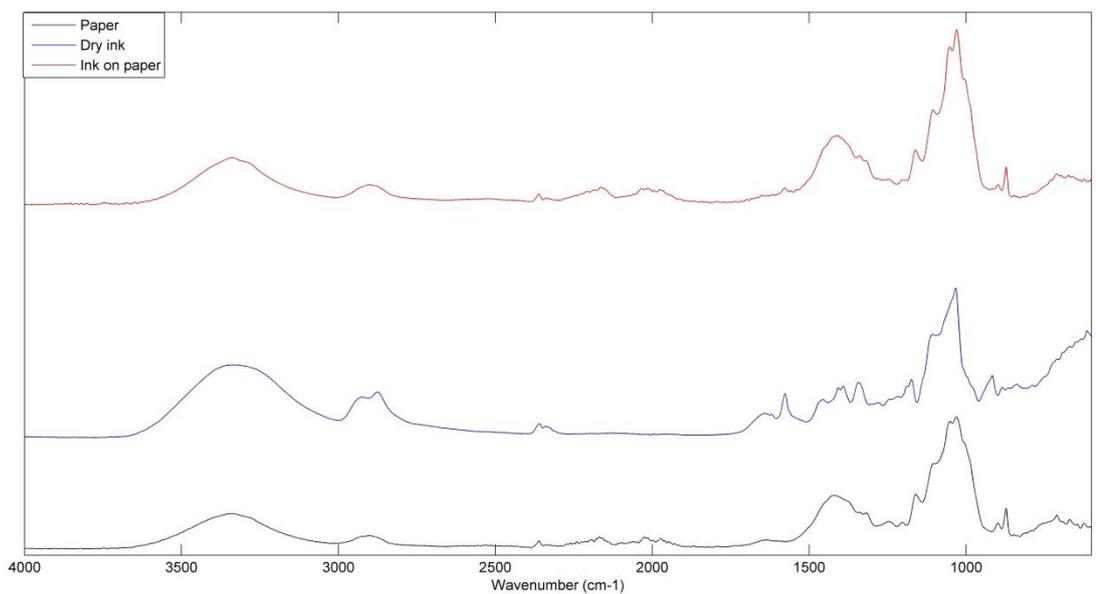


Figure 6: Comparison between paper, ink on paper and dry ink for Papermate green ink

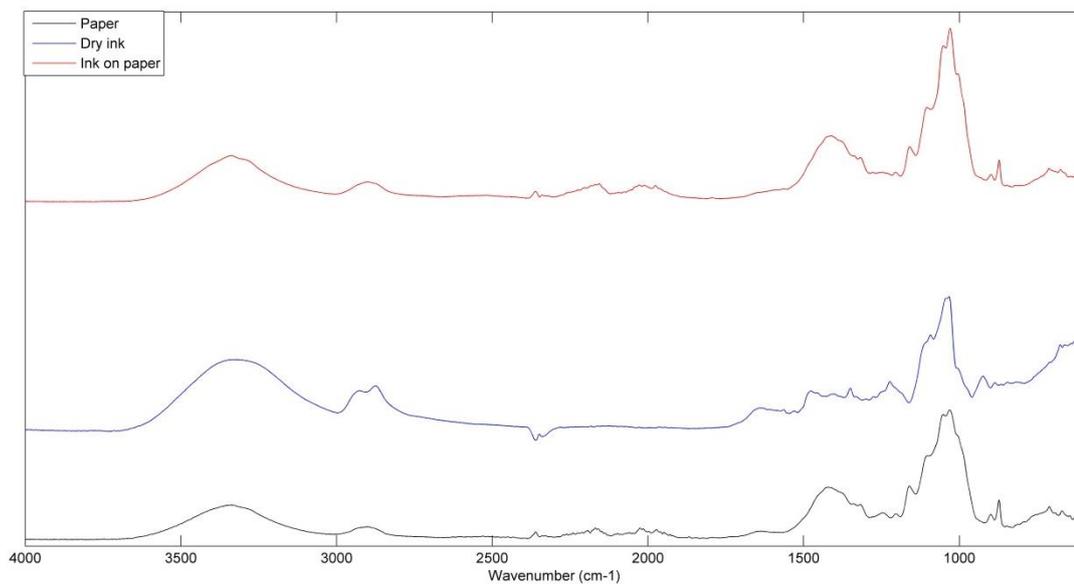


Figure 7: Comparison between paper, ink on paper and dry ink for Papermate red ink

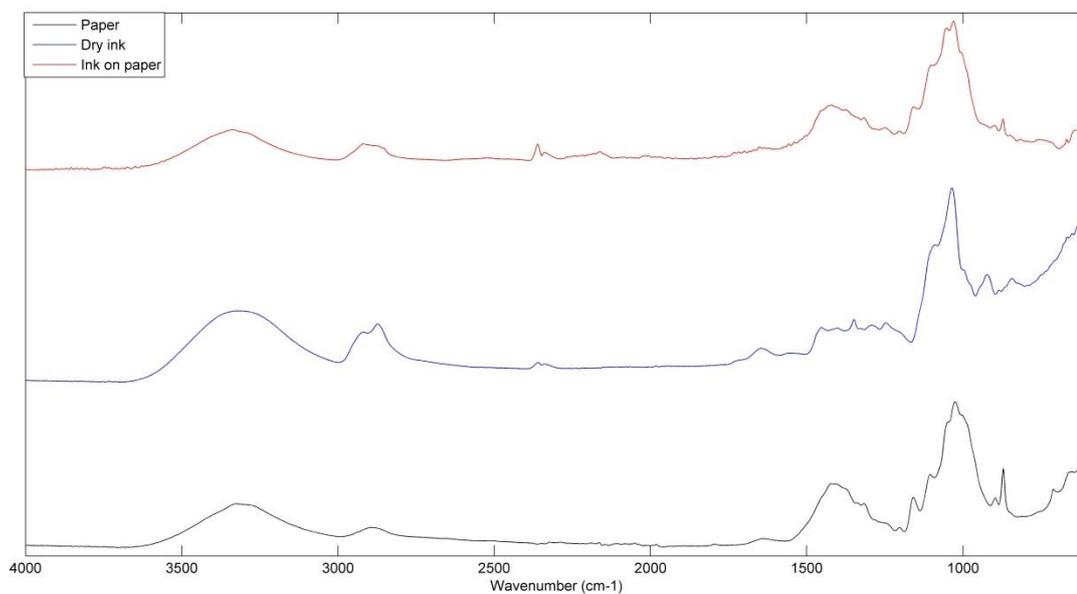


Figure 8: Comparison between paper, ink on paper and dry ink for WHSmith black ink

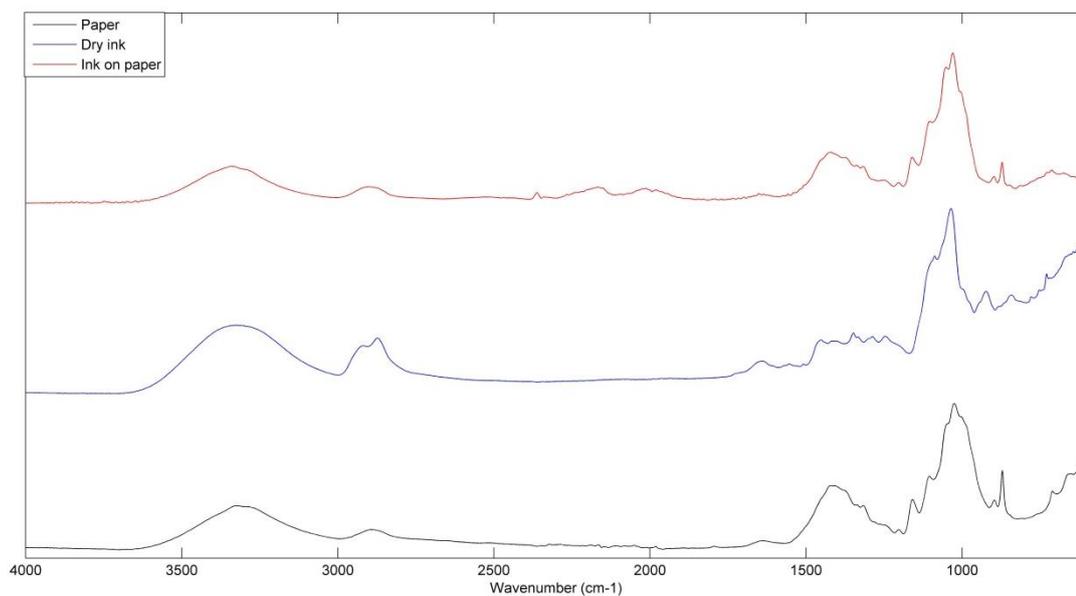


Figure 9: Comparison between paper, ink on paper and dry ink for WHSmith blue ink

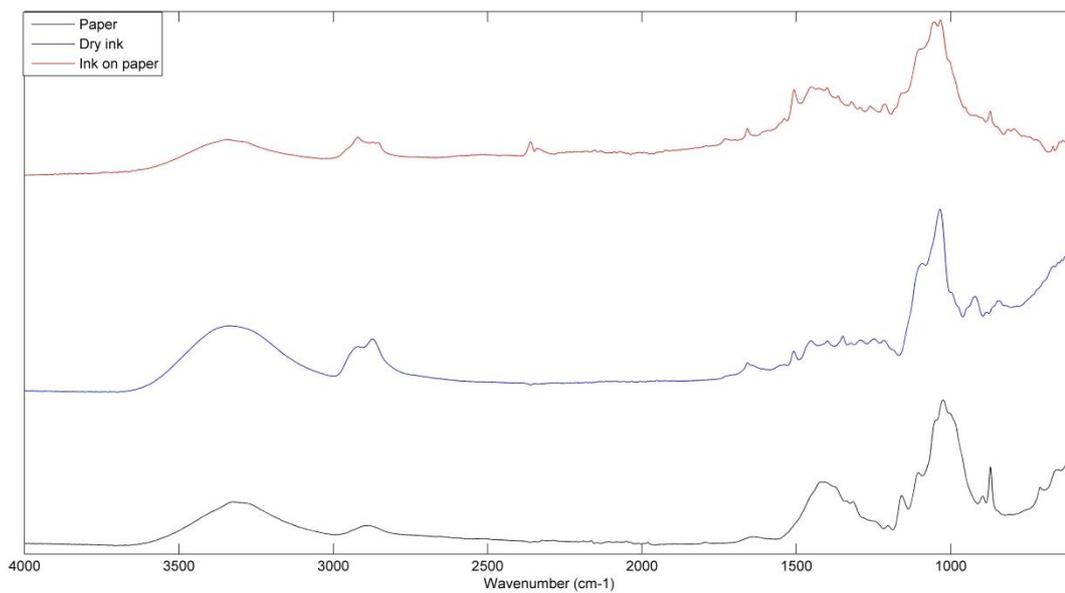


Figure 10: Comparison between paper, ink on paper and dry ink for WHSmith brown ink

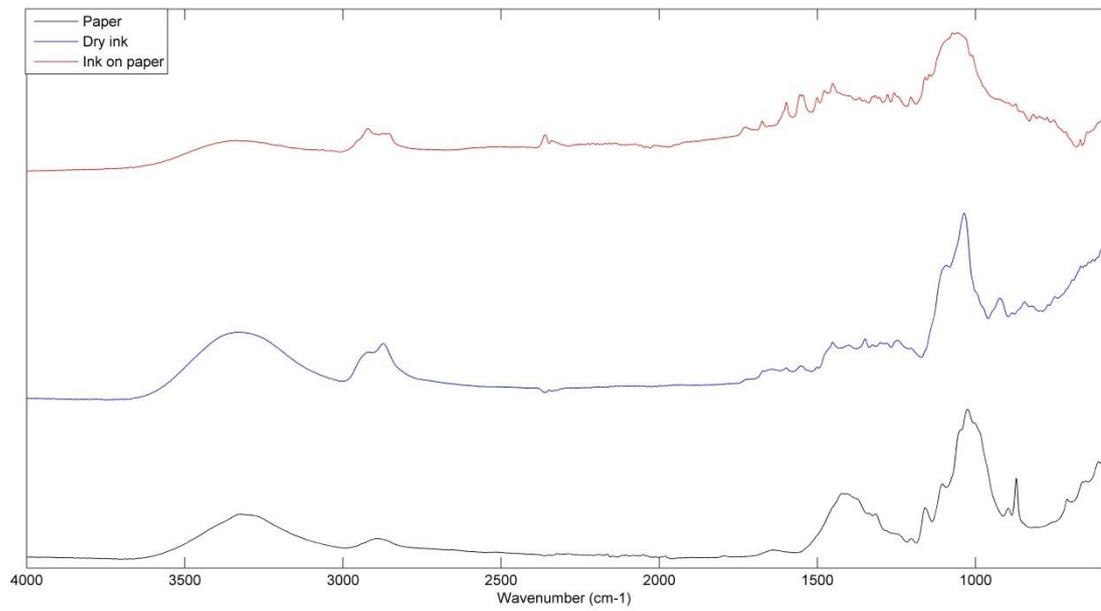


Figure 11: Comparison between paper, ink on paper and dry ink for WHSmith gold ink

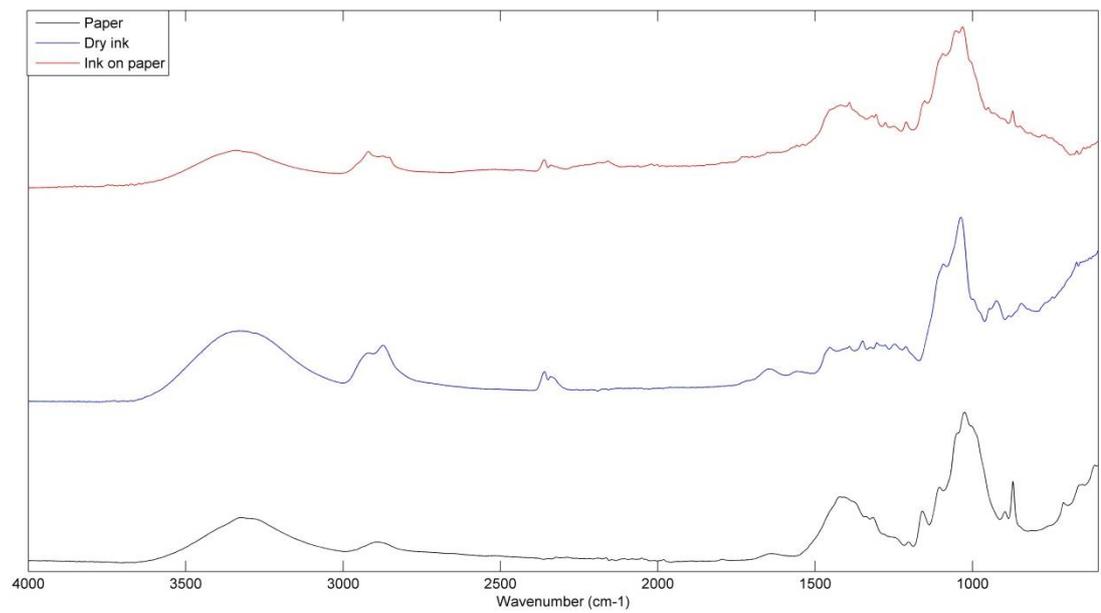


Figure 12: Comparison between paper, ink on paper and dry ink for WHSmith green ink

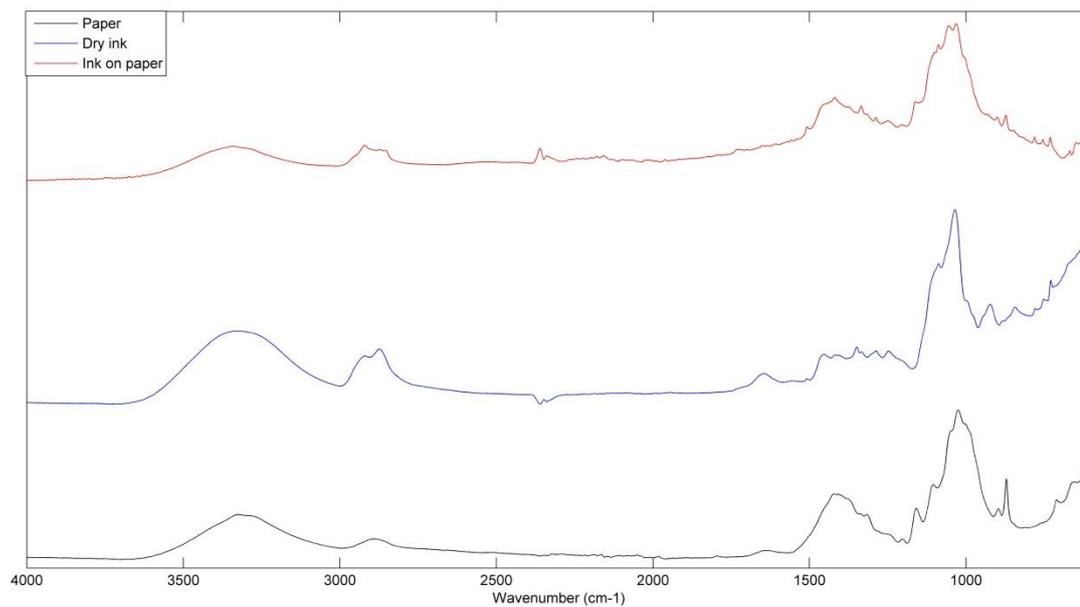


Figure 13: Comparison between paper, ink on paper and dry ink for WHSmith light blue ink

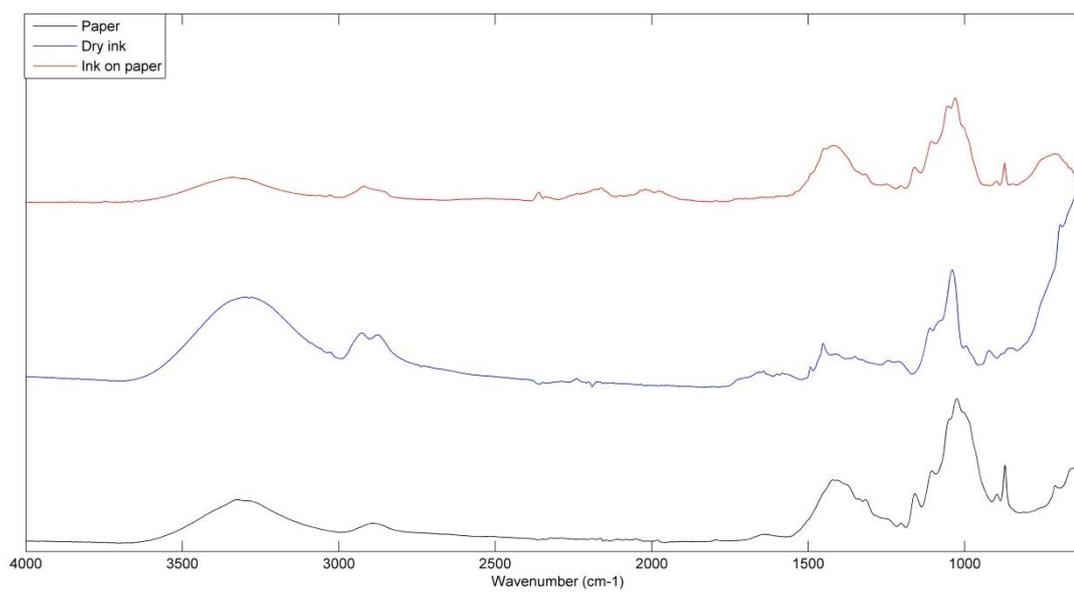


Figure 14: Comparison between paper, ink on paper and dry ink for WHSmith lime

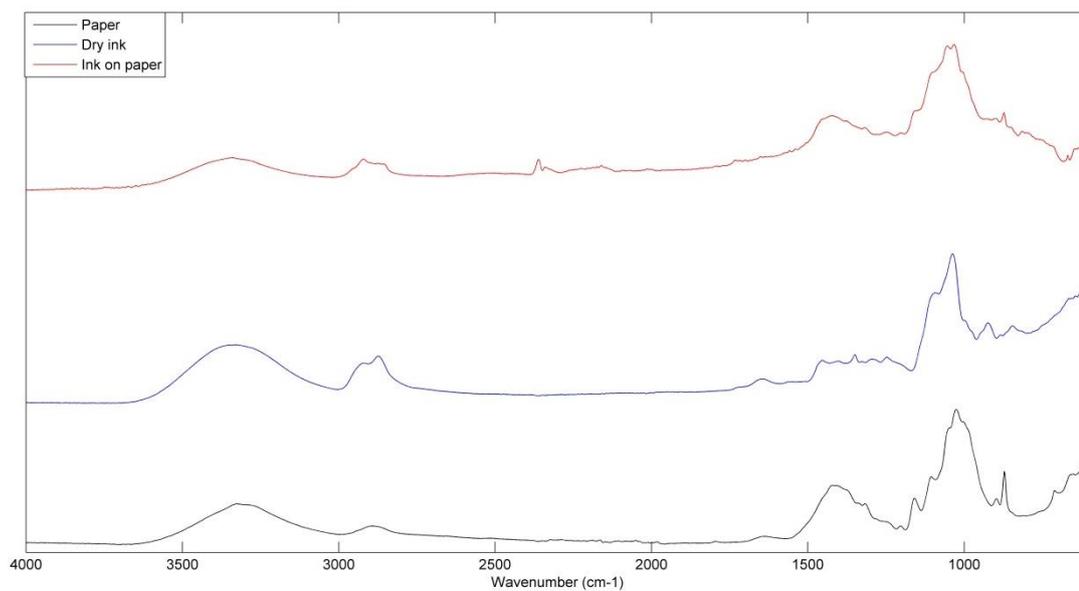


Figure 15: Comparison between paper, ink on paper and dry ink for WHSmith mauve ink

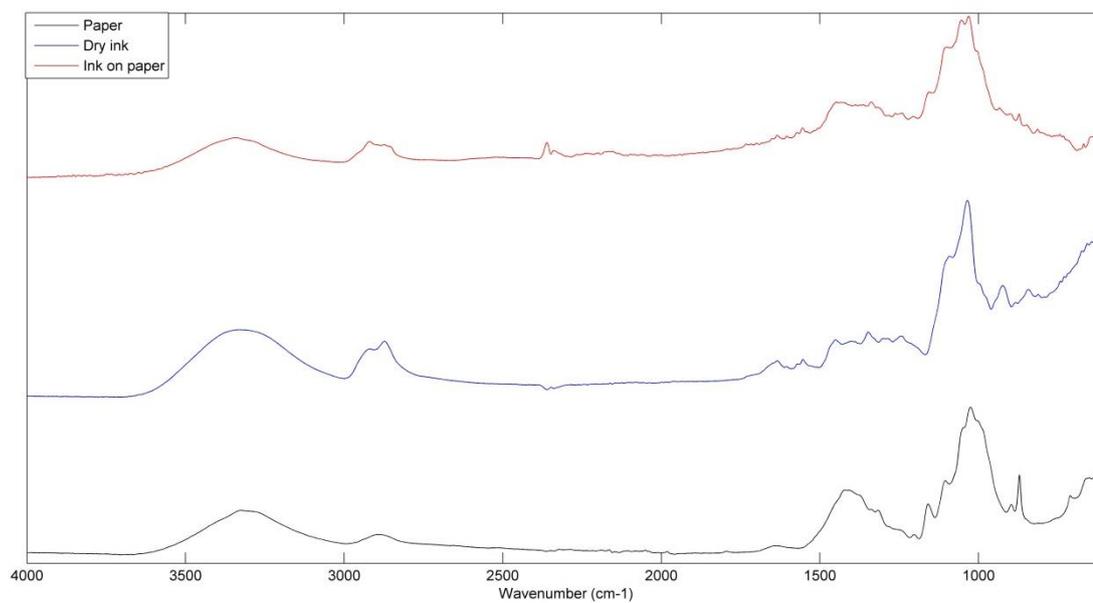


Figure 16: Comparison between paper, ink on paper and dry ink for WHSmith orange ink

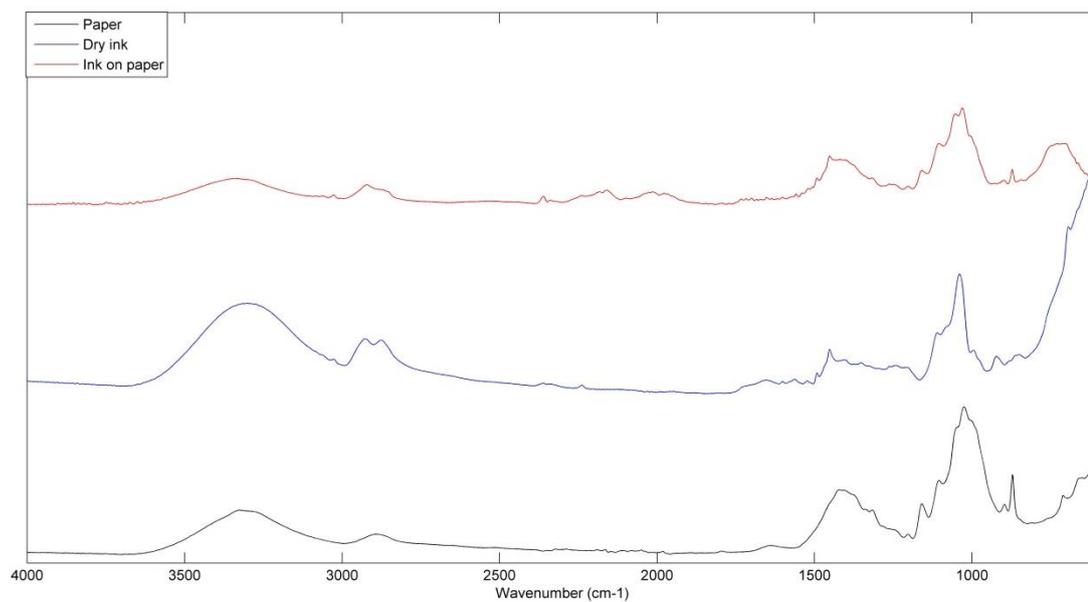


Figure 17: Comparison between paper, ink on paper and dry ink for WHSmith peach ink

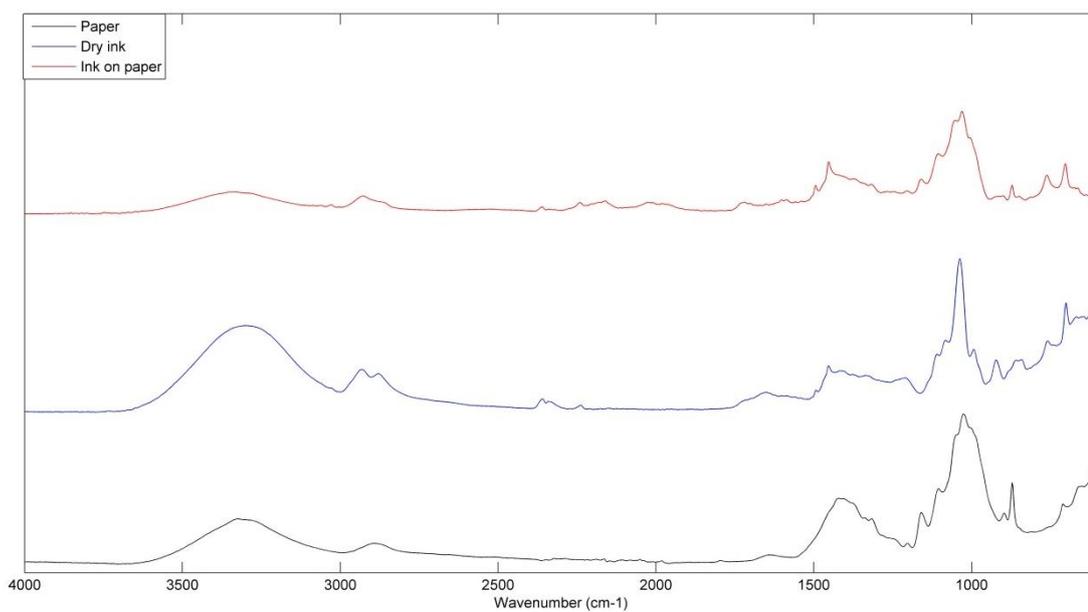


Figure 18: Comparison between paper, ink on paper and dry ink for WHSmith pink ink

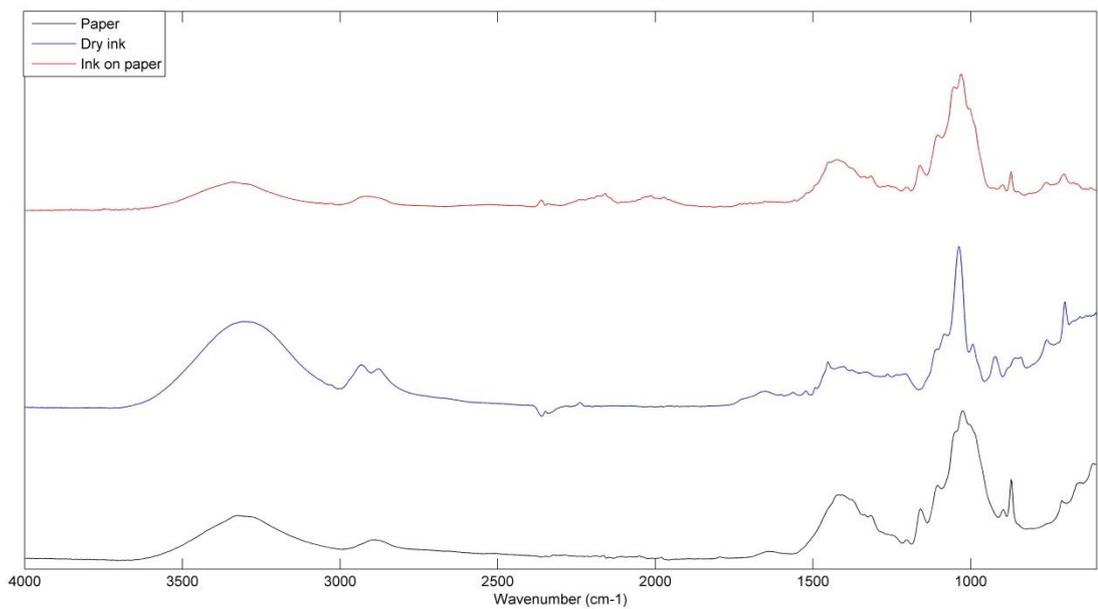


Figure 19: Comparison between paper, ink on paper and dry ink for WHSmith purple ink

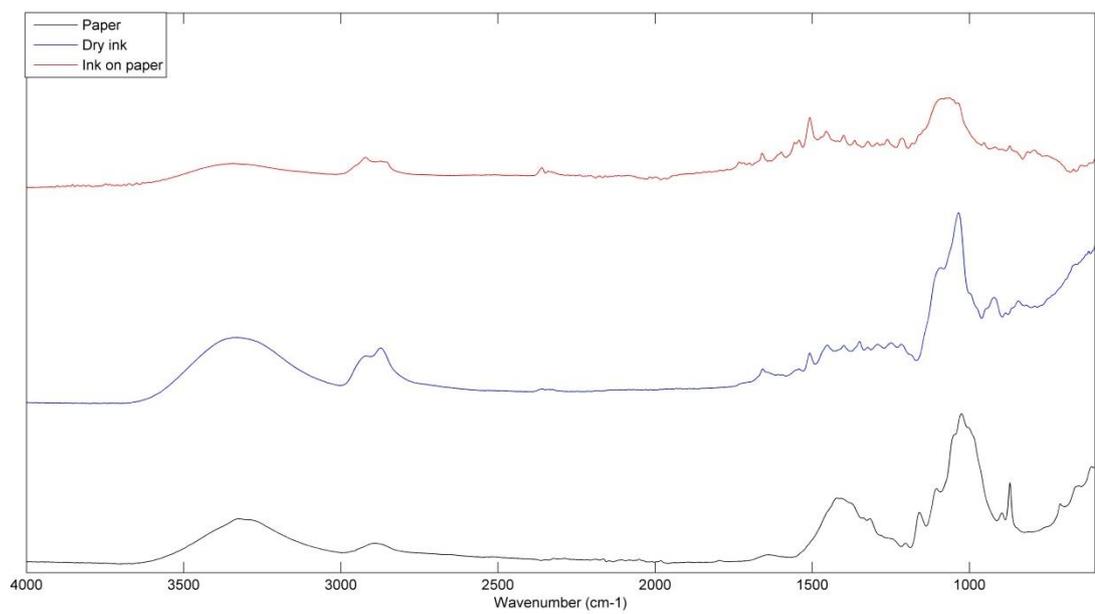


Figure 20: Comparison between paper, ink on paper and dry ink for WHSmith silver ink

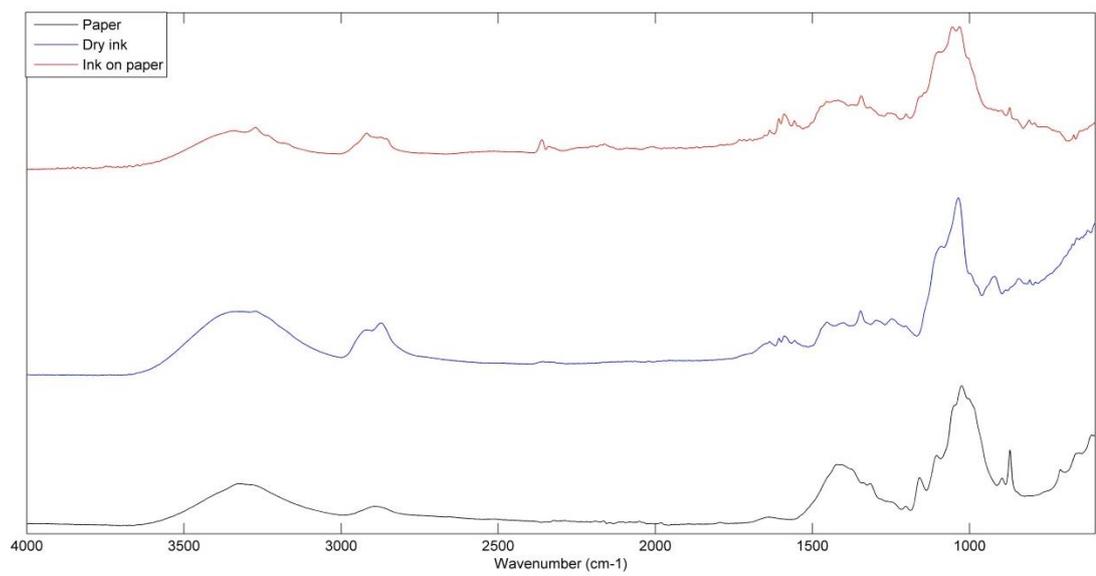


Figure 21: Comparison between paper, ink on paper and dry ink for WHSmith violet ink

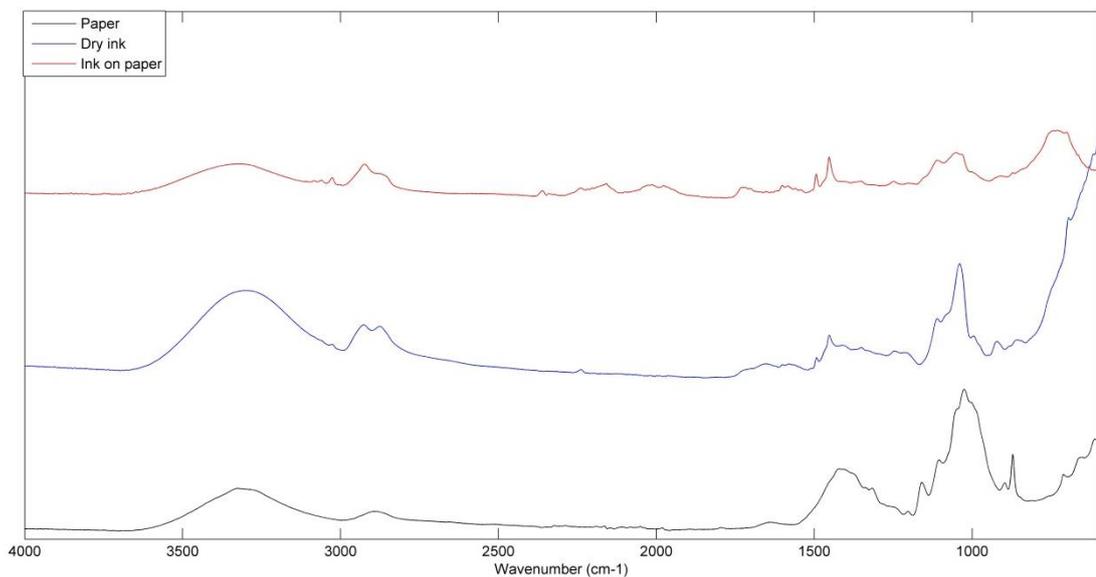


Figure 22: Comparison between paper, ink on paper and dry ink for WHSmith yellow ink

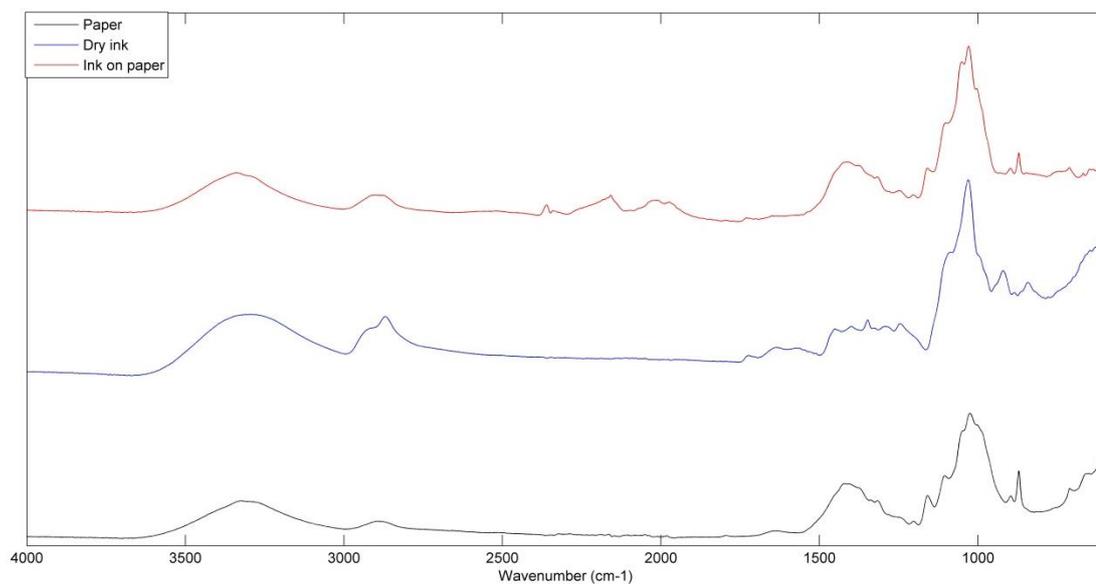


Figure 23: Comparison between paper, ink on paper and dry ink for WHSmith glitter black ink

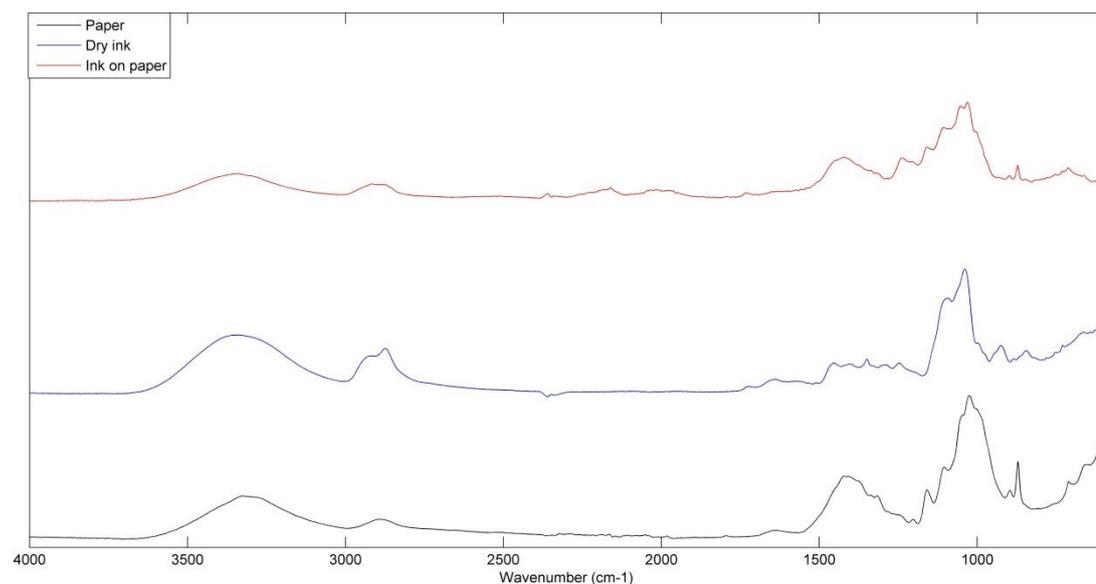


Figure 24: Comparison between paper, ink on paper and dry ink for WHSmith glitter blue ink

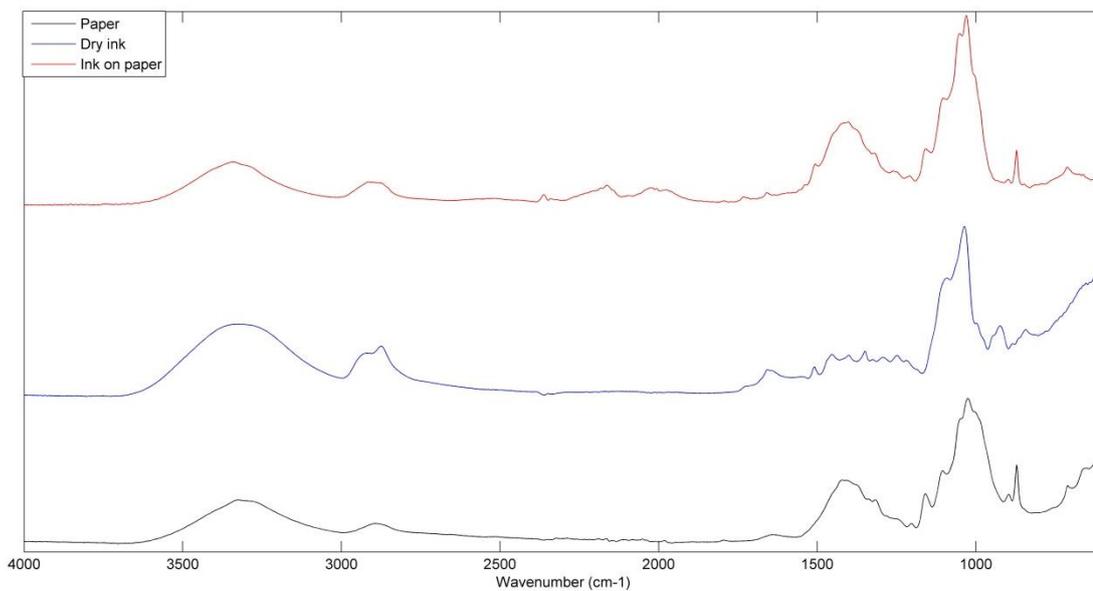


Figure 25: Comparison between paper, ink on paper and dry ink for WHSmith glitter gold ink

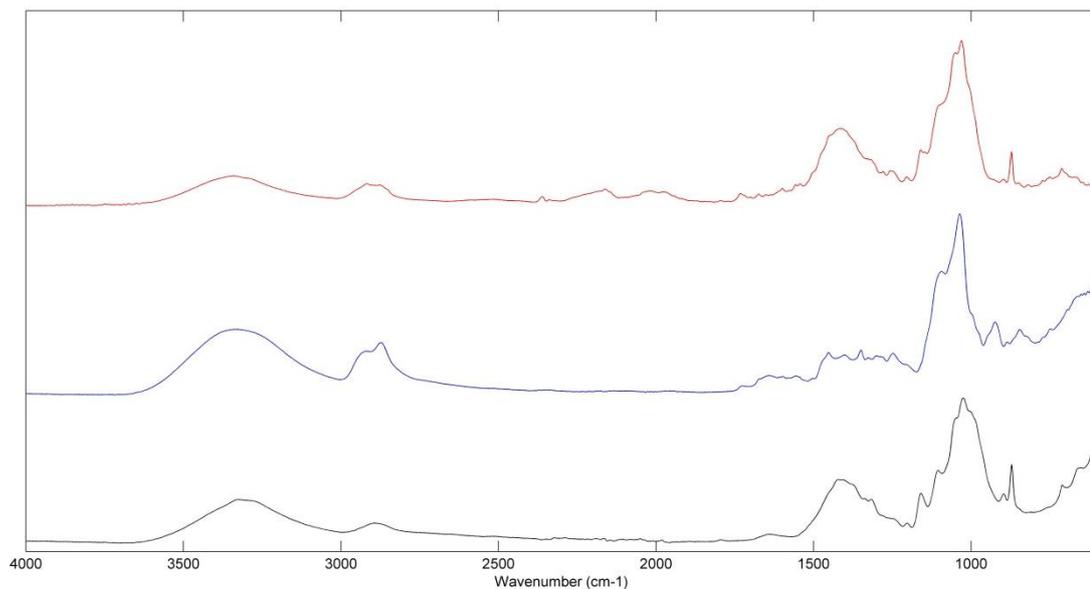


Figure 26: Comparison between paper, ink on paper and dry ink for WHSmith glitter green ink

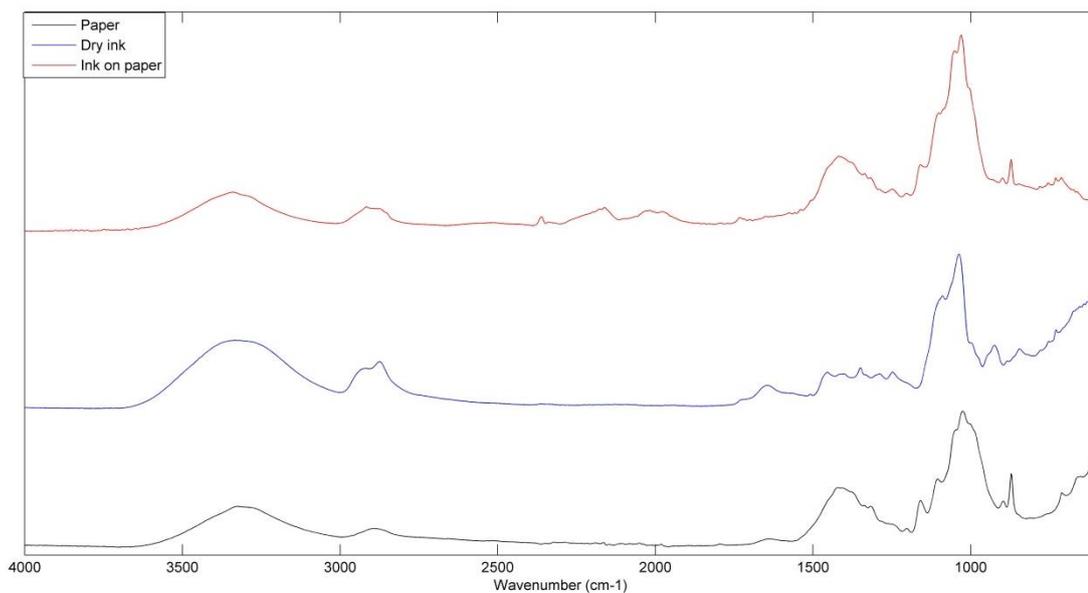


Figure 27: Comparison between paper, ink on paper and dry ink for WHSmith glitter light blue ink

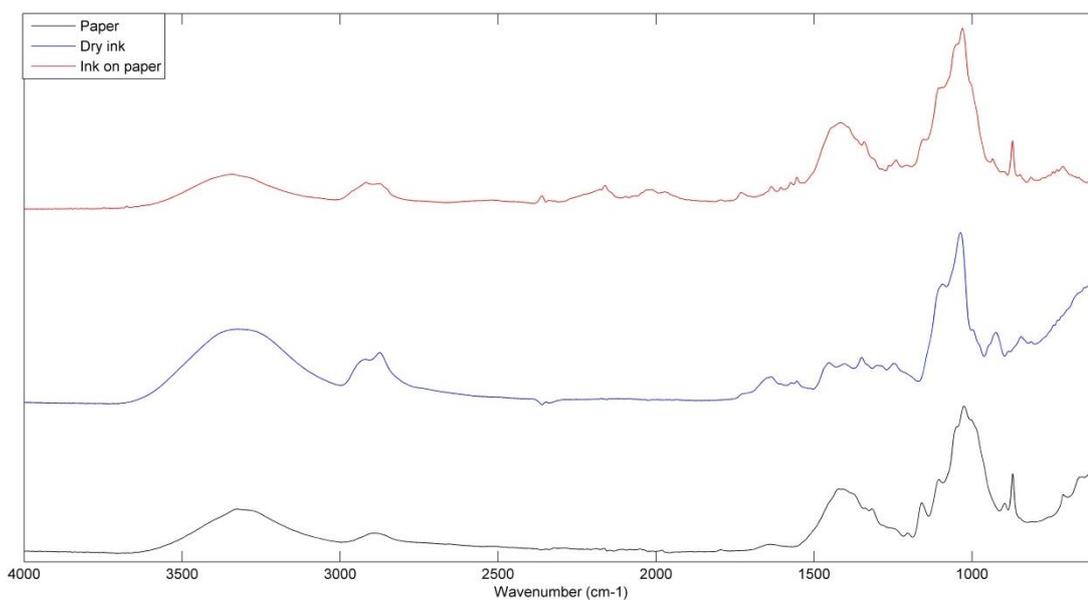


Figure 28: Comparison between paper, ink on paper and dry ink for WHSmith glitter orange ink

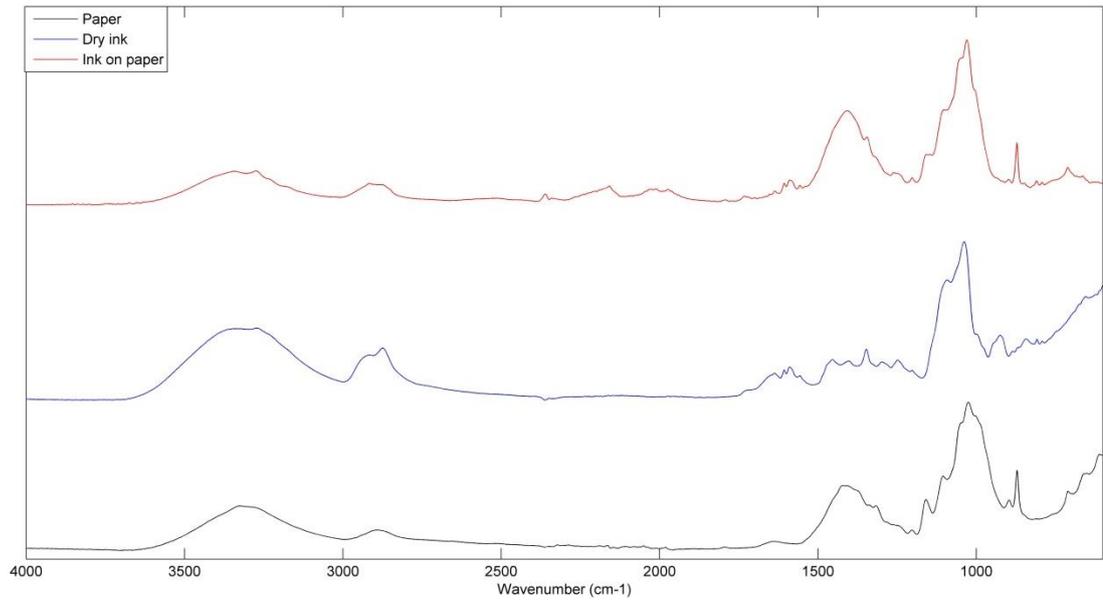


Figure 29: Comparison between paper, ink on paper and dry ink for WHSmith glitter pink ink

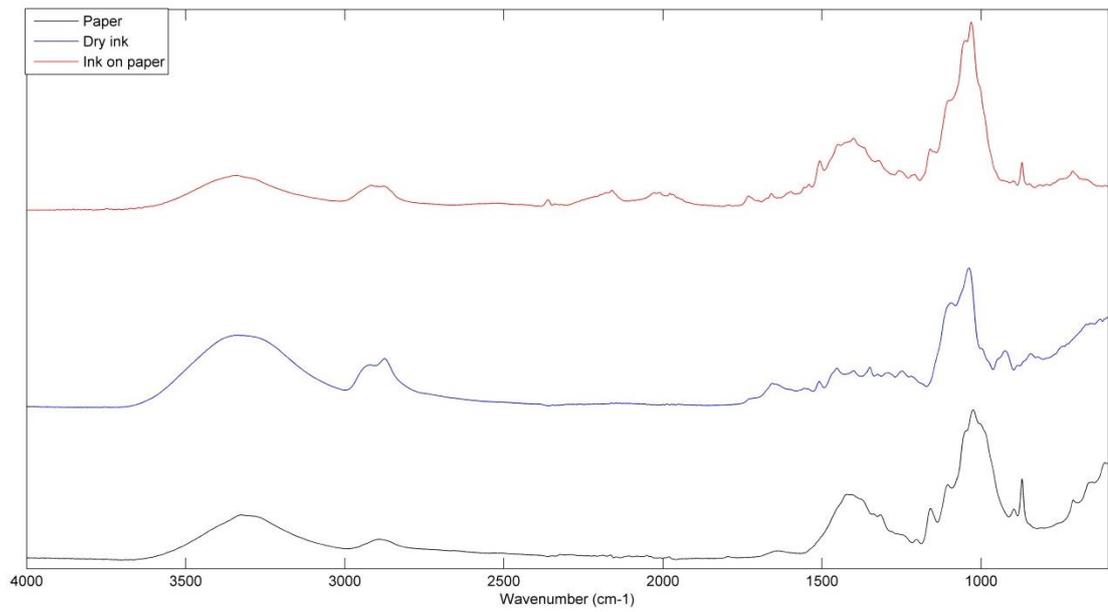


Figure 30: Comparison between paper, ink on paper and dry ink for WHSmith glitter purple ink

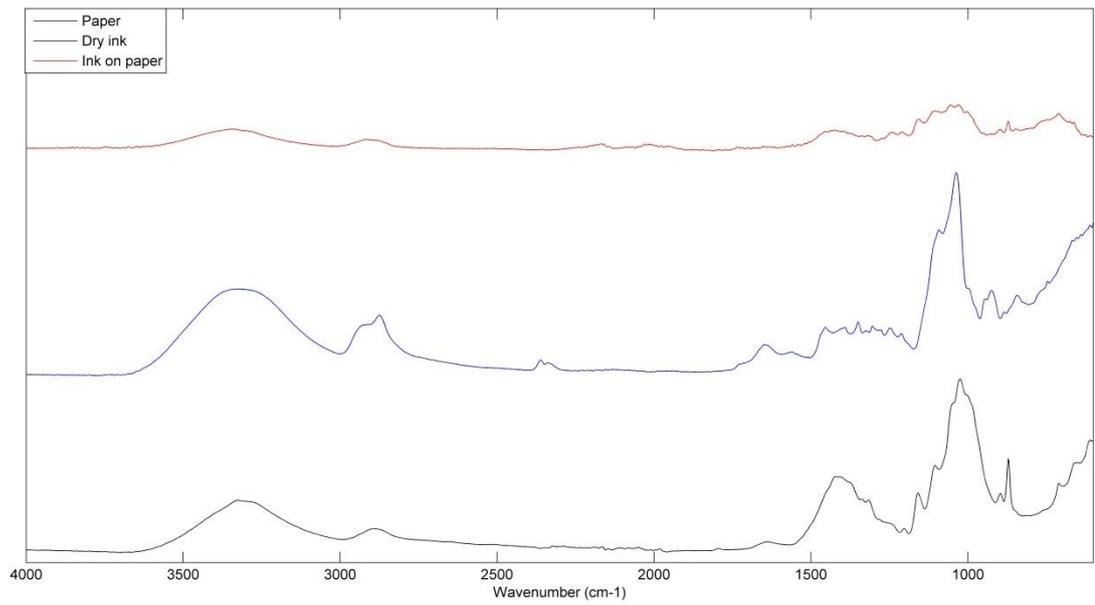


Figure 31: Comparison between paper, ink on paper and dry ink for WHSmith glitter red ink

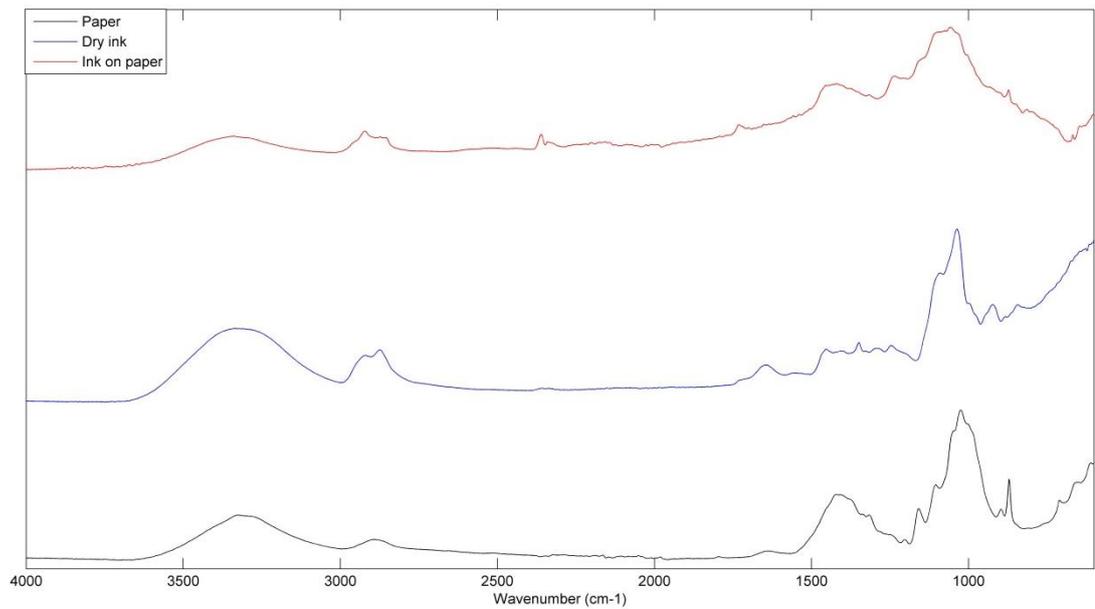


Figure 32: Comparison between paper, ink on paper and dry ink for WHSmith glitter silver ink

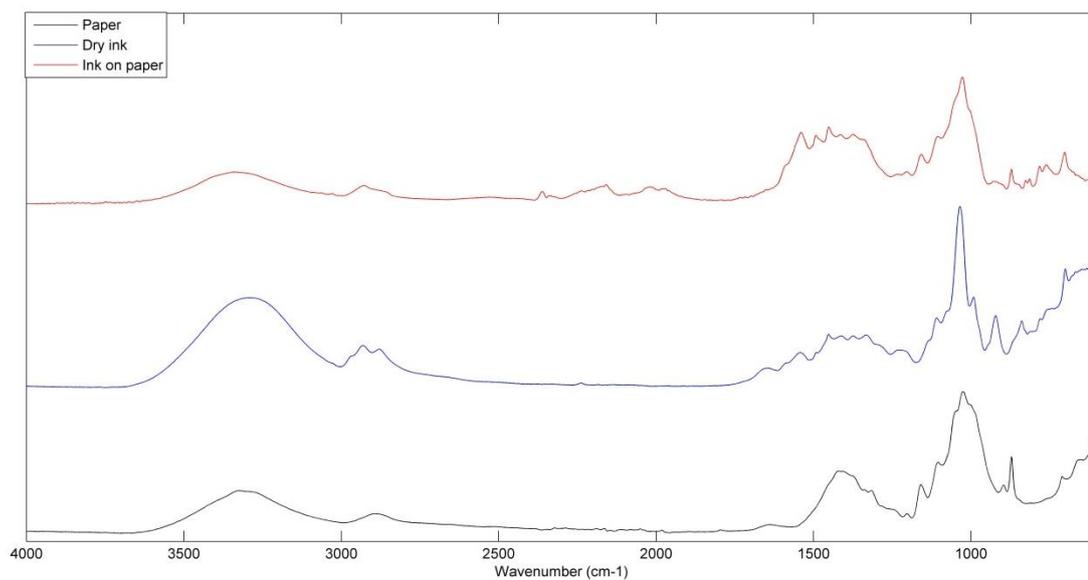


Figure 33: Comparison between paper, ink on paper and dry ink for Wilko green ink

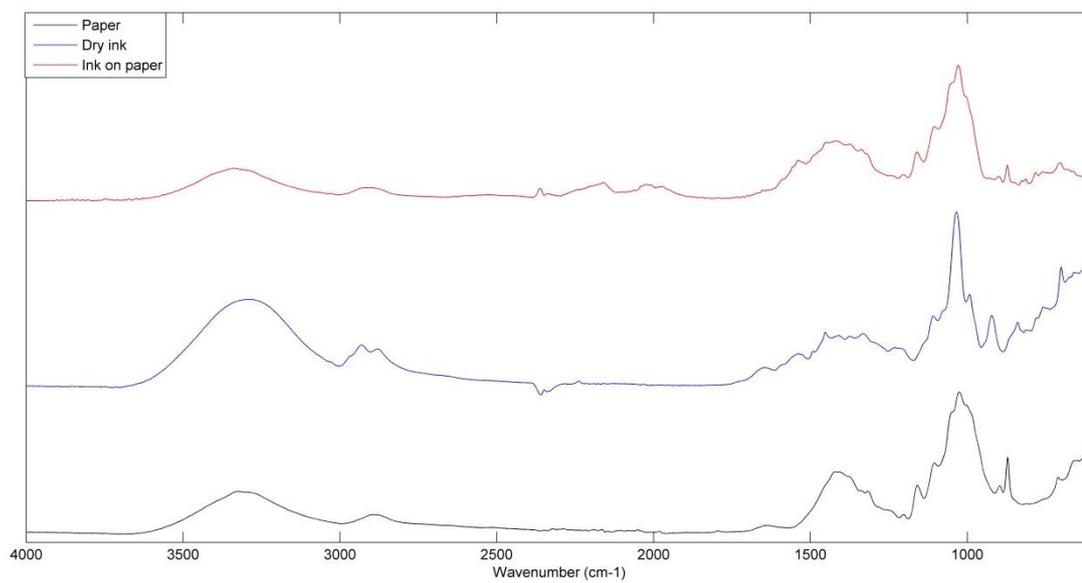


Figure 34: Comparison between paper, ink on paper and dry ink for Wilko orange ink

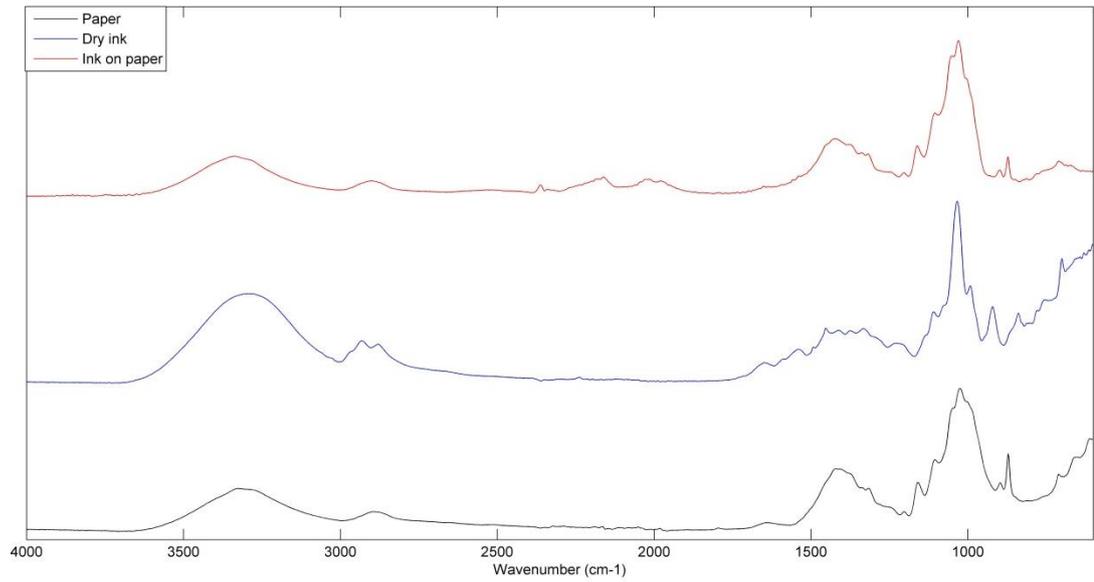


Figure 35: Comparison between paper, ink on paper and dry ink for Wilko pink ink

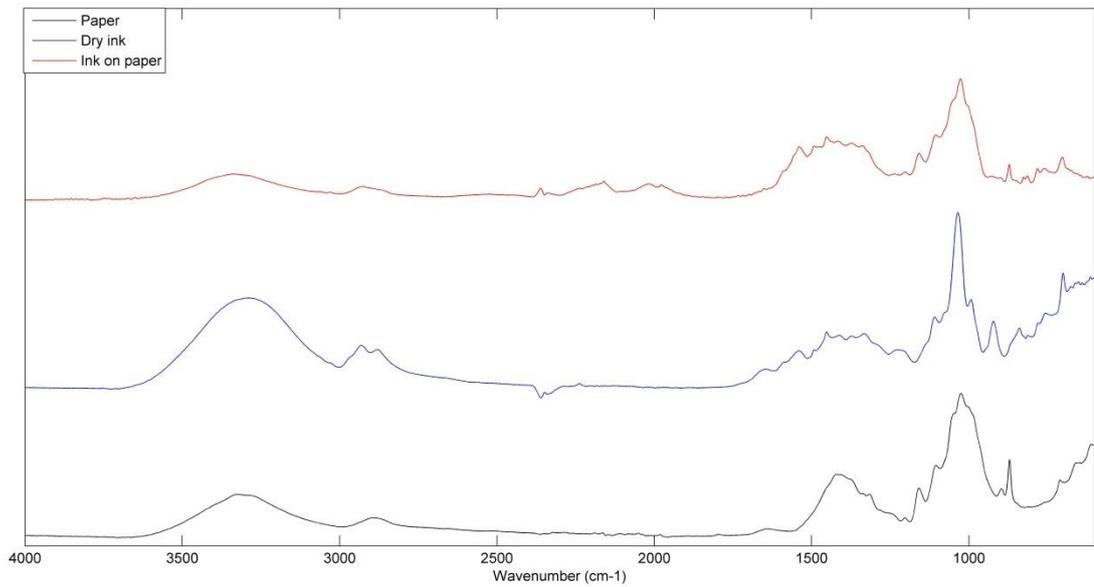


Figure 36: Comparison between paper, ink on paper and dry ink for Wilko purple ink

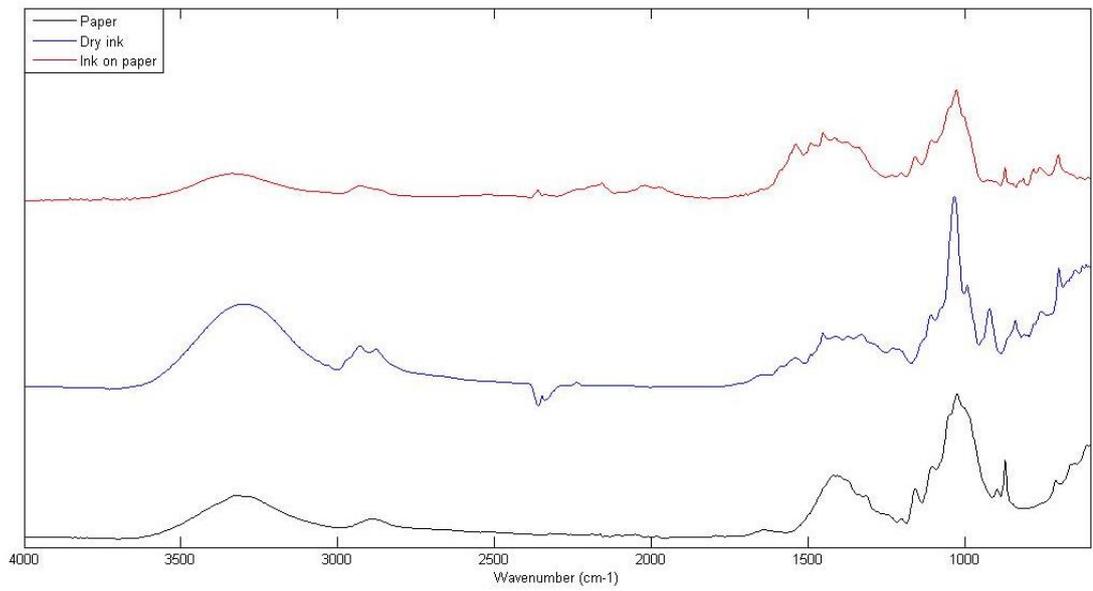


Figure 37: Comparison between paper, ink on paper and dry ink for Wilko yellow ink

Appendix E

Appendix E contains a collection of second derivatised spectra for the inks manufactured by club, papermate and WHSmith. These spectra are concentrated on the most discriminative wavenumbers at 929.51cm^{-1} and 1348cm^{-1} .

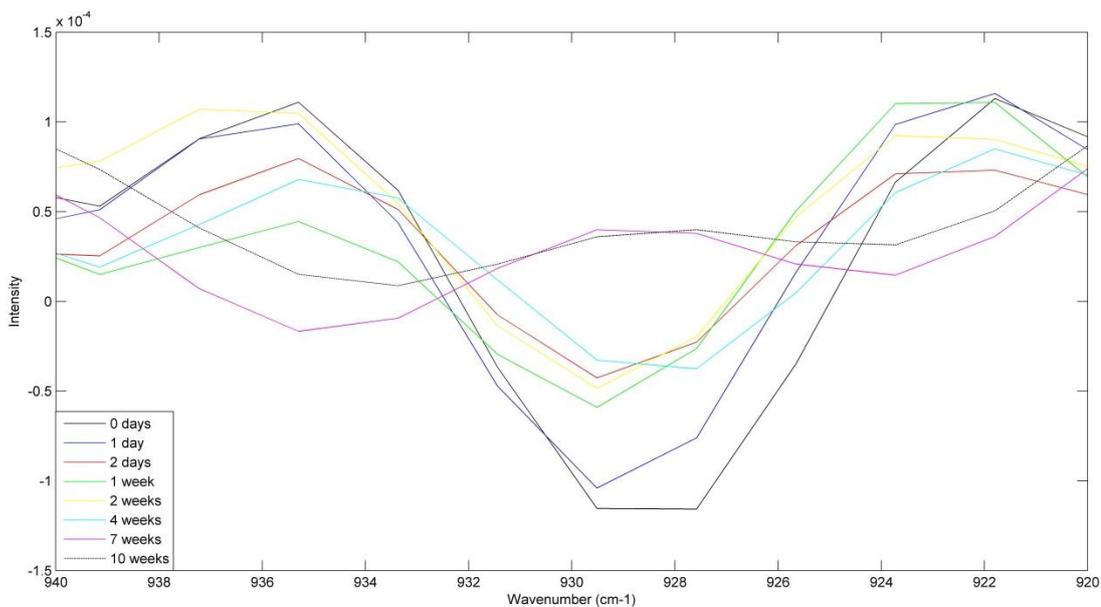


Figure 1: Second derivatised spectrum of Club black ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

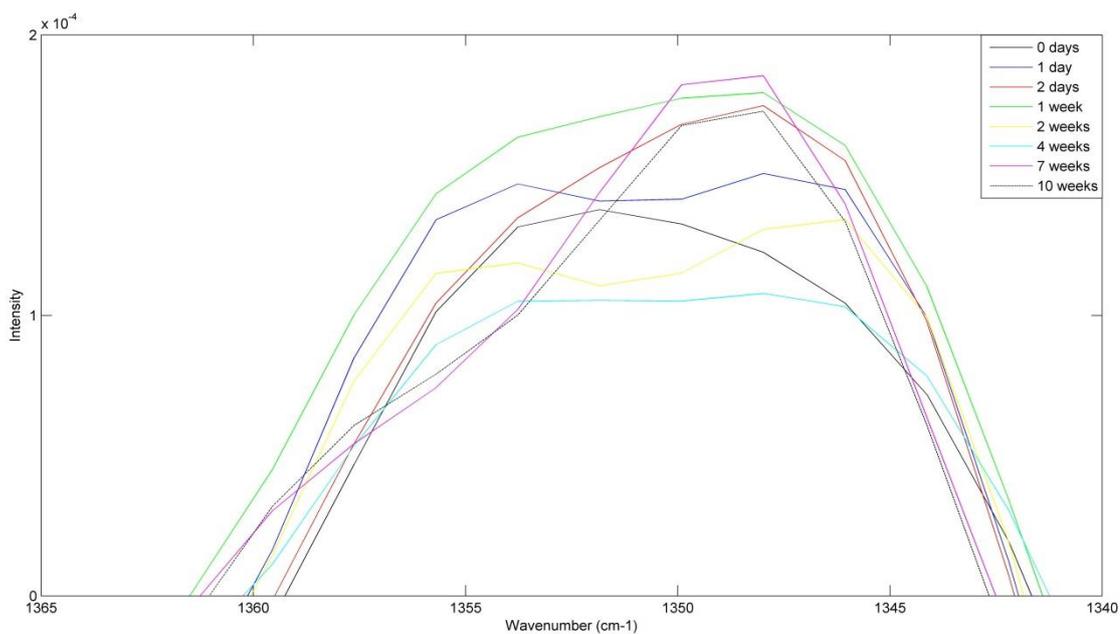


Figure 2: Second derivatised spectrum of Club black ink over the wavenumber range of 1340cm^{-1} to 1365cm^{-1} .

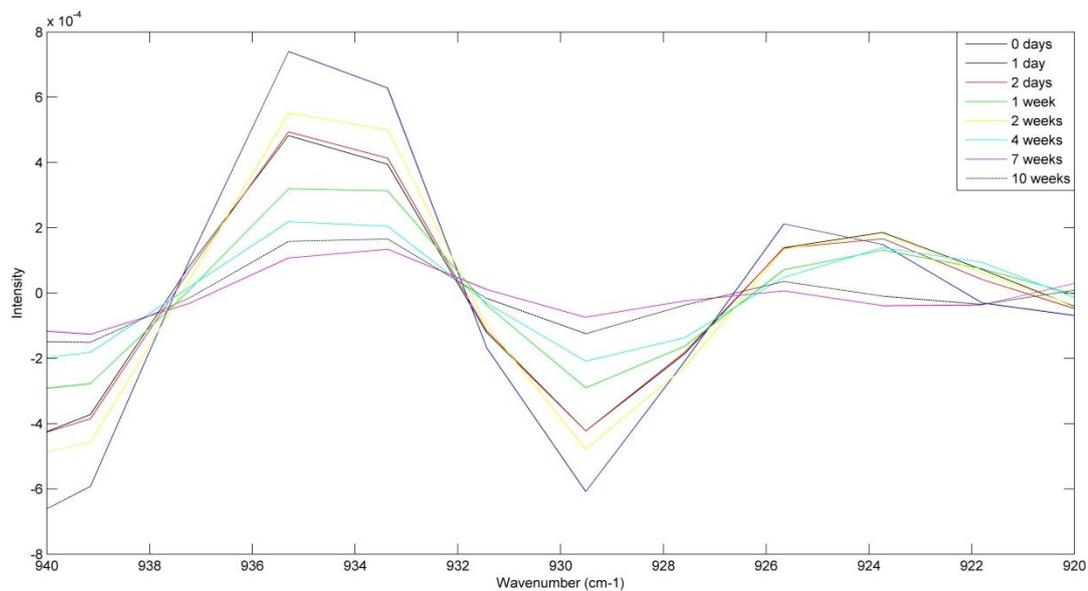


Figure 3: Second derivatised spectrum of Club blue ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

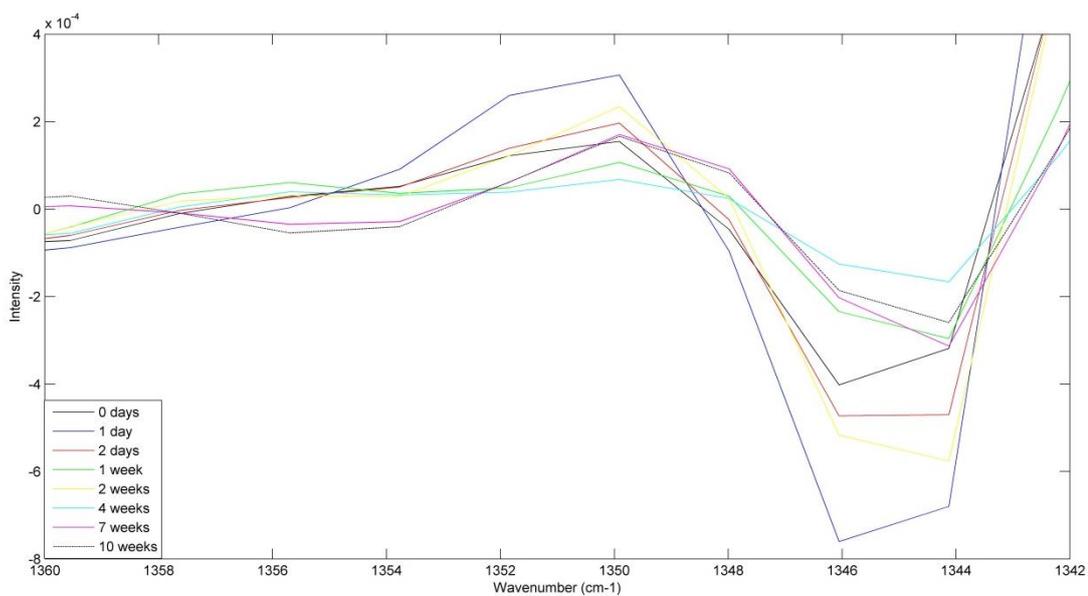


Figure 4: Second derivatised spectrum of Club blue ink over the wavenumber range of 1342cm^{-1} to 1360cm^{-1} .

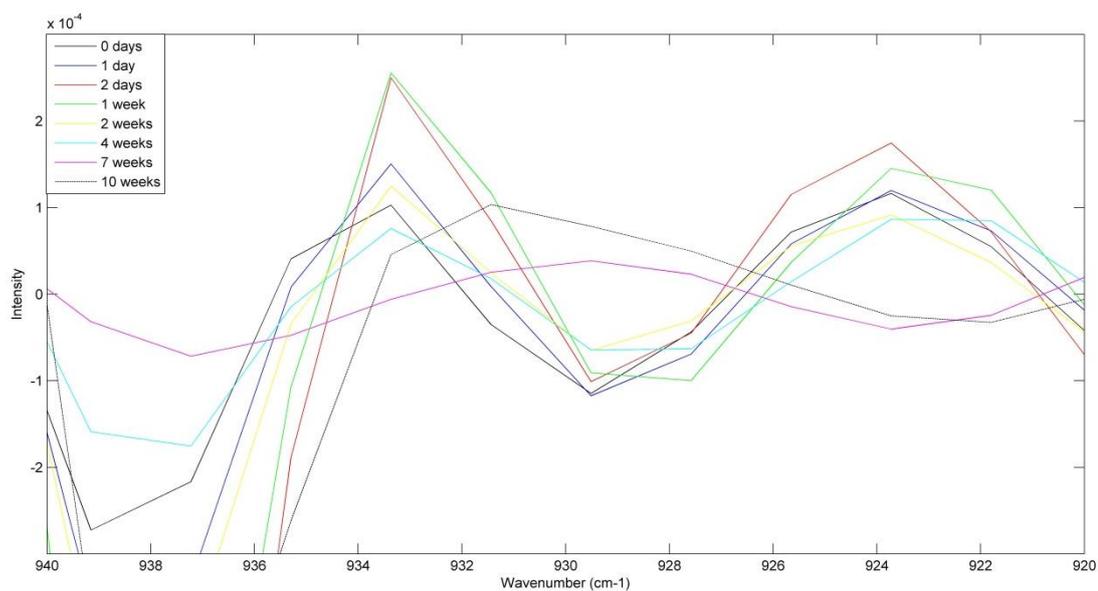


Figure 5: Second derivatised spectrum of Club green ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

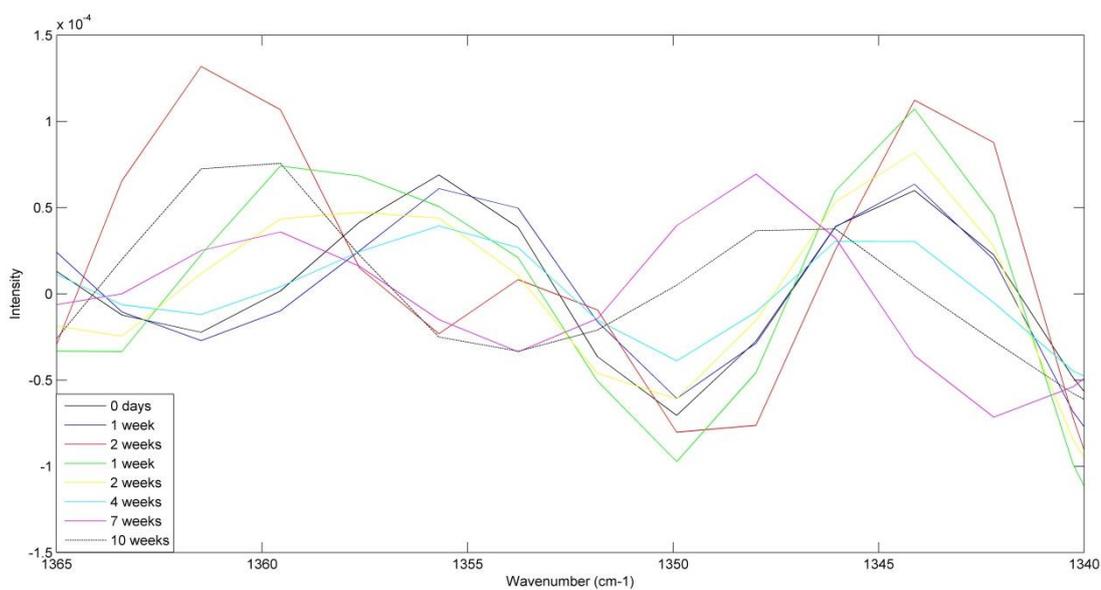


Figure 6: Second derivatised spectrum of Club green ink over the wavenumber range of 1340cm^{-1} to 1365cm^{-1} .

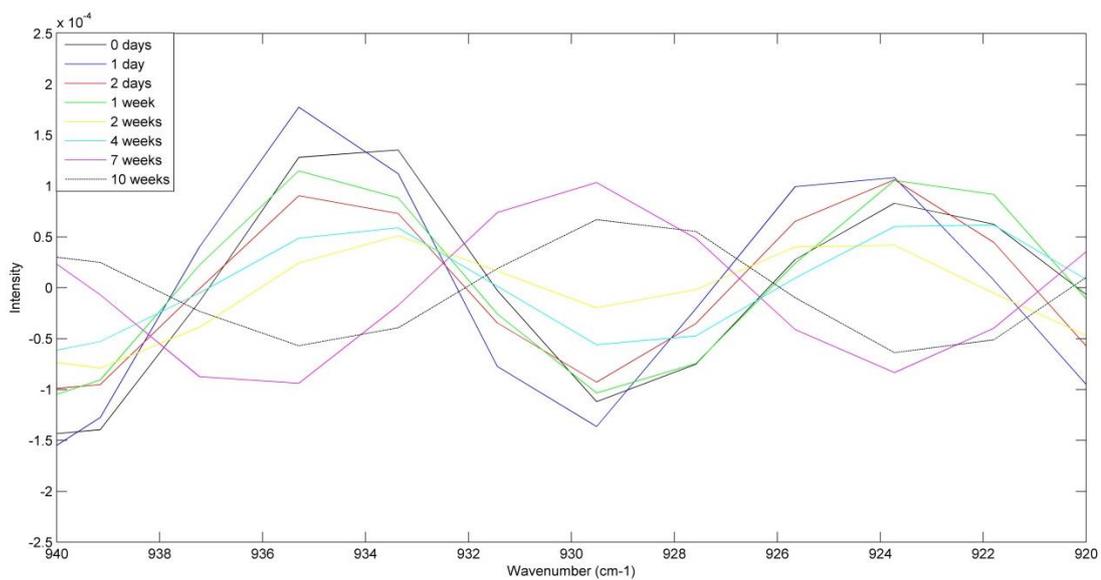


Figure 7: Second derivatised spectrum of Club red ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

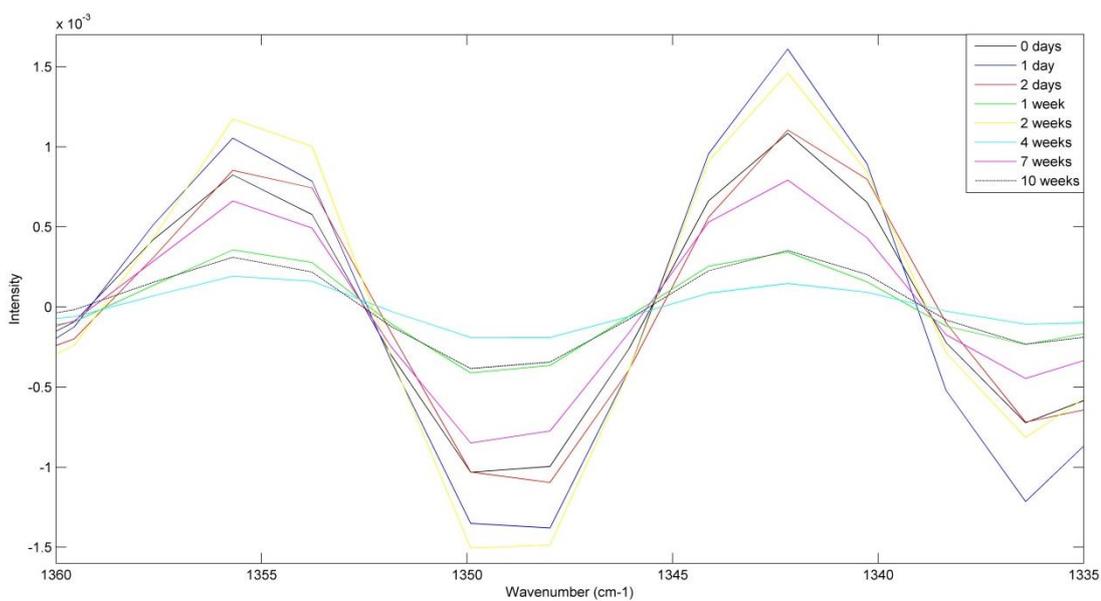


Figure 8: Second derivatised spectrum of Club red ink over the wavenumber range of 1335cm^{-1} to 1360cm^{-1} .

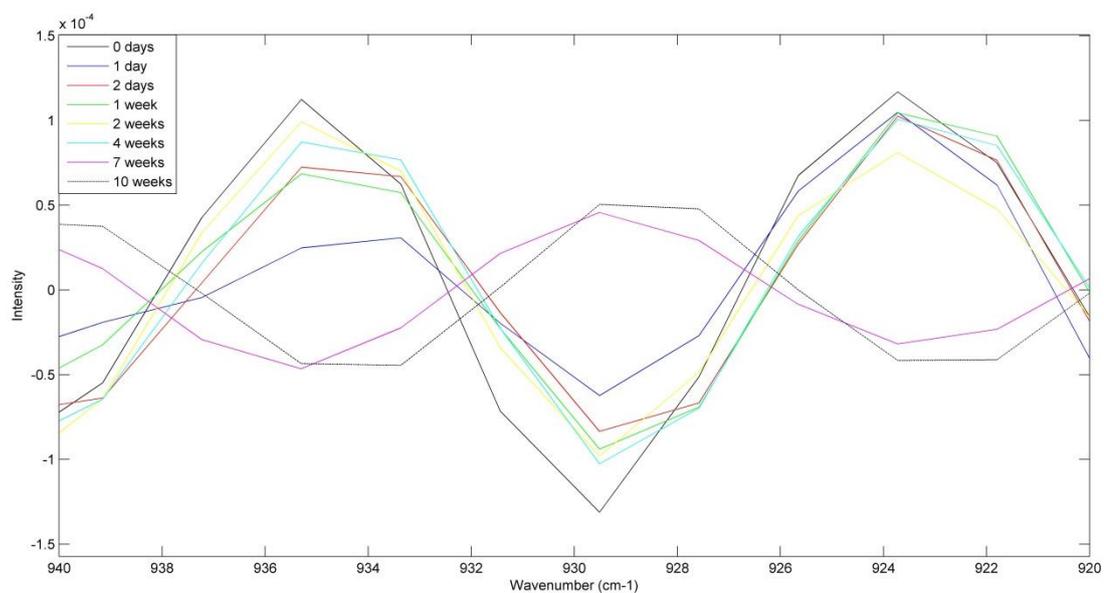


Figure 9: Second derivatised spectrum of Papermate black ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

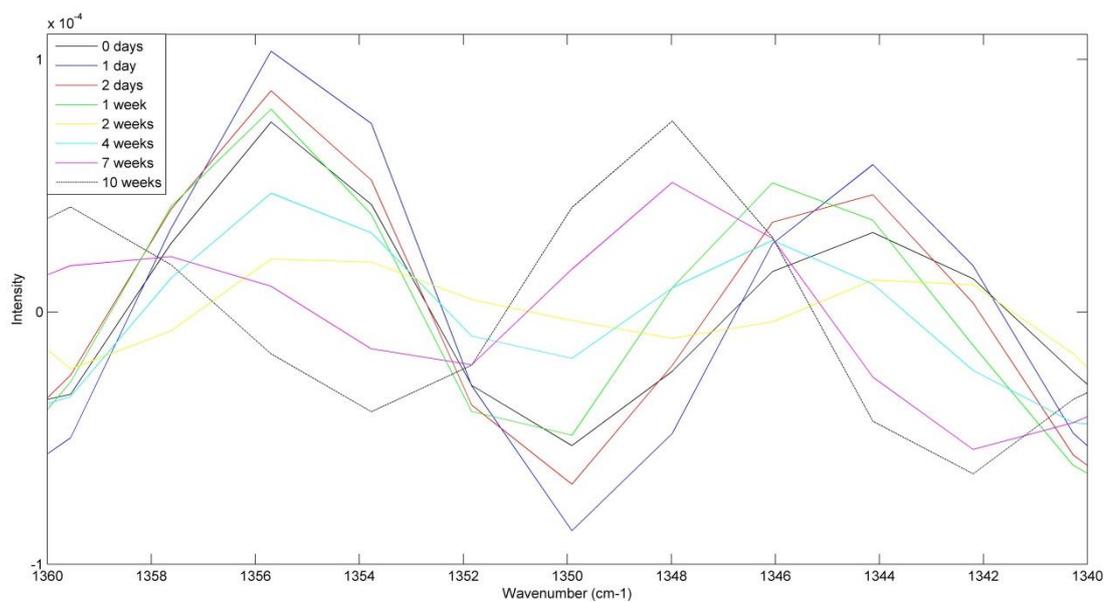


Figure 10: Second derivatised spectrum of Papermate black ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

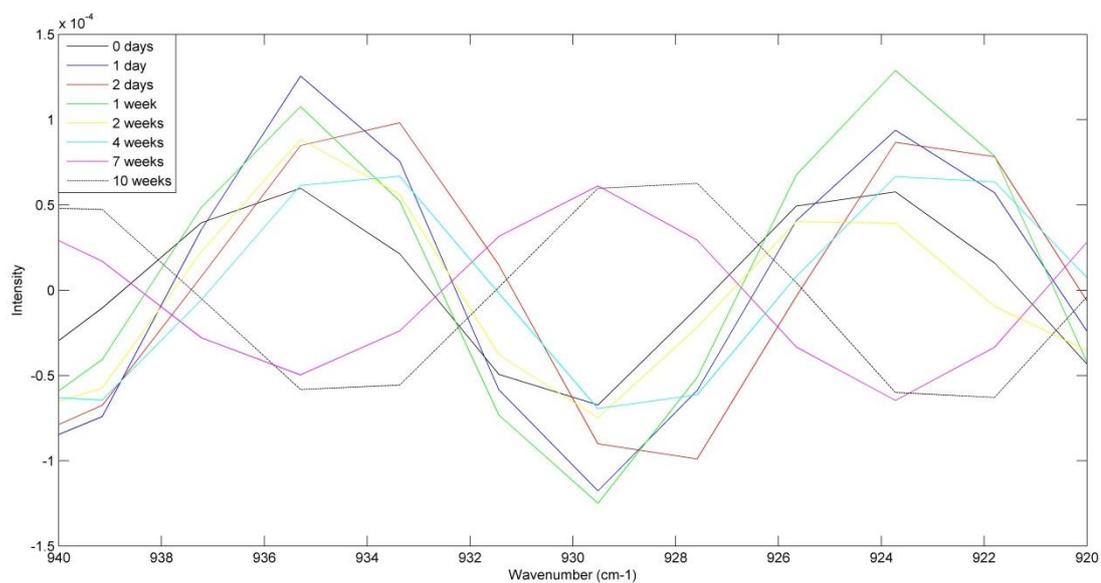


Figure 11: Second derivatised spectrum of Papermate blue ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

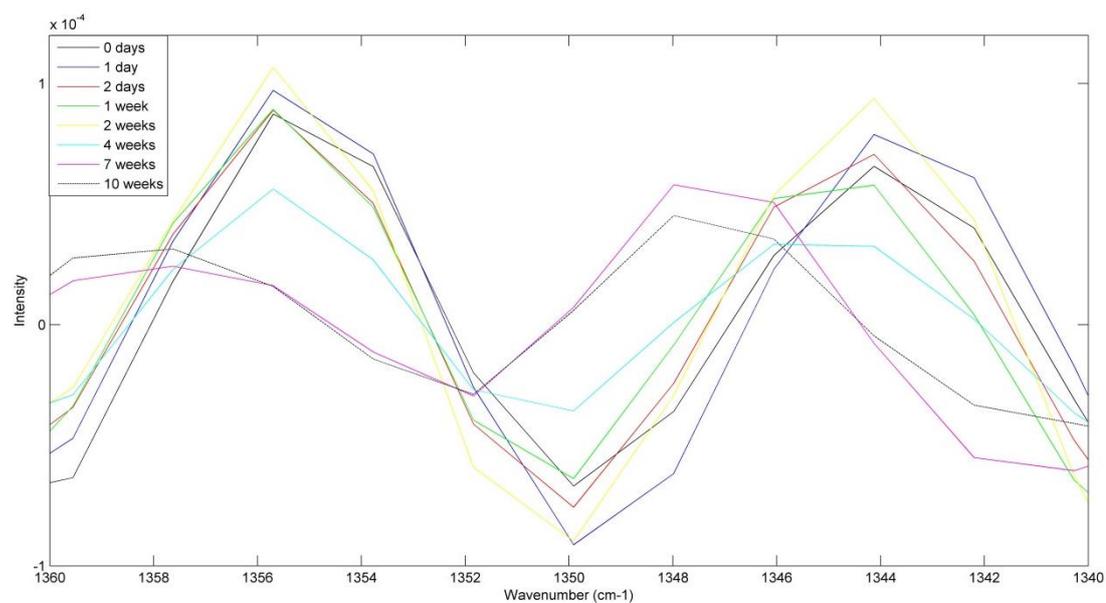


Figure 12: Second derivatised spectrum of Papermate blue ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

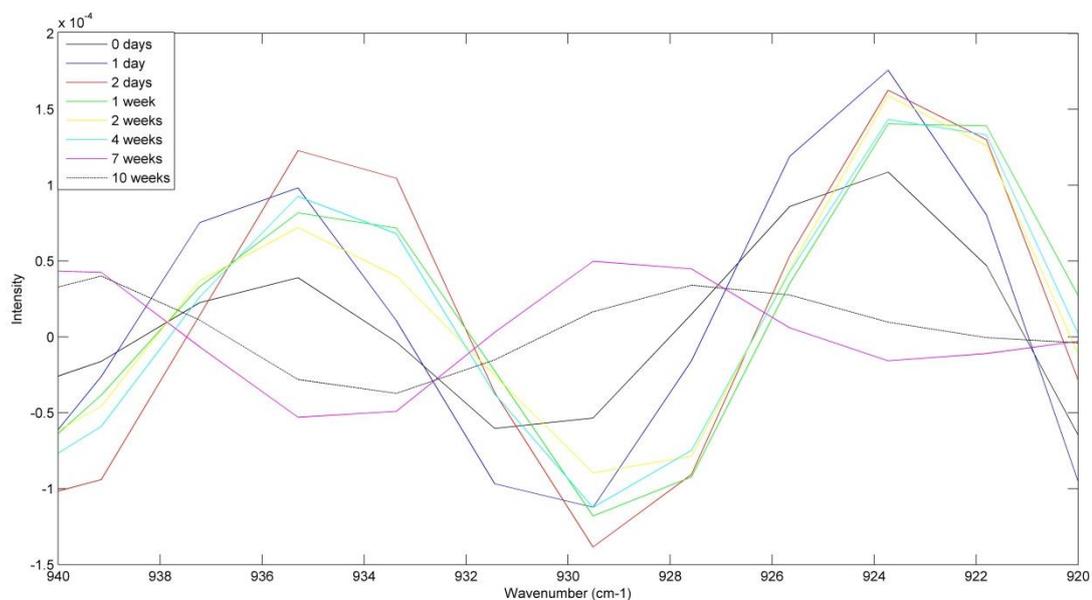


Figure 13: Second derivatised spectrum of Papermate green ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

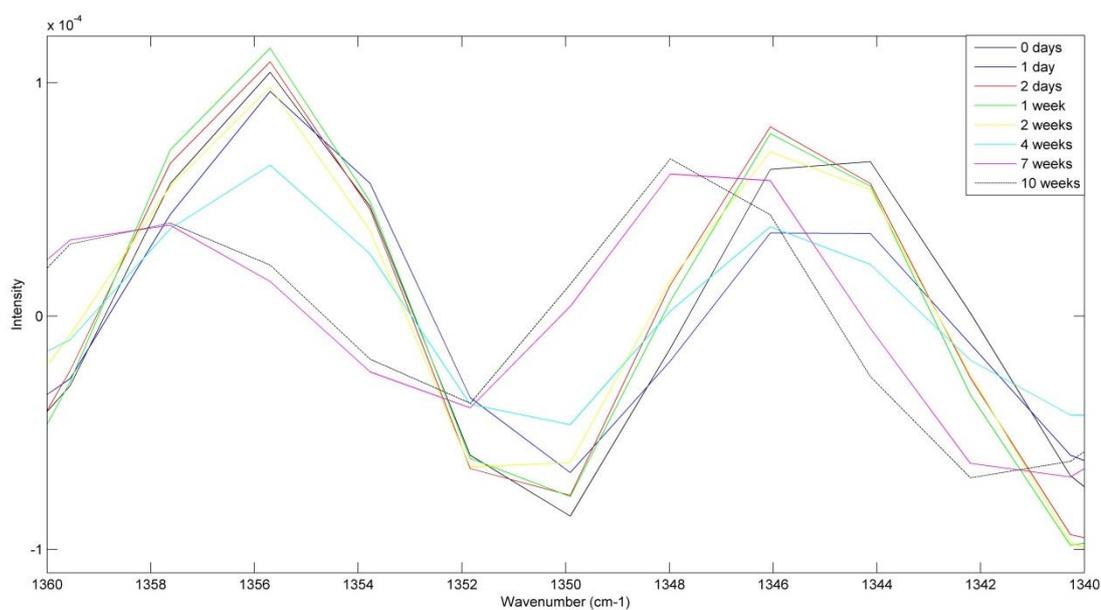


Figure 14: Second derivatised spectrum of Papermate green ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

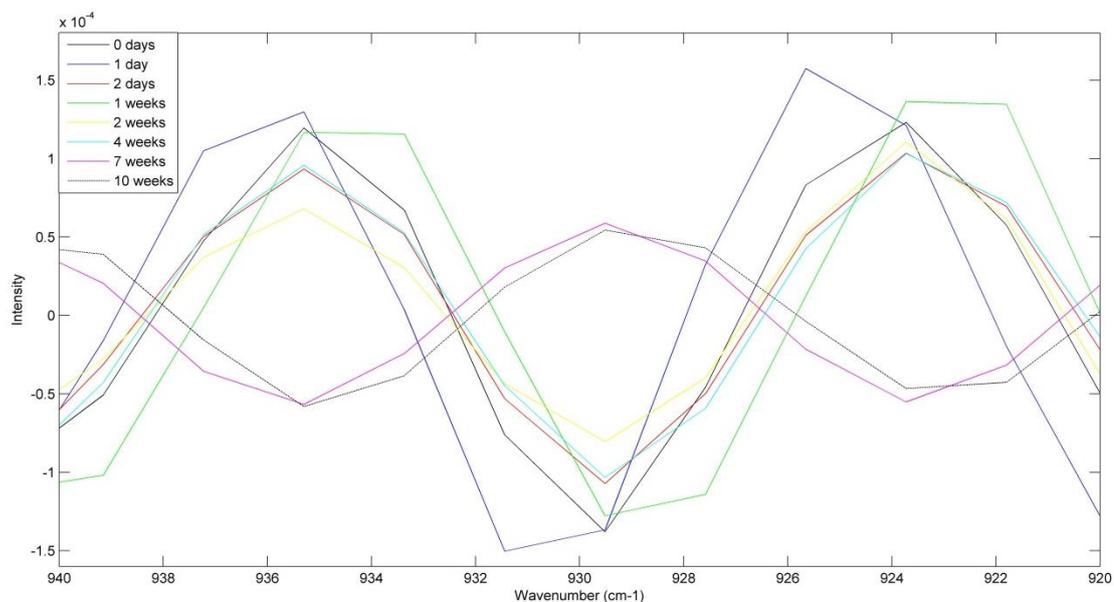


Figure 15: Second derivatised spectrum of Papermate red ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

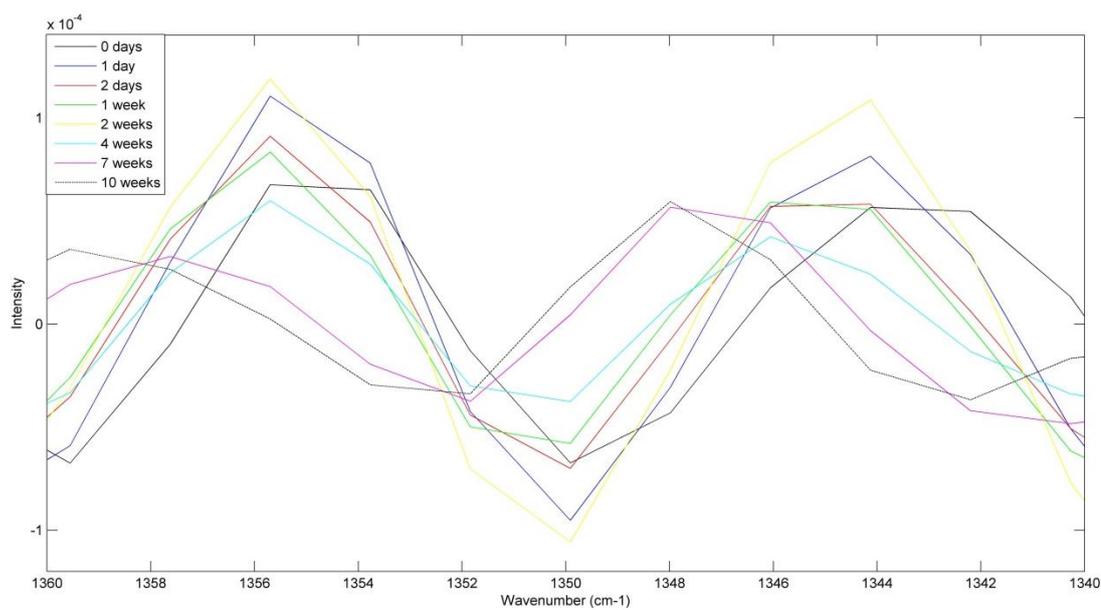


Figure 16: Second derivatised spectrum of Club red ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

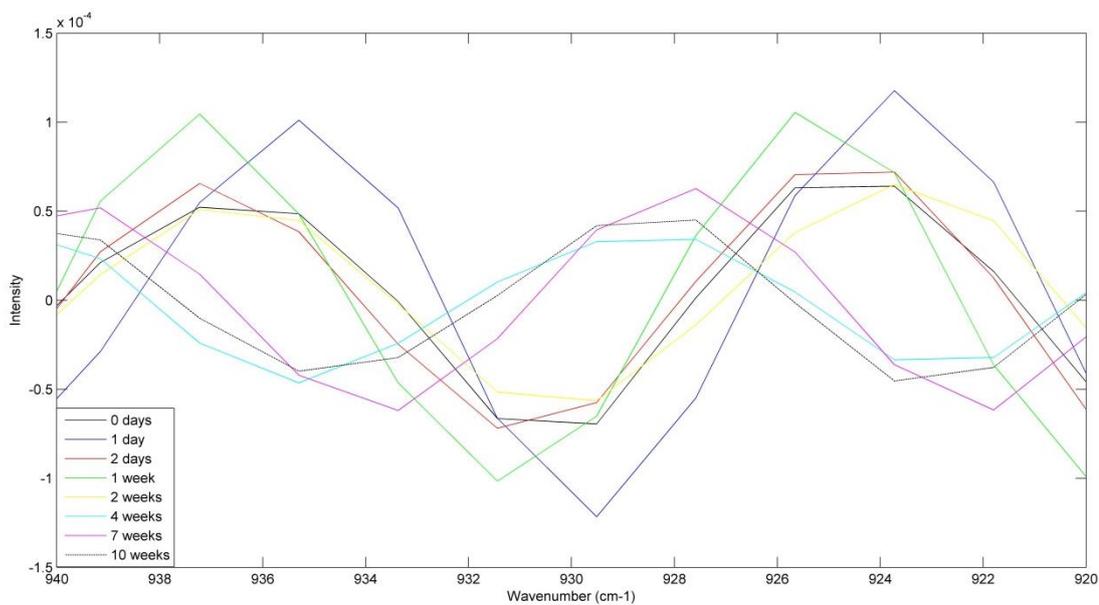


Figure 17: Second derivatised spectrum of WHSmith black ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

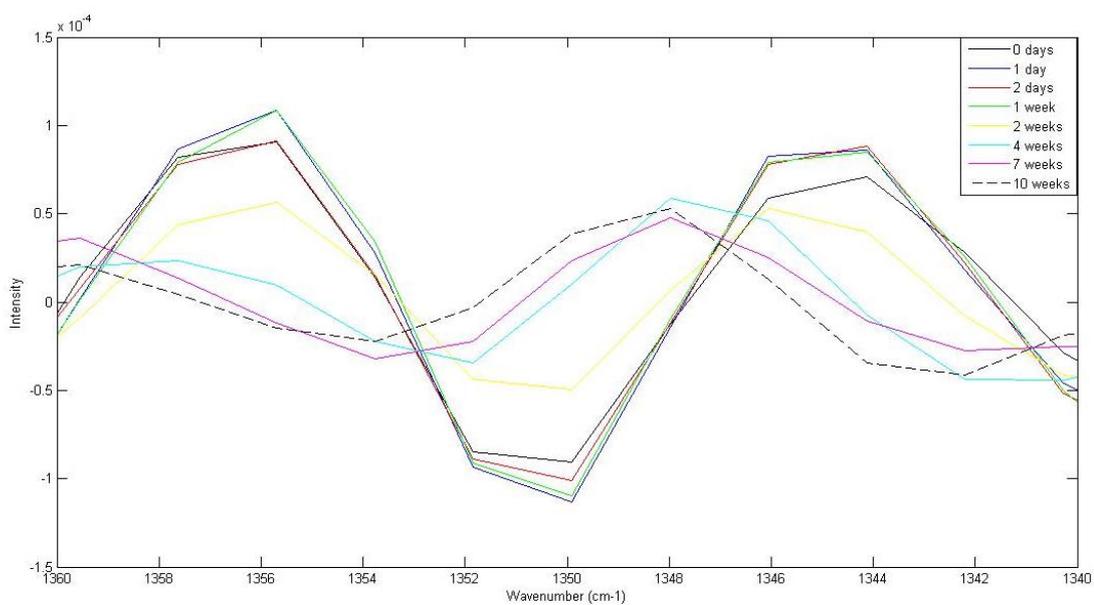


Figure 18: Second derivatised spectrum of WHSmith black ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

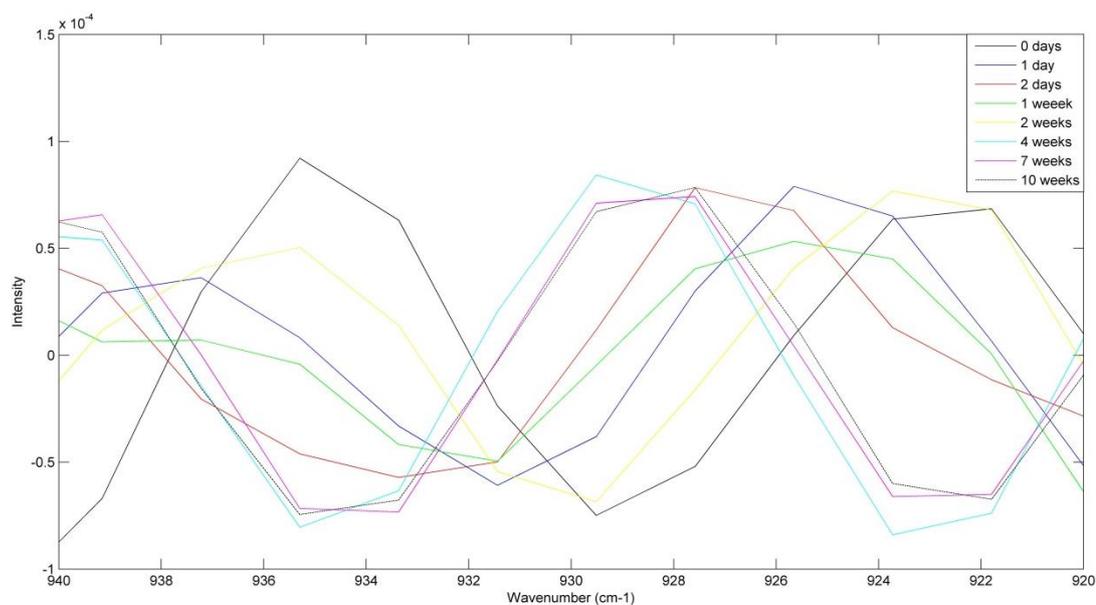


Figure 19: Second derivatised spectrum of WHSmith blue ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

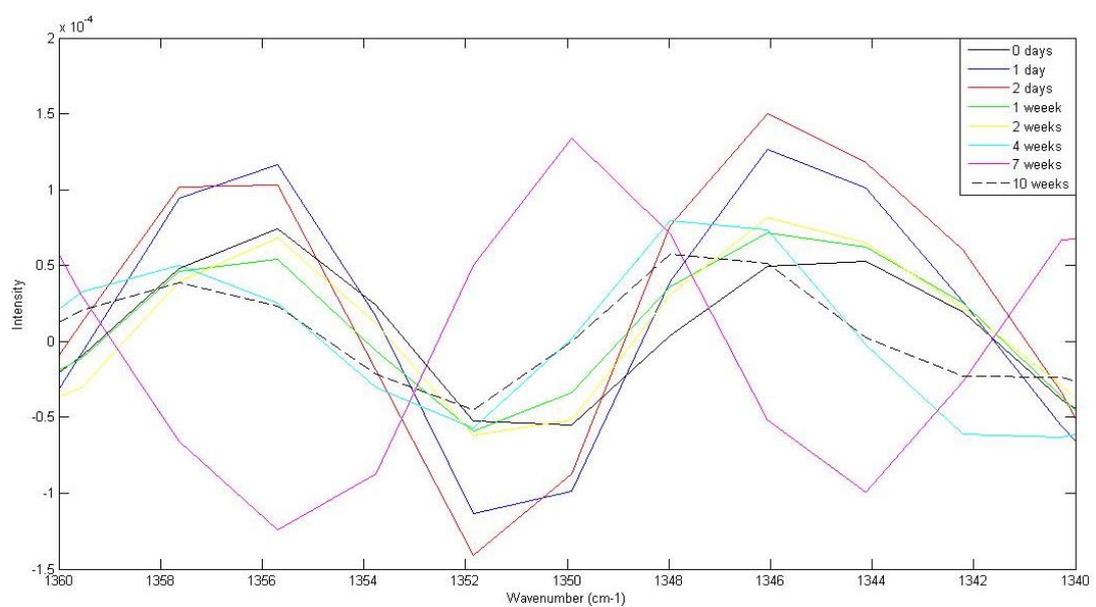


Figure 20: Second derivatised spectrum of WHSmith blue ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

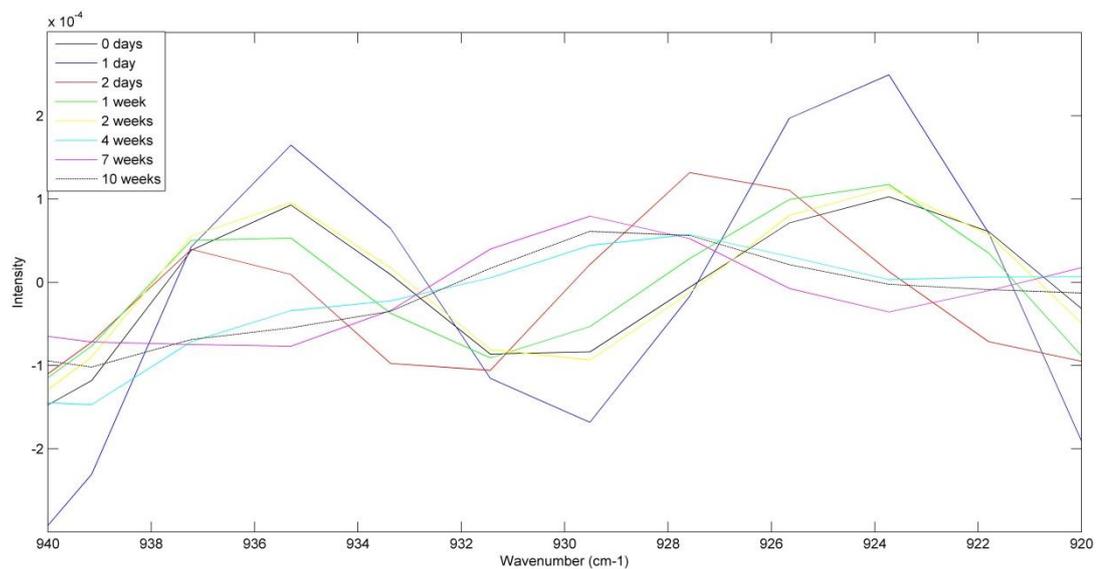


Figure 21: Second derivatised spectrum of WHSmith brown ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

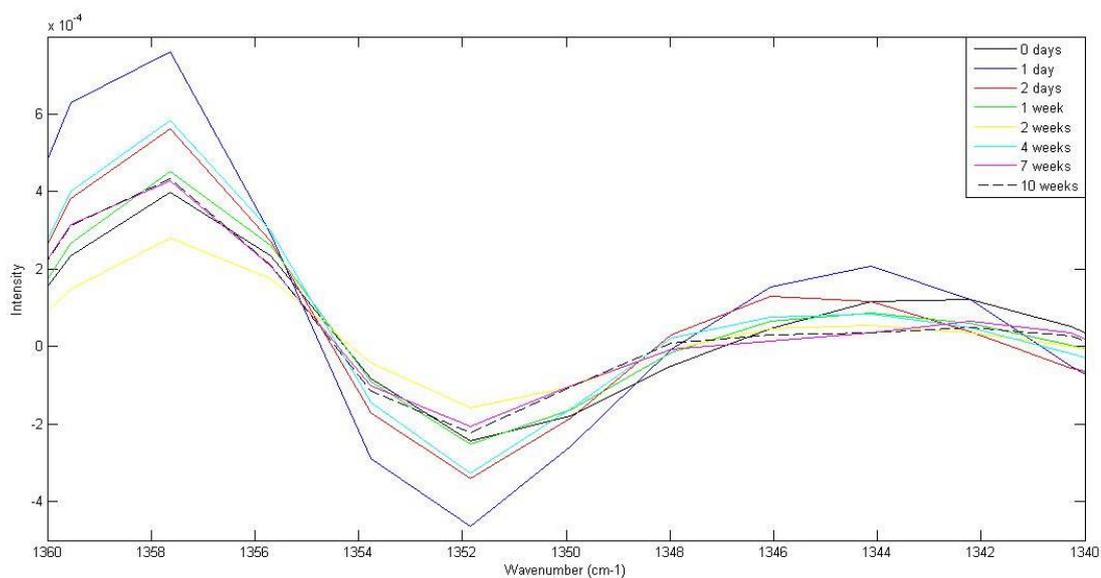


Figure 22: Second derivatised spectrum of WHSmith brown ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

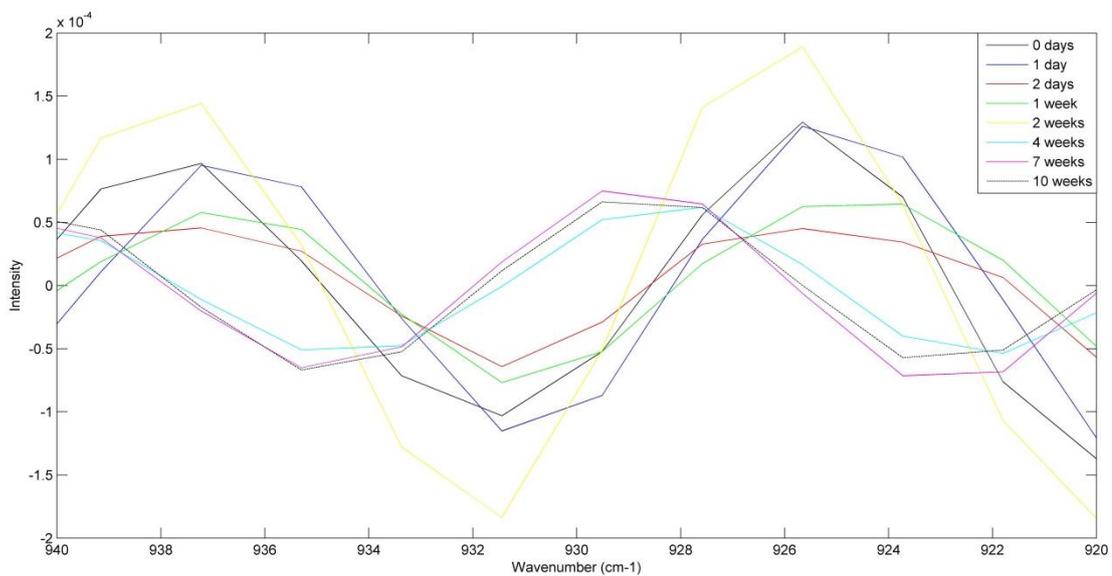


Figure 23: Second derivatised spectrum of WHSmith gold ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

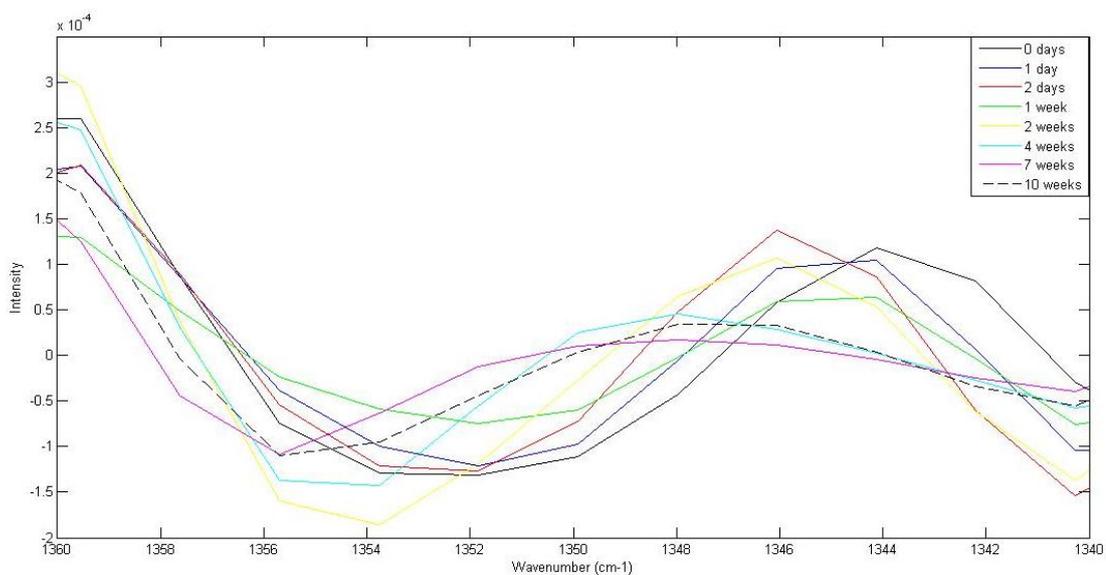


Figure 24: Second derivatised spectrum of WHSmith gold ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

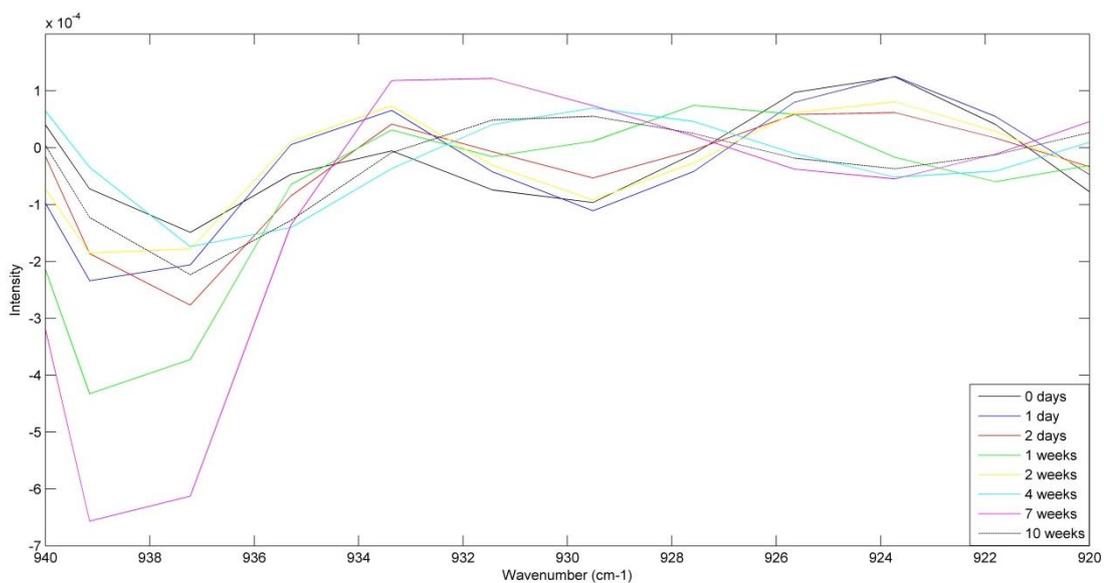


Figure 25: Second derivatised spectrum of WHSmith green ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

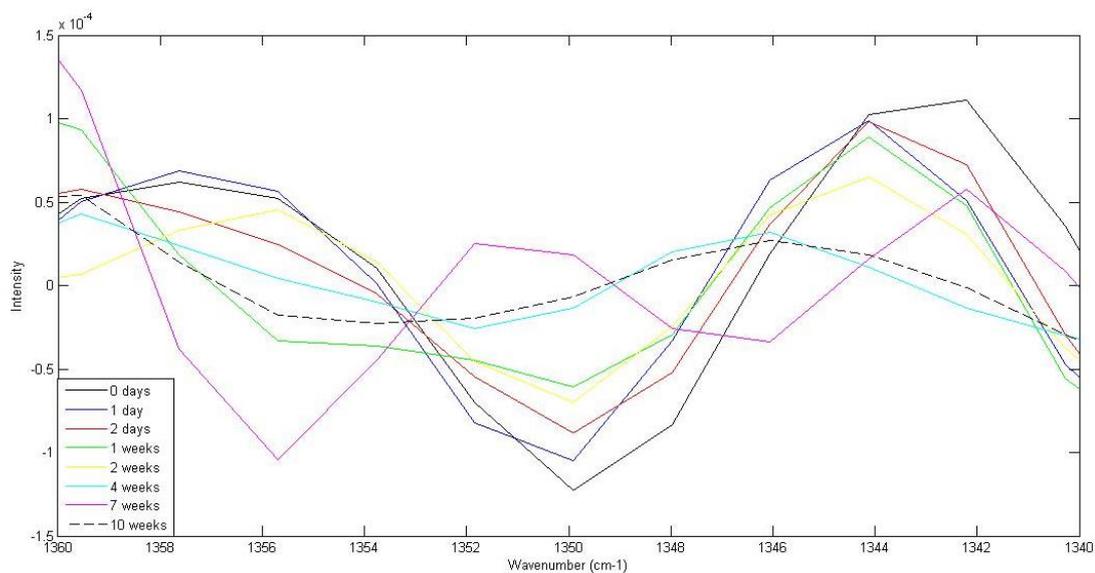


Figure 26: Second derivatised spectrum of WHSmith green ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

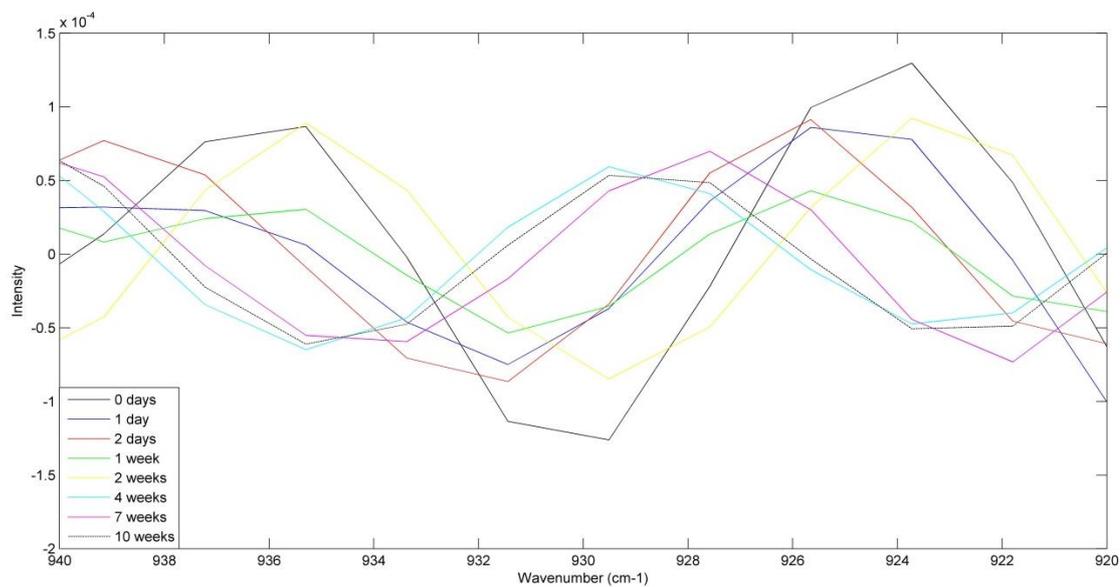


Figure 27: Second derivatised spectrum of WHSmith light blue ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

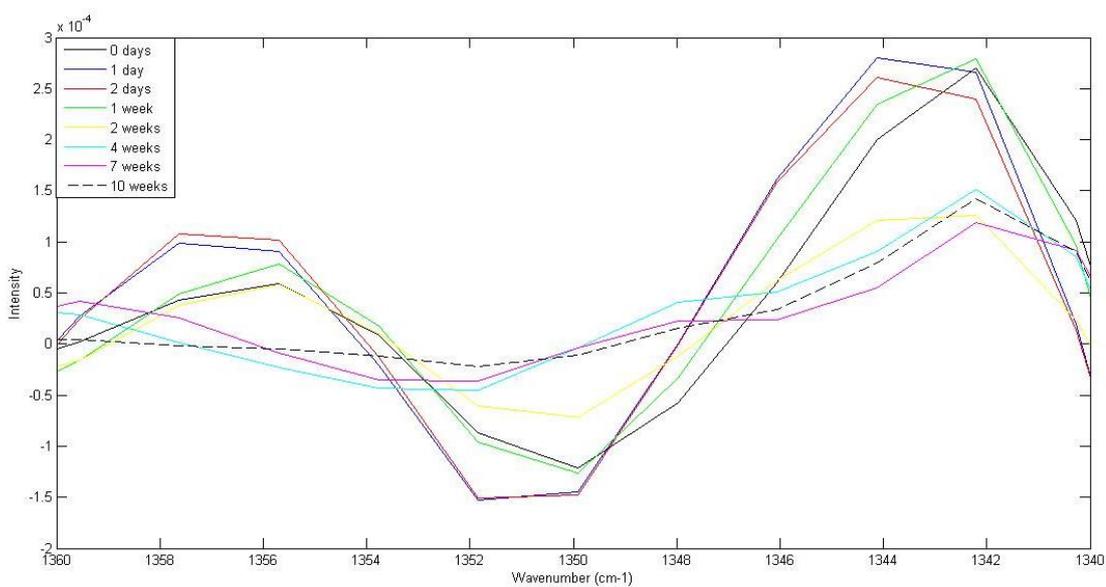


Figure 28: Second derivatised spectrum of WHSmith light blue ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

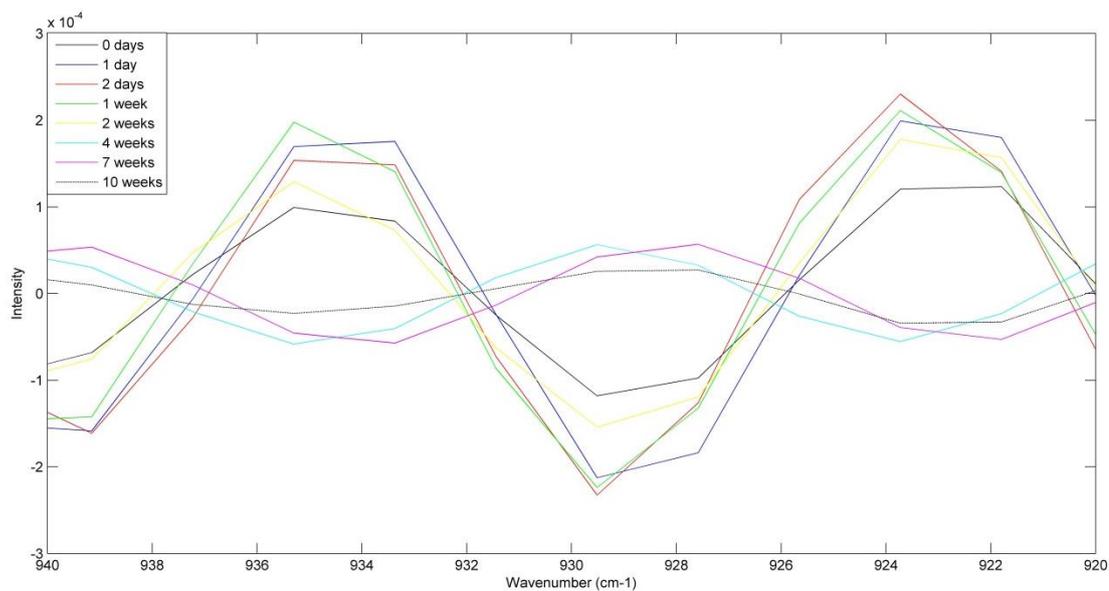


Figure 29: Second derivatised spectrum of WHSmith lime ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

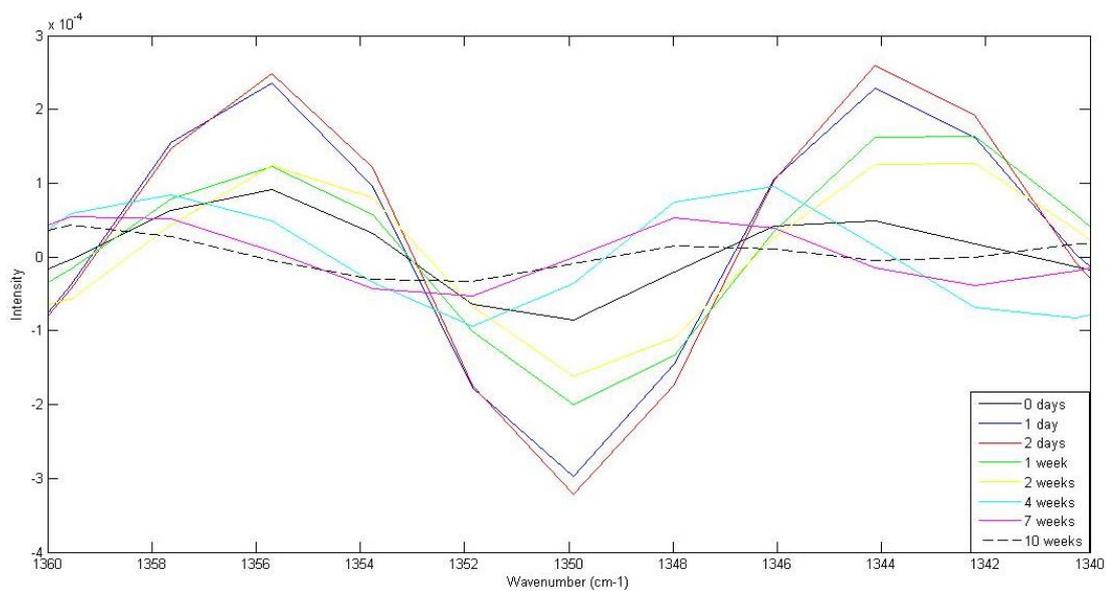


Figure 30: Second derivatised spectrum of WHSmith lime ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

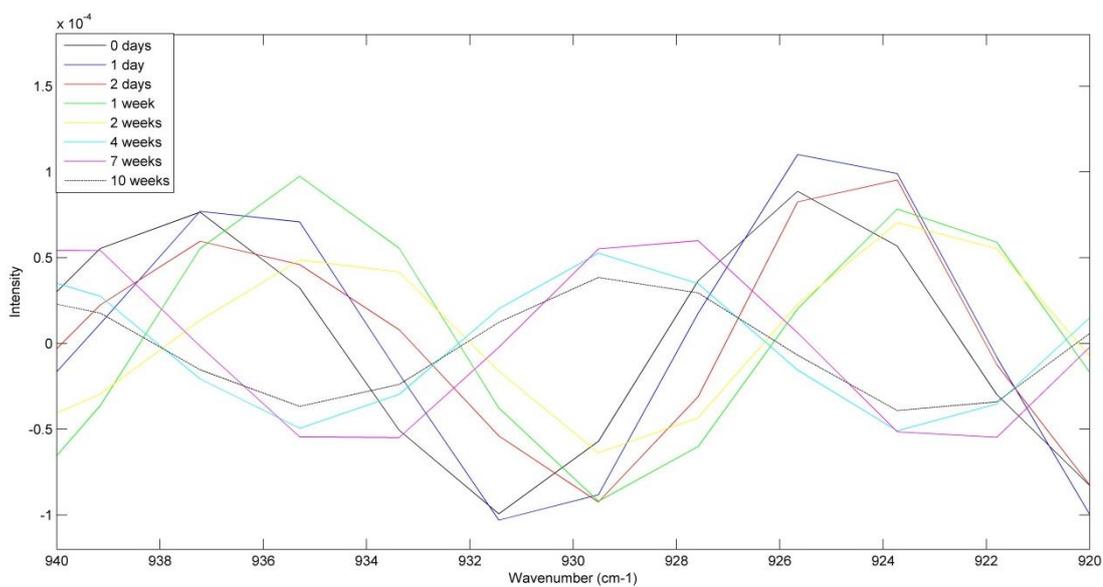


Figure 31: Second derivatised spectrum of WHSmith mauve ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

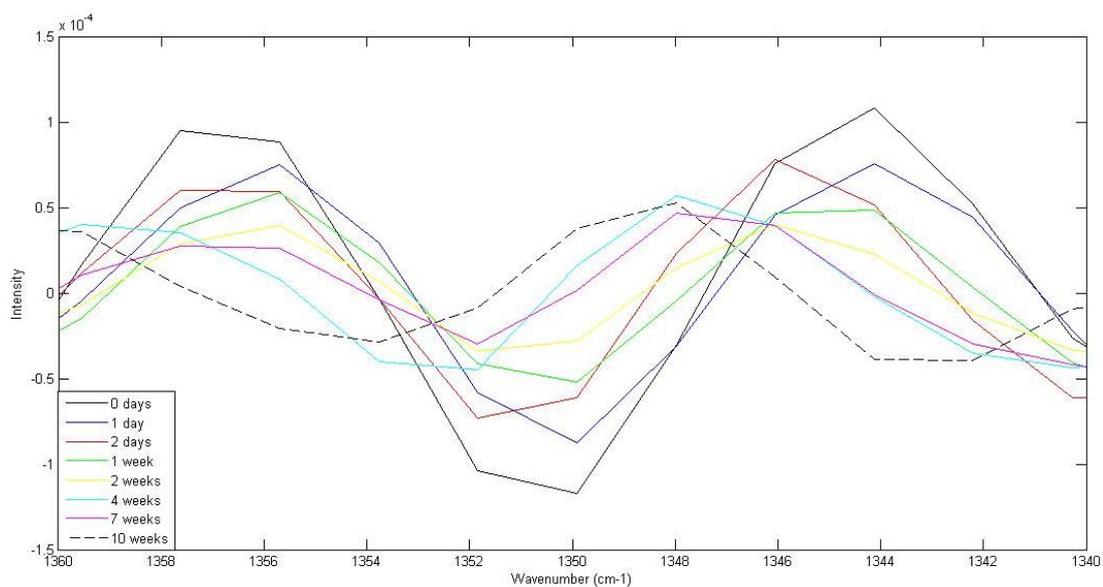


Figure 32: Second derivatised spectrum of WHSmith mauve ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

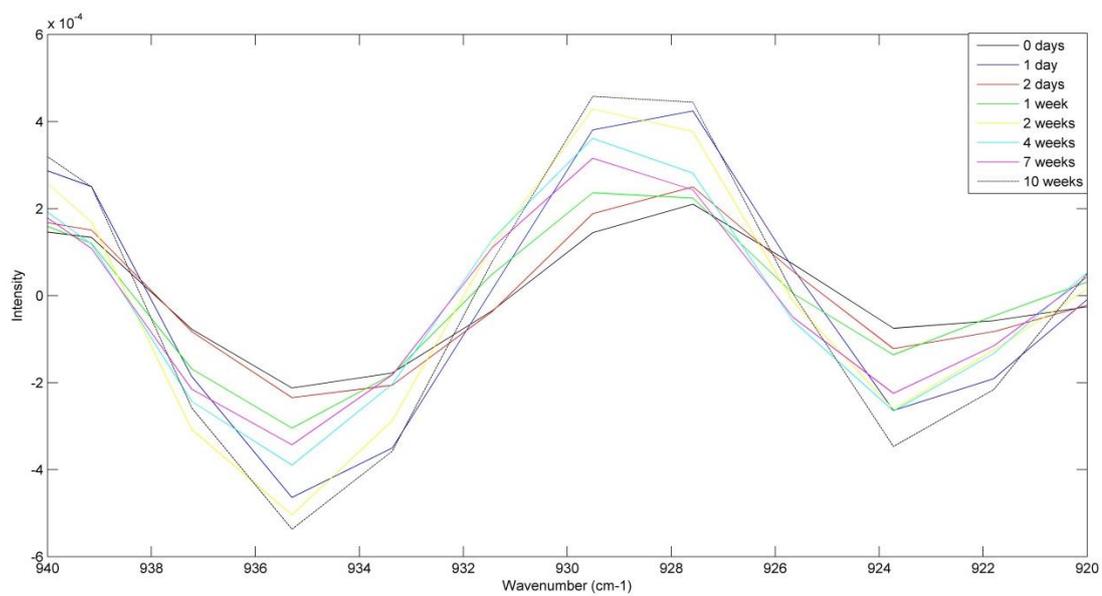


Figure 33: Second derivatised spectrum of WHSmith orange ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

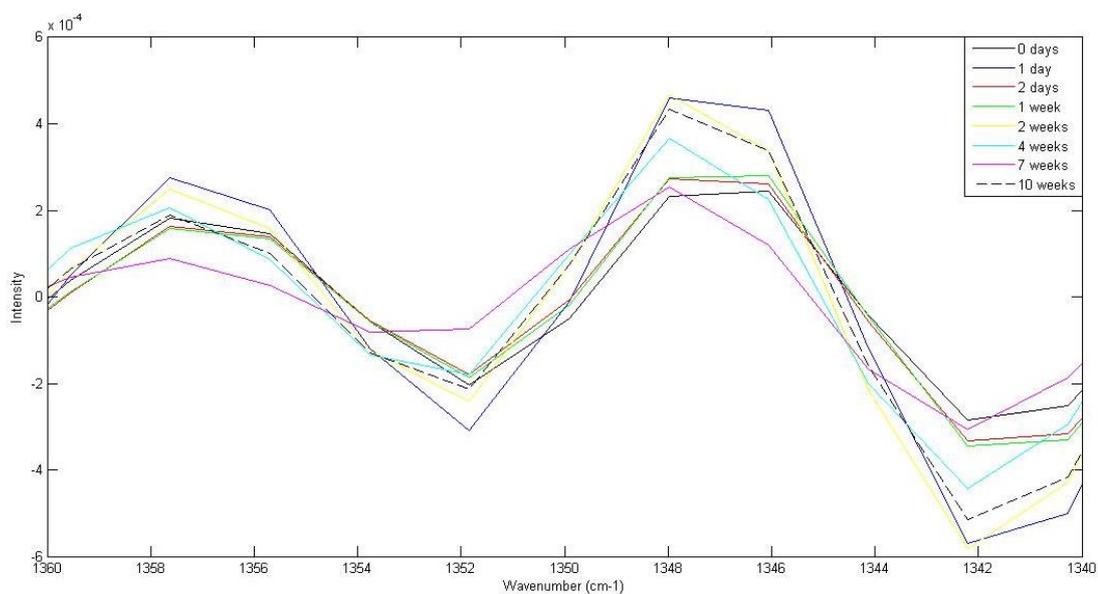


Figure 34: Second derivatised spectrum of WHSmith orange ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

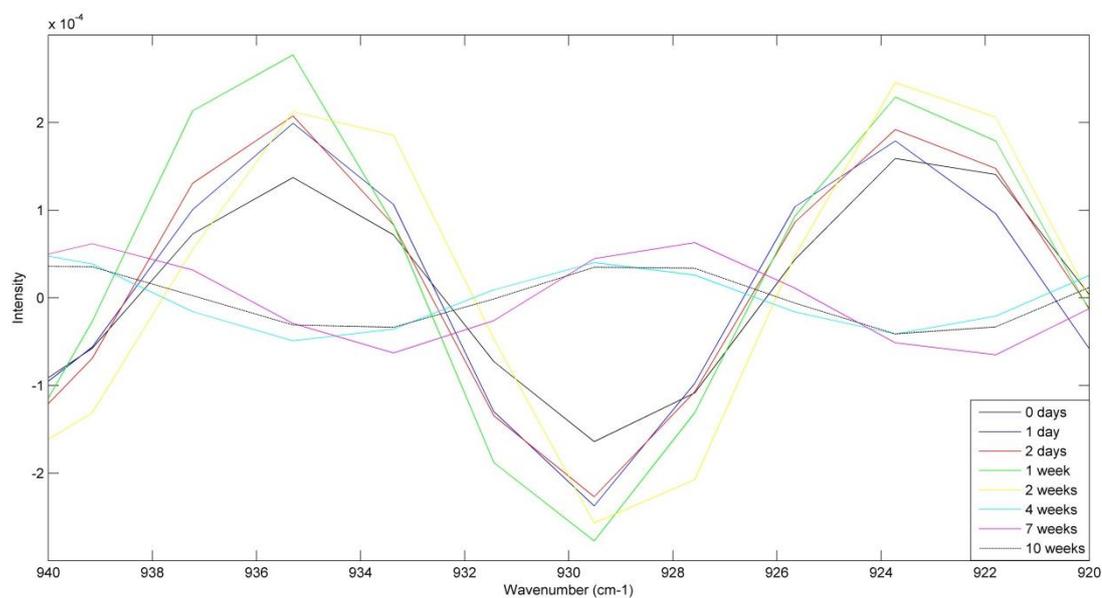


Figure 35: Second derivatised spectrum of WHSmith peach ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

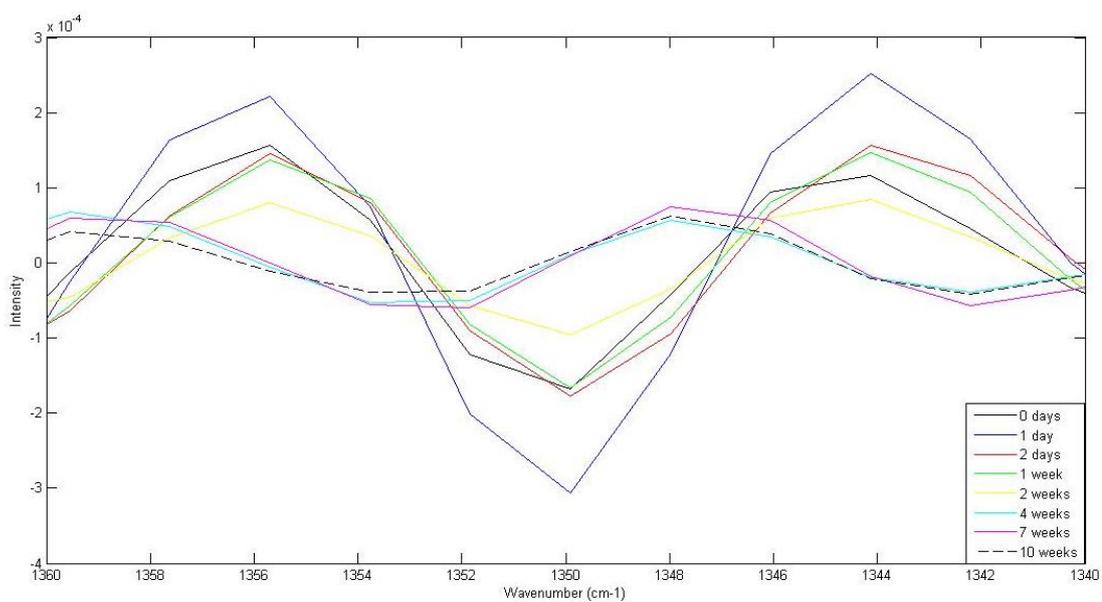


Figure 36: Second derivatised spectrum of WHSmith peach ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

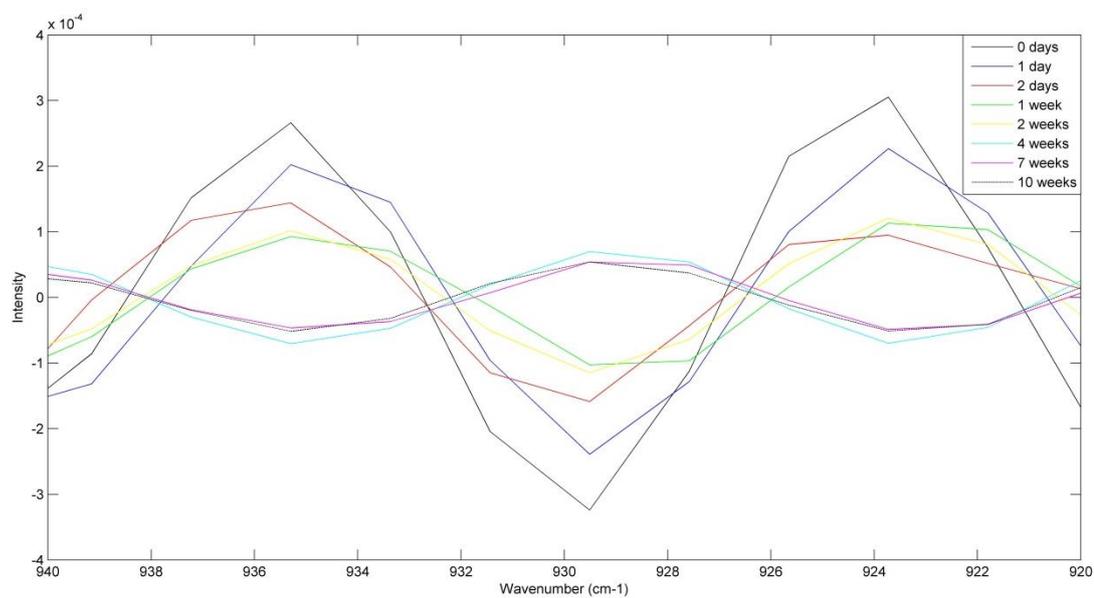


Figure 37: Second derivatised spectrum of WHSmith pink ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

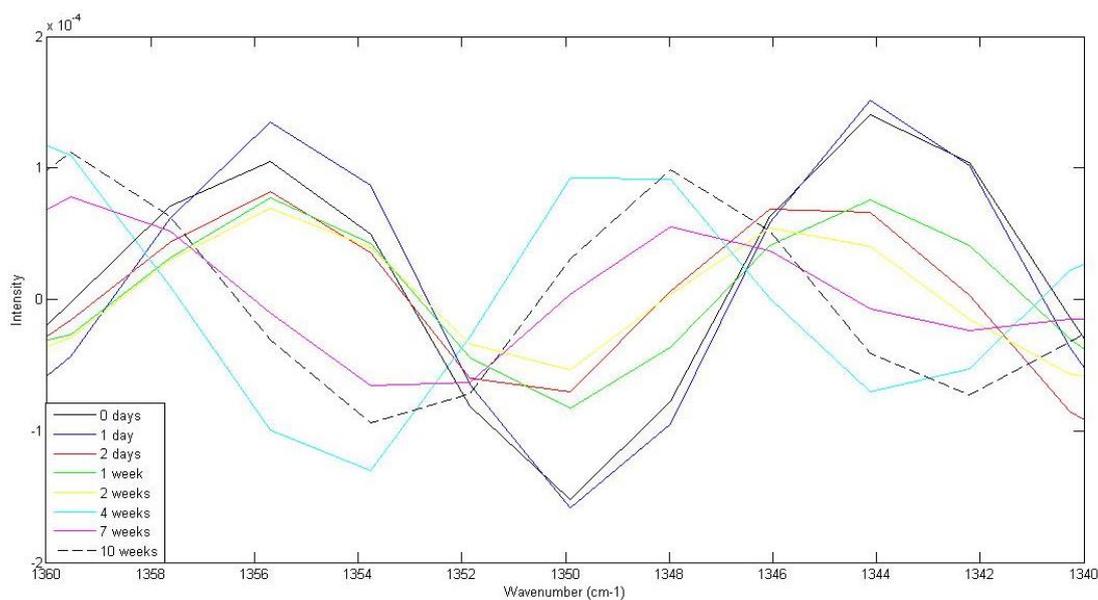


Figure 38: Second derivatised spectrum of WHSmith pink ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

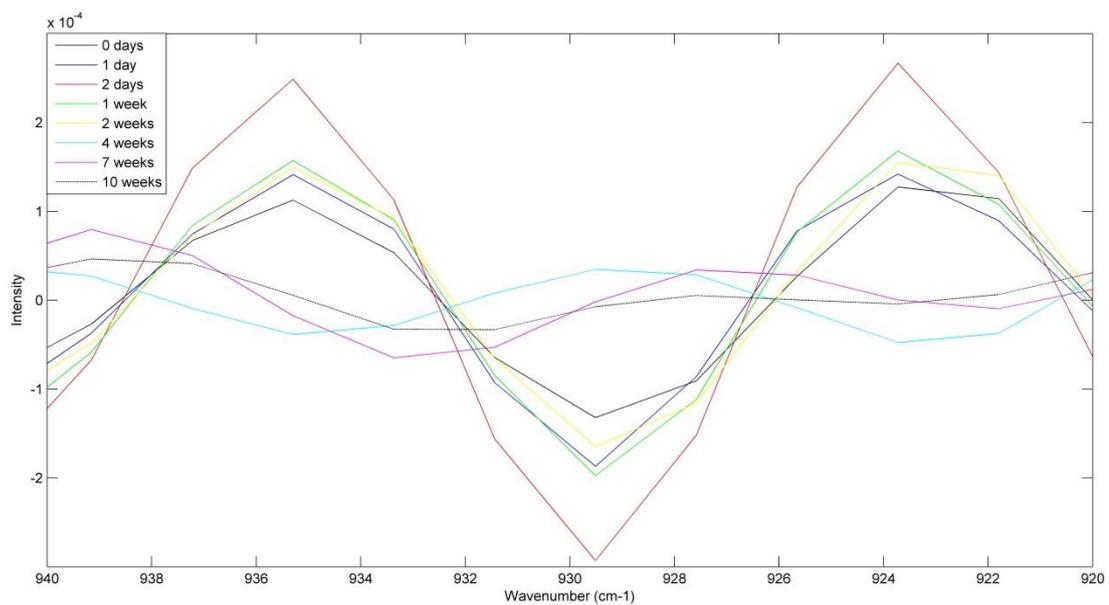


Figure 39: Second derivatised spectrum of WHSmith purple ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

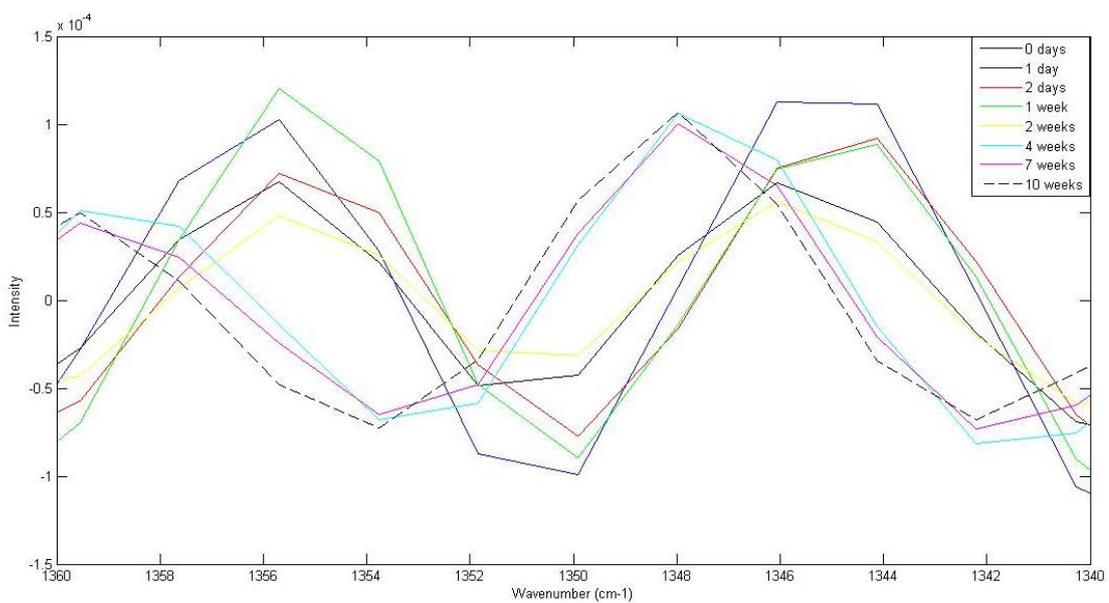


Figure 40: Second derivatised spectrum of WHSmith purple ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

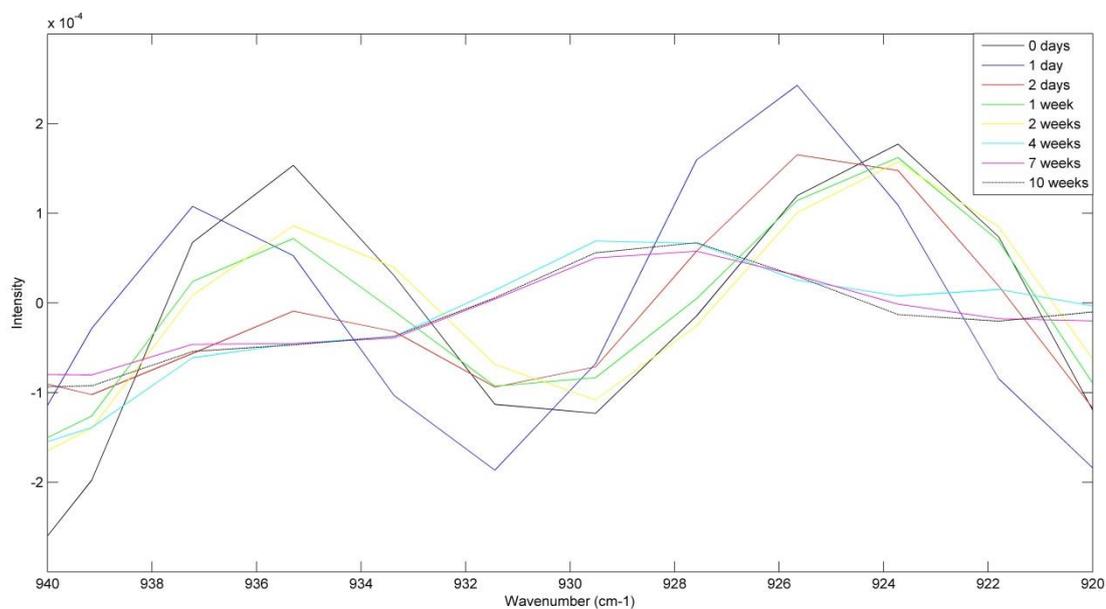


Figure 41: Second derivatised spectrum of WHSmith silver ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

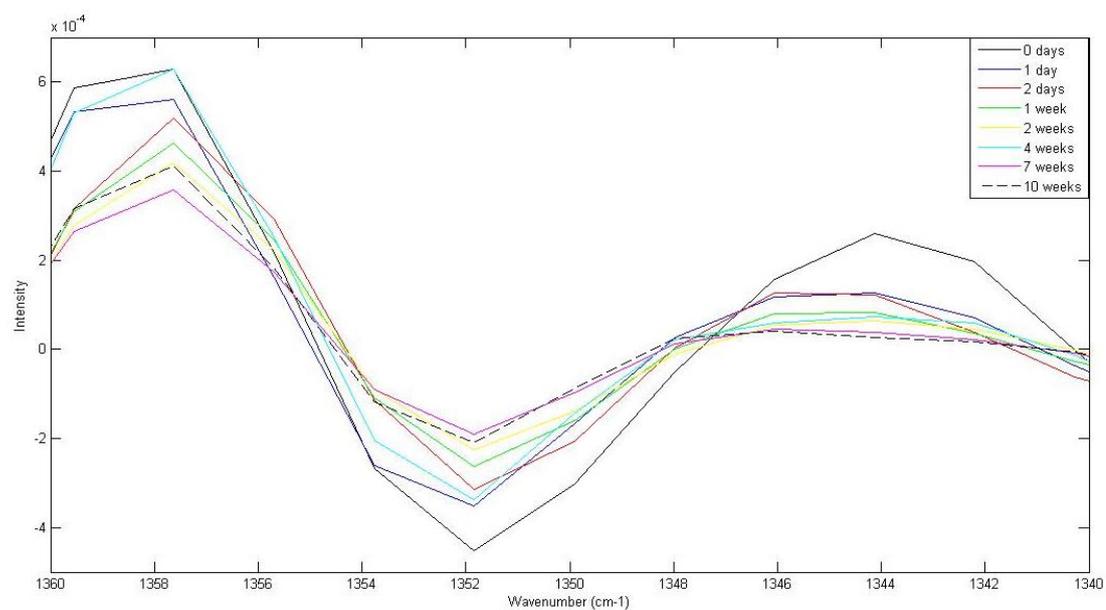


Figure 42: Second derivatised spectrum of WHSmith silver ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

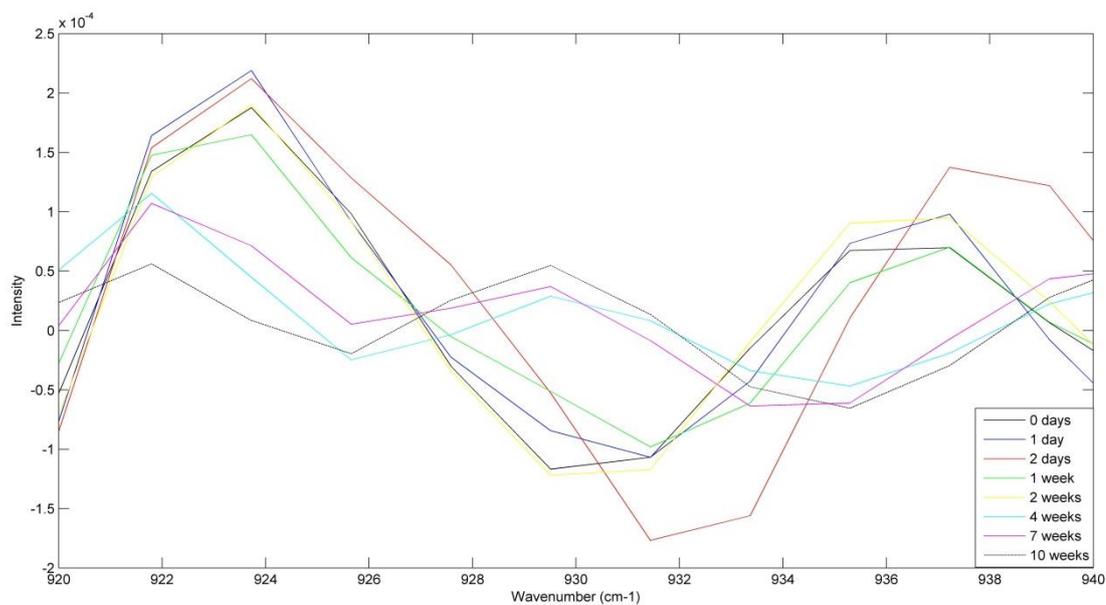


Figure 43: Second derivatised spectrum of WHSmith violet ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

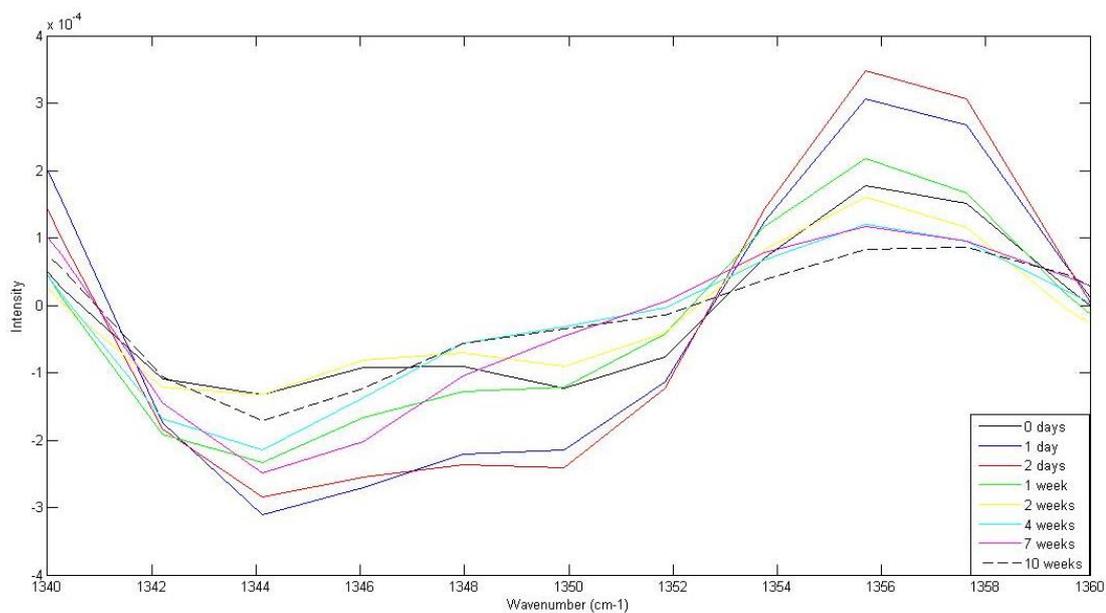


Figure 44: Second derivatised spectrum of WHSmith violet ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

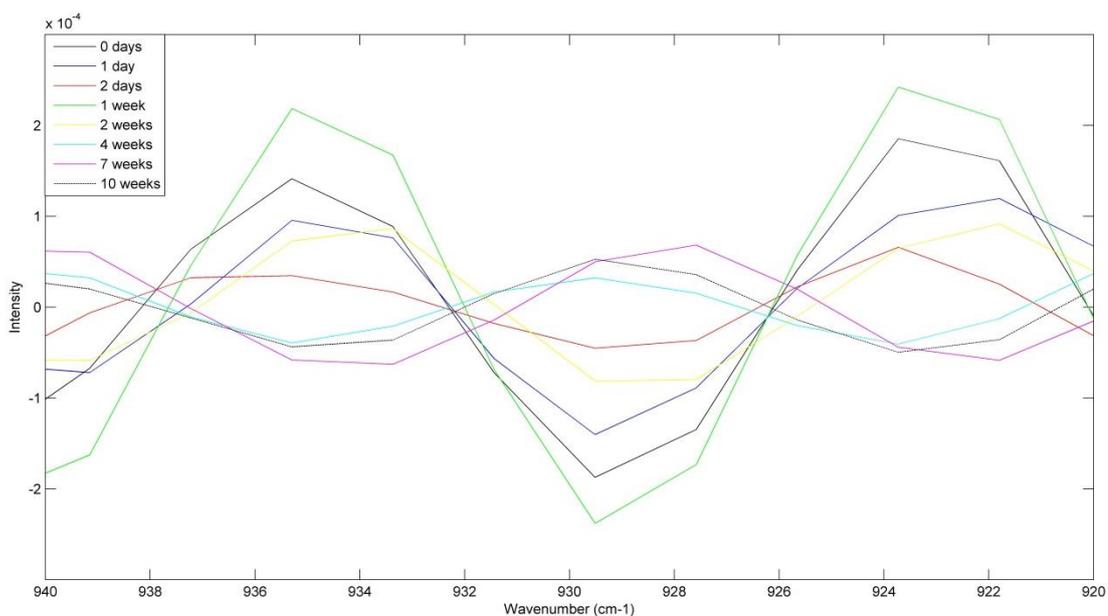


Figure 45: Second derivatised spectrum of WHSmith yellow ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

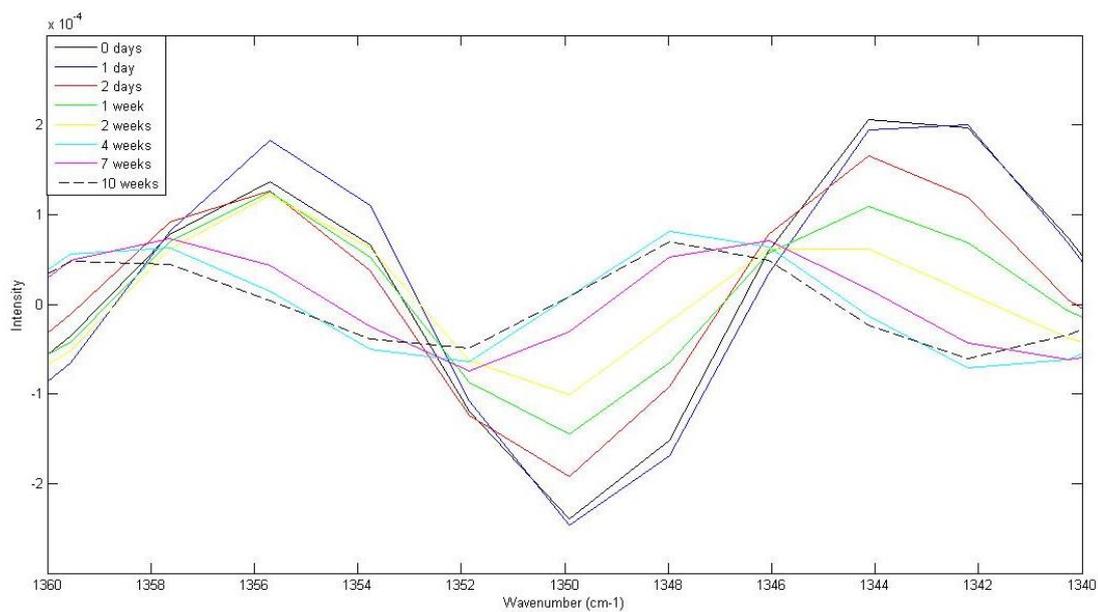


Figure 46: Second derivatised spectrum of WHSmith yellow ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

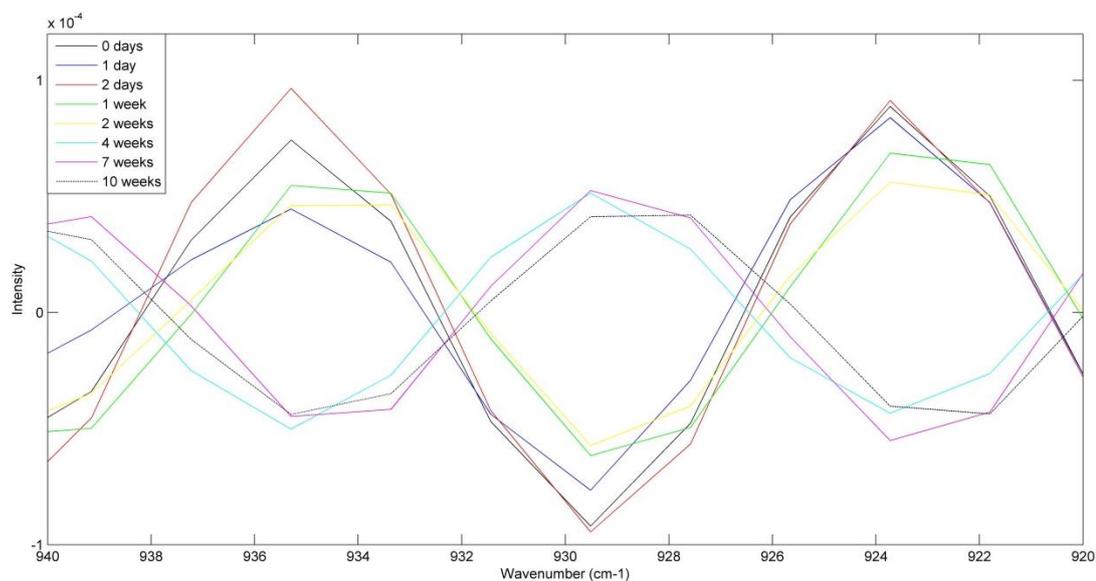


Figure 47: Second derivatised spectrum of WHSmith glitter black ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

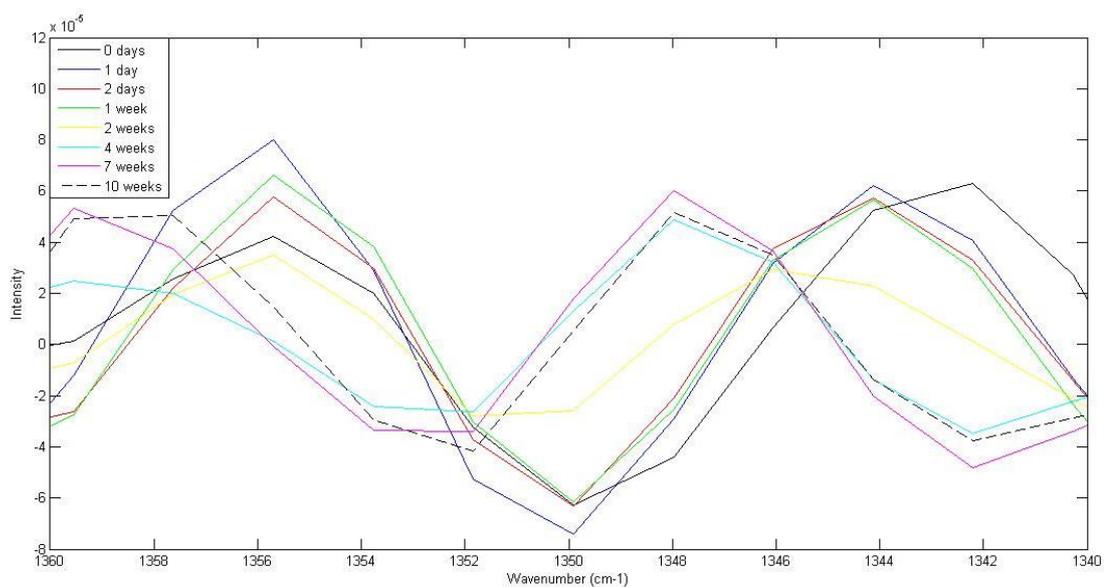


Figure 48: Second derivatised spectrum of WHSmith glitter black ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

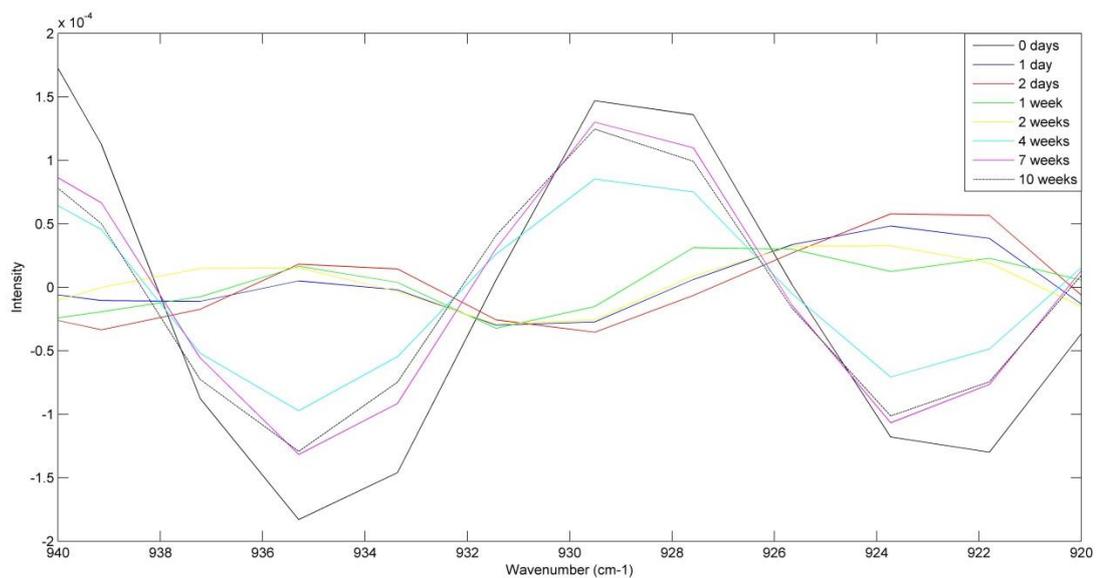


Figure 49: Second derivatised spectrum of WHSmith glitter blue ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

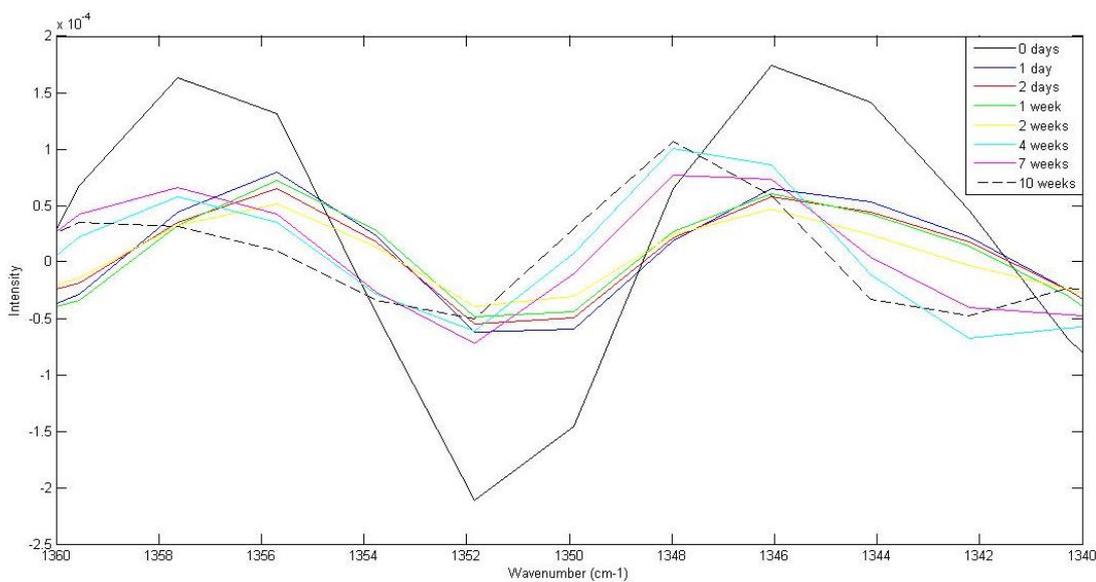


Figure 50: Second derivatised spectrum of WHSmith glitter blue ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

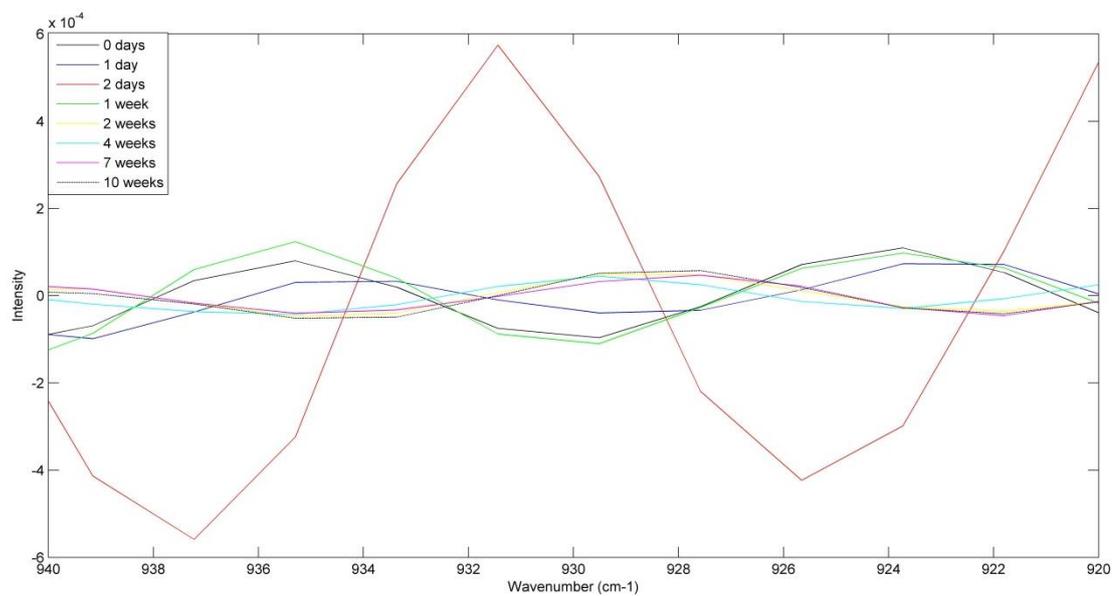


Figure 51: Second derivatised spectrum of WHSmith glitter gold ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

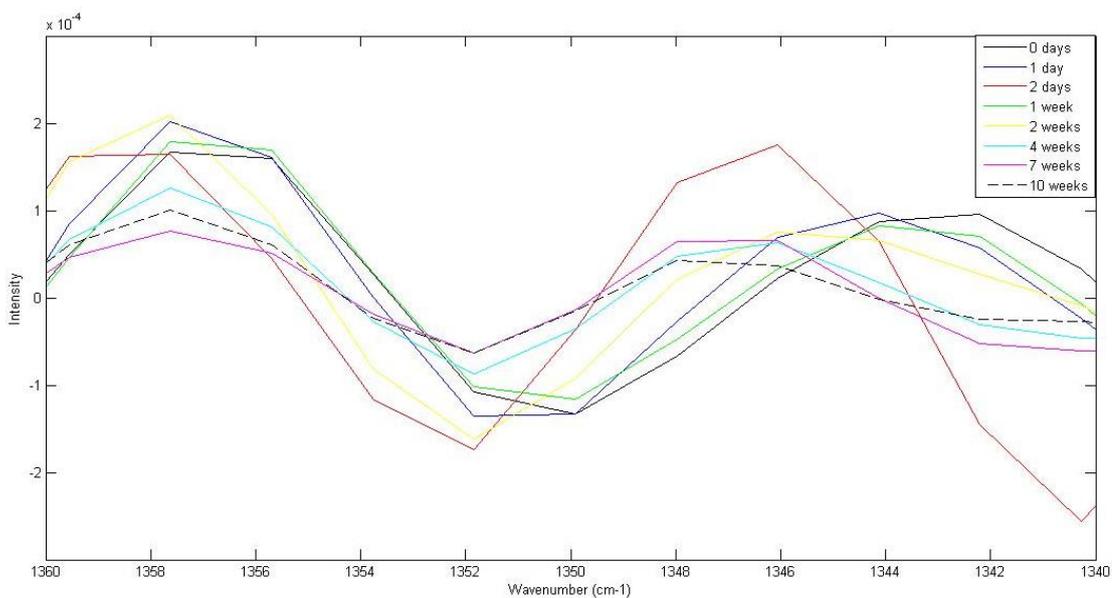


Figure 52: Second derivatised spectrum of WHSmith glitter gold ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

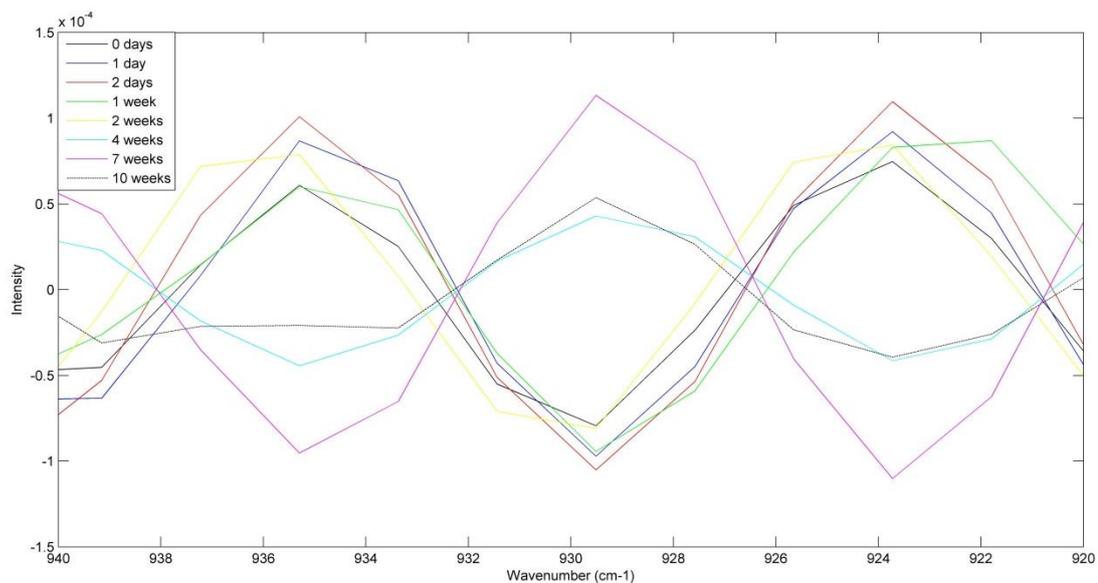


Figure 53: Second derivatised spectrum of WHSmith glitter green ink over the wavenumber range of 920cm⁻¹ to 940cm⁻¹.

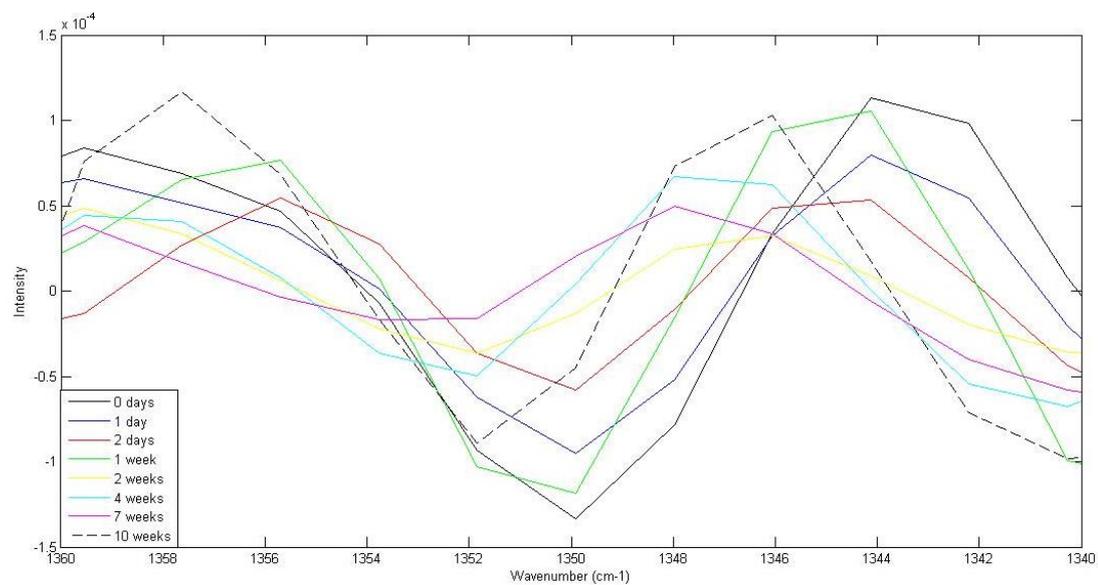


Figure 54: Second derivatised spectrum of WHSmith glitter green ink over the wavenumber range of 1340cm⁻¹ to 1360cm⁻¹.

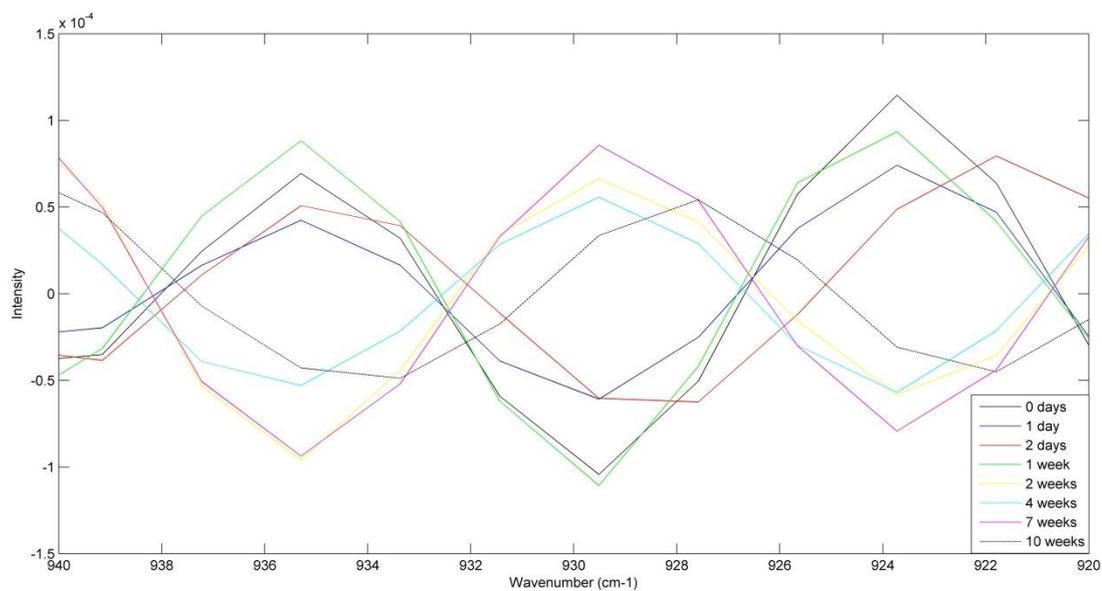


Figure 55: Second derivatised spectrum of WHSmith glitter light blue ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

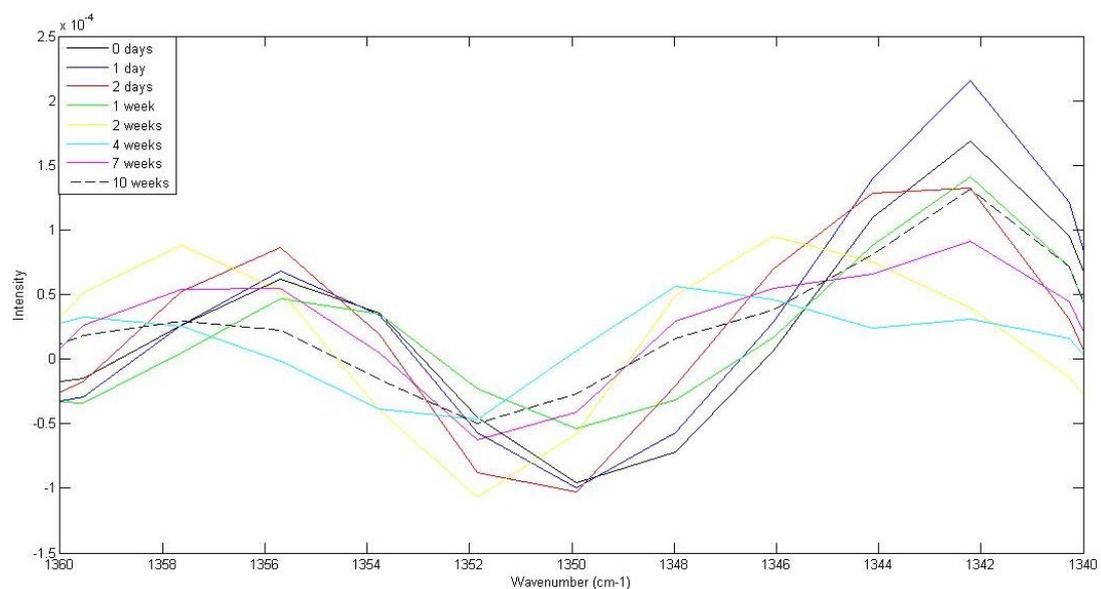


Figure 56: Second derivatised spectrum of WHSmith glitter light blue ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

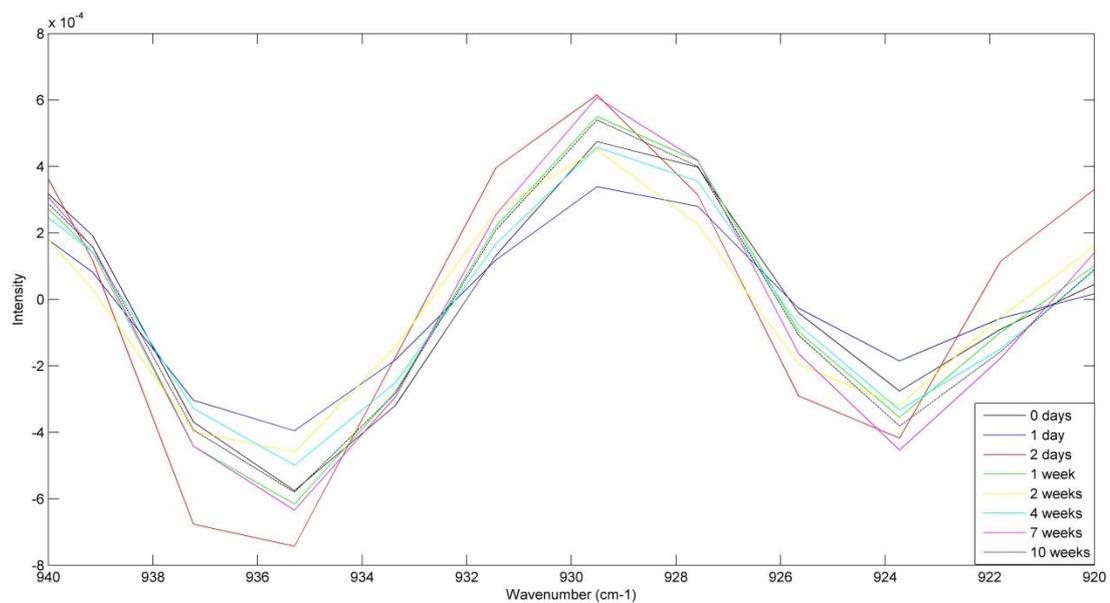


Figure 57: Second derivatised spectrum of WHSmith glitter orange ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

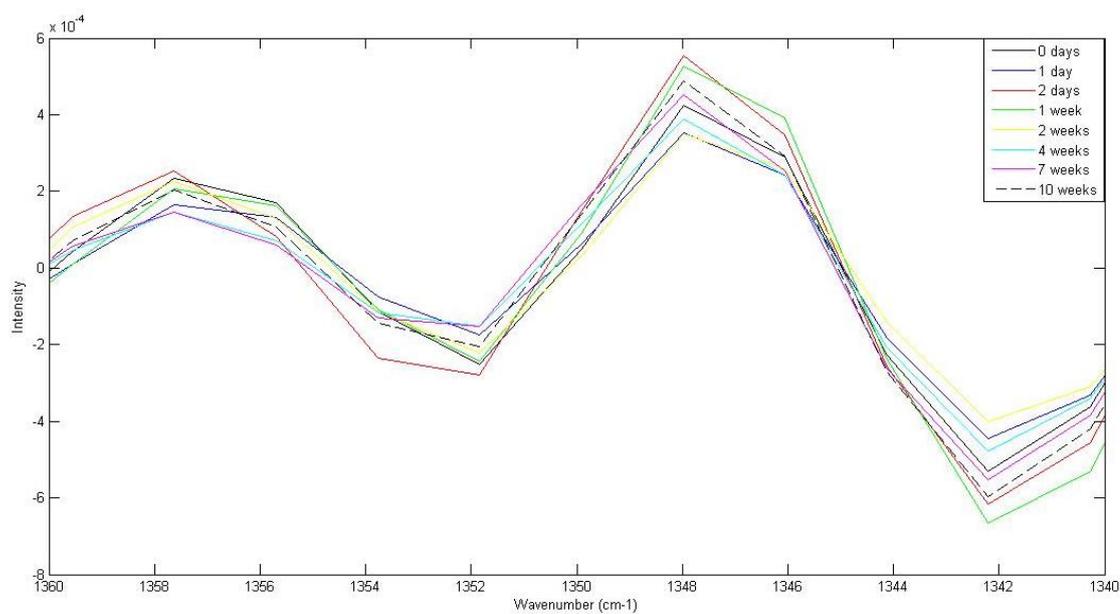


Figure 58: Second derivatised spectrum of WHSmith glitter orange ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

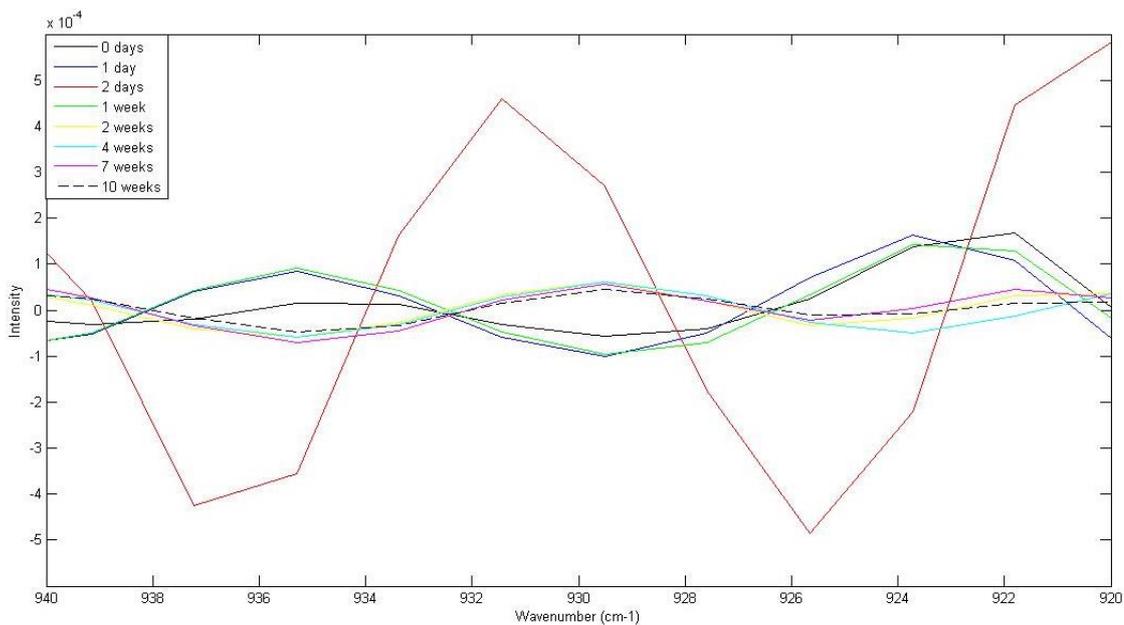


Figure 59: Second derivatised spectrum of WHSmith glitter pink ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

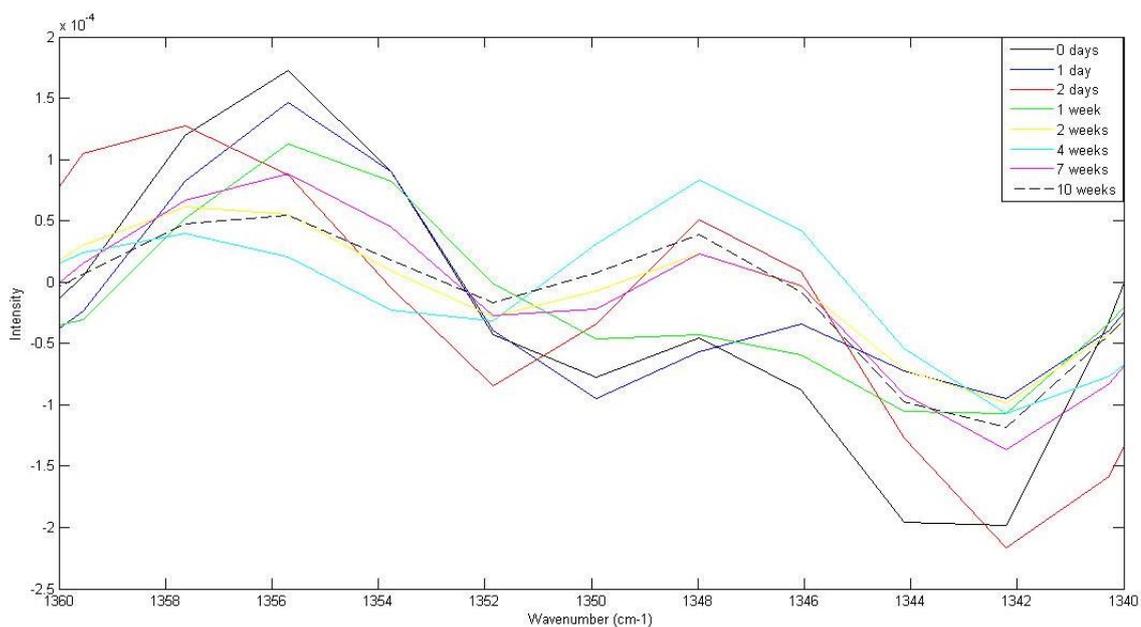


Figure 60: Second derivatised spectrum of WHSmith glitter pink ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

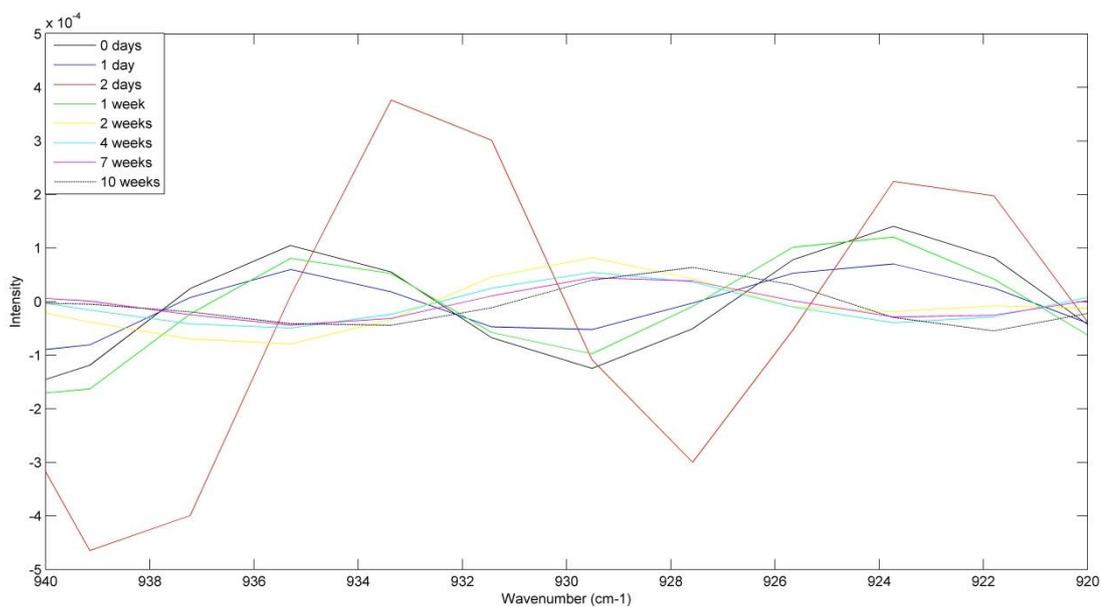


Figure 61: Second derivatised spectrum of WHSmith glitter purple ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

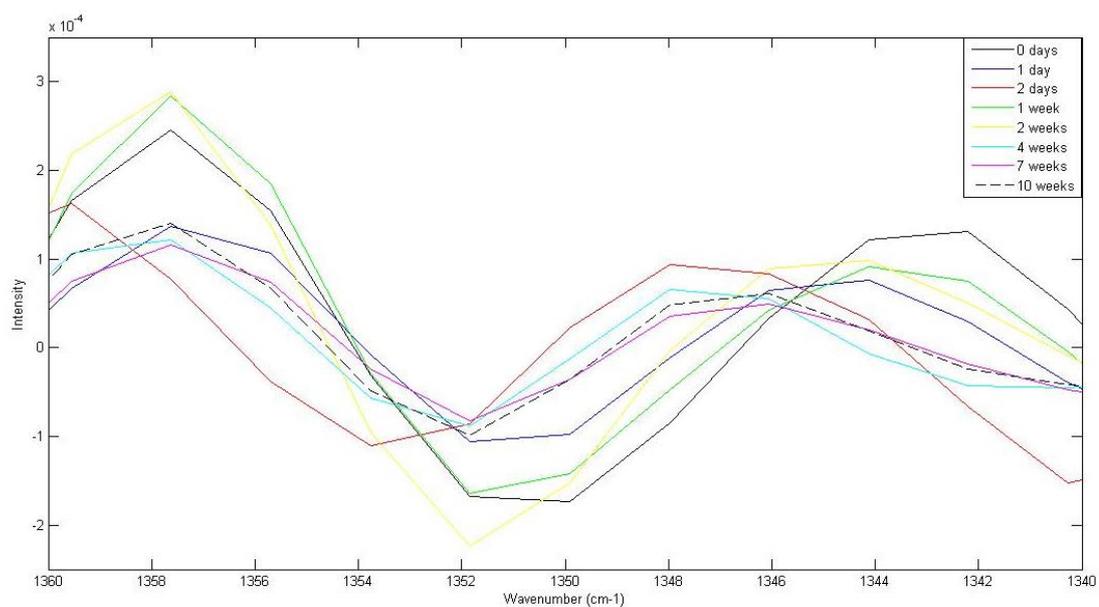


Figure 62: Second derivatised spectrum of WHSmith glitter purple ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

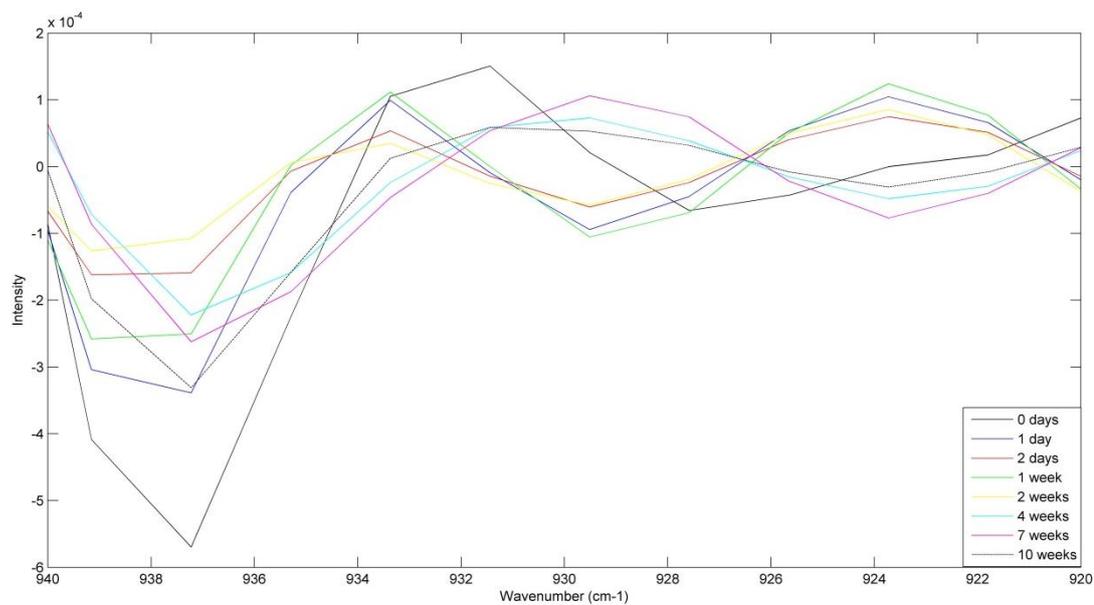


Figure 63: Second derivatised spectrum of WHSmith glitter red ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

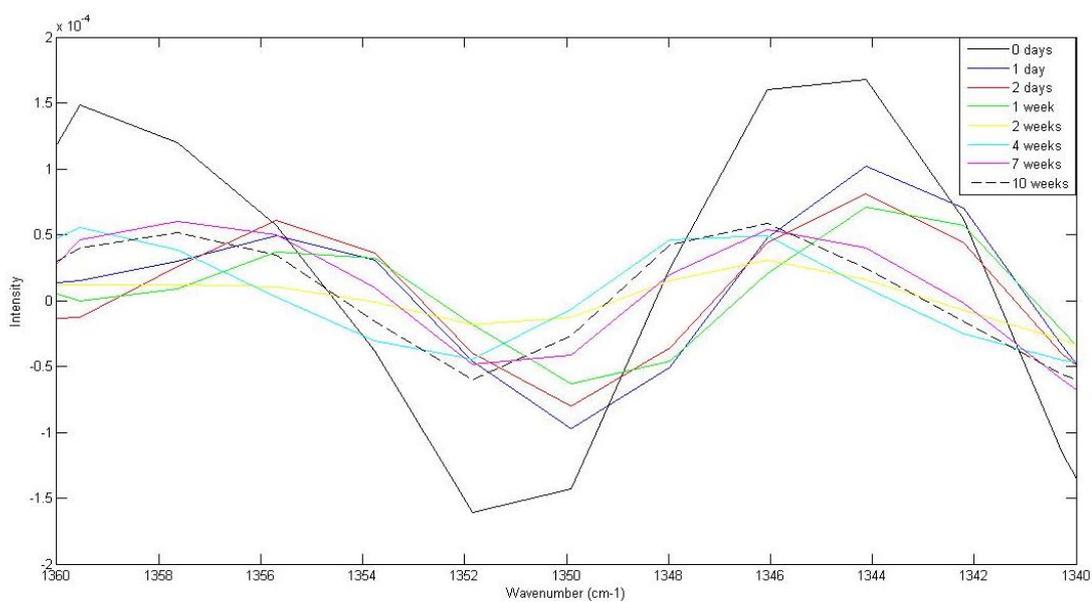


Figure 64: Second derivatised spectrum of WHSmith glitter red ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

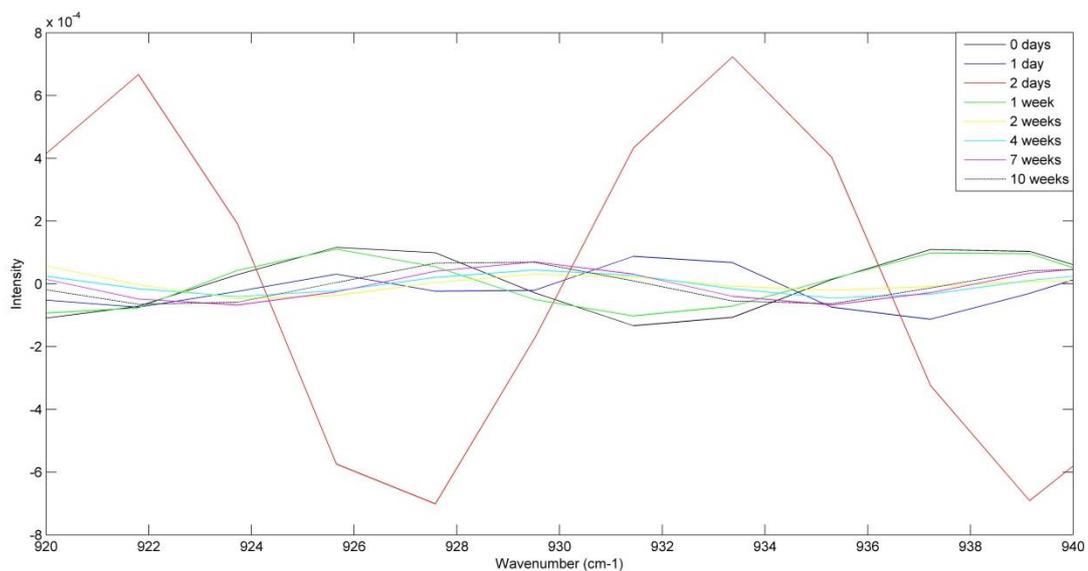


Figure 65: Second derivatised spectrum of WHSmith glitter silver ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

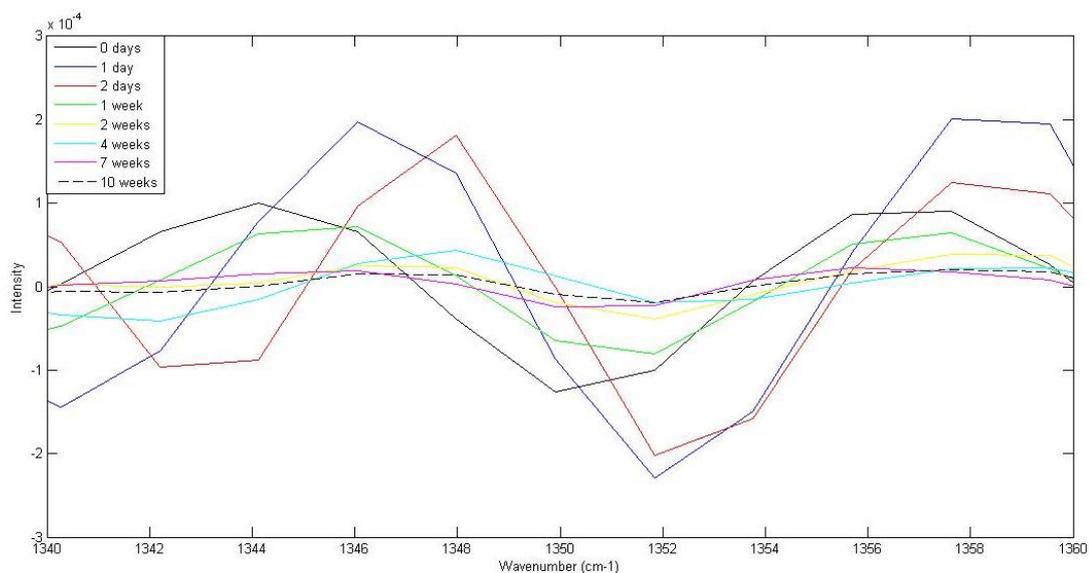


Figure 66: Second derivatised spectrum of WHSmith glitter silver ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

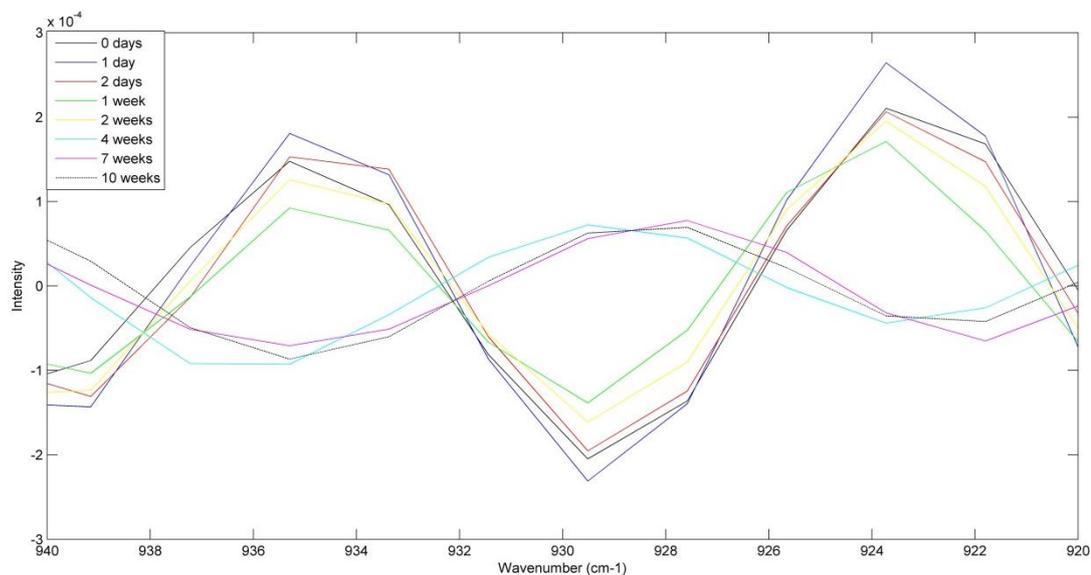


Figure 67: Second derivatised spectrum of Wilko green ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

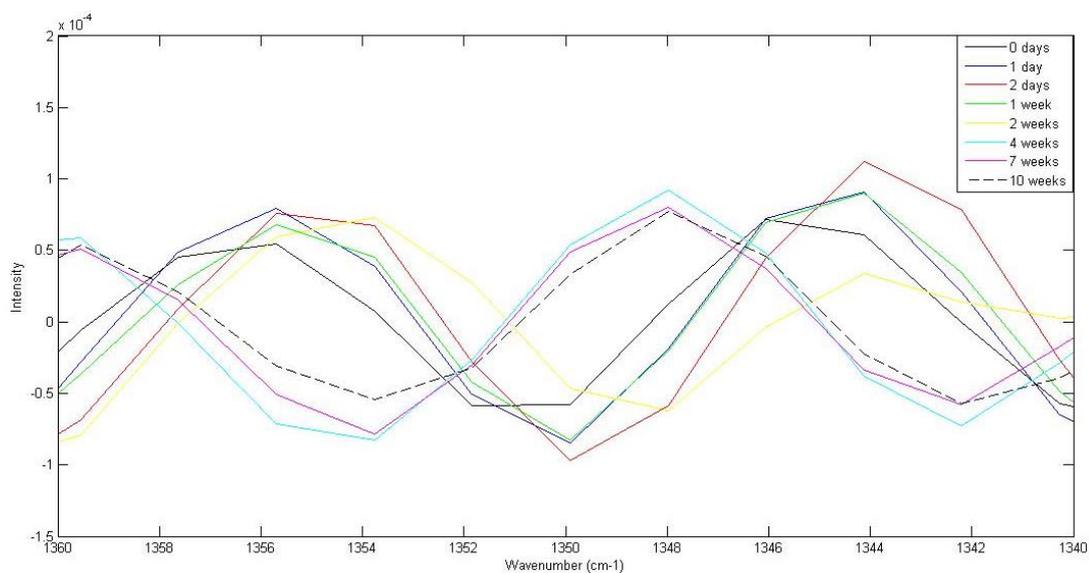


Figure 68: Second derivatised spectrum of Wilko green ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

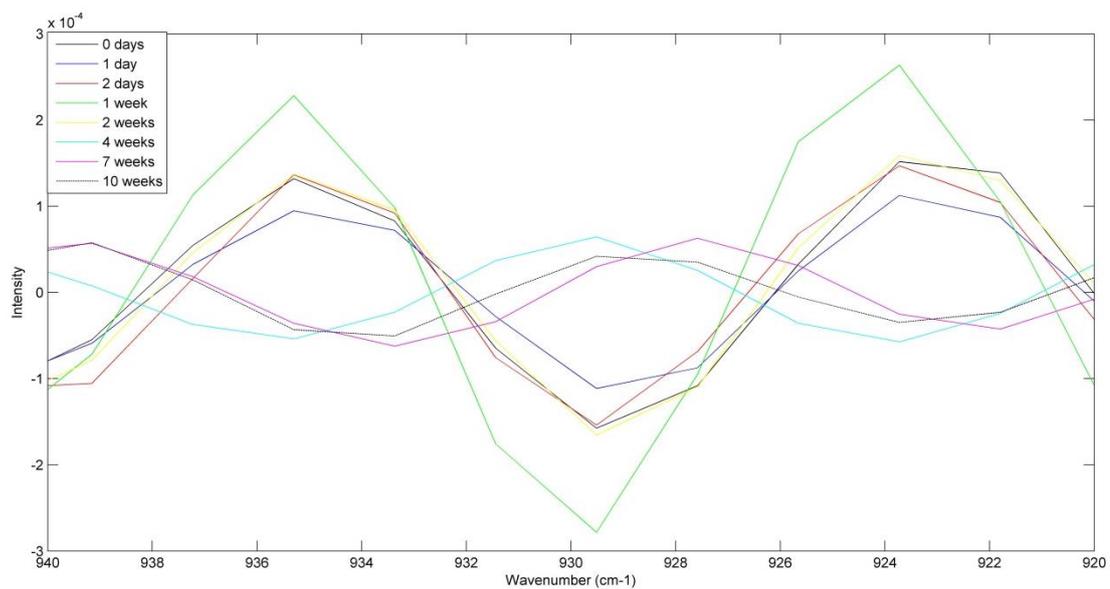


Figure 69: Second derivatised spectrum of Wilko orange ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

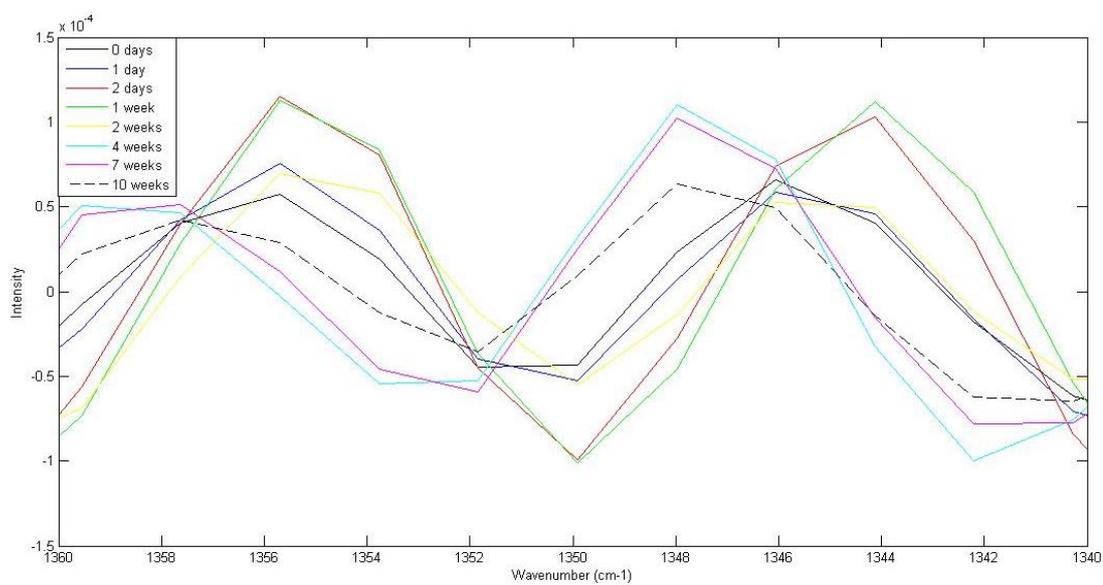


Figure 70: Second derivatised spectrum of Wilko orange ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

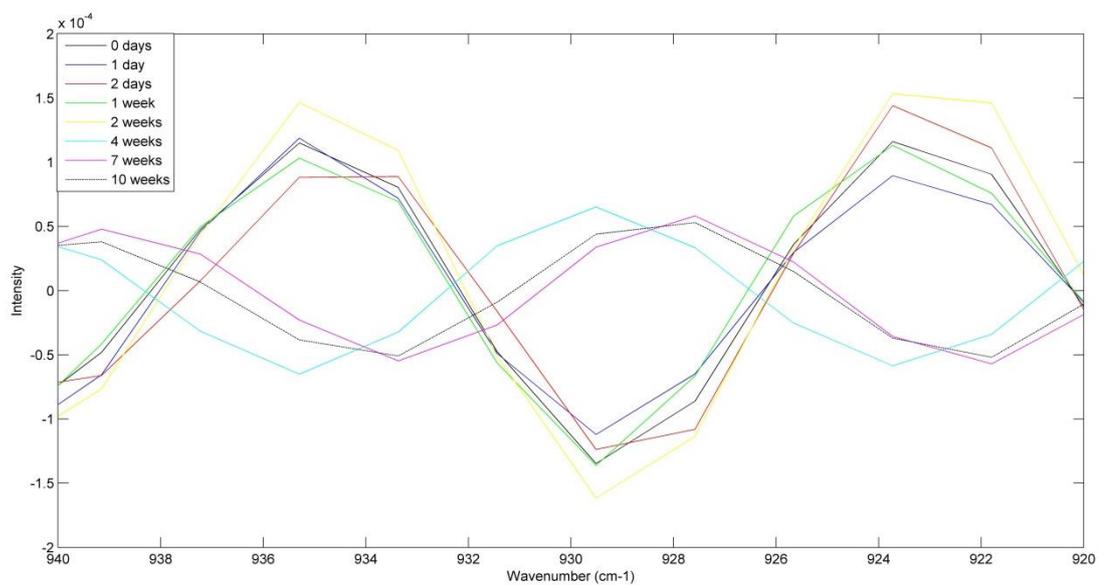


Figure 71: Second derivatised spectrum of Wilko pink ink over the wavenumber range of 922 cm^{-1} to 940 cm^{-1} .

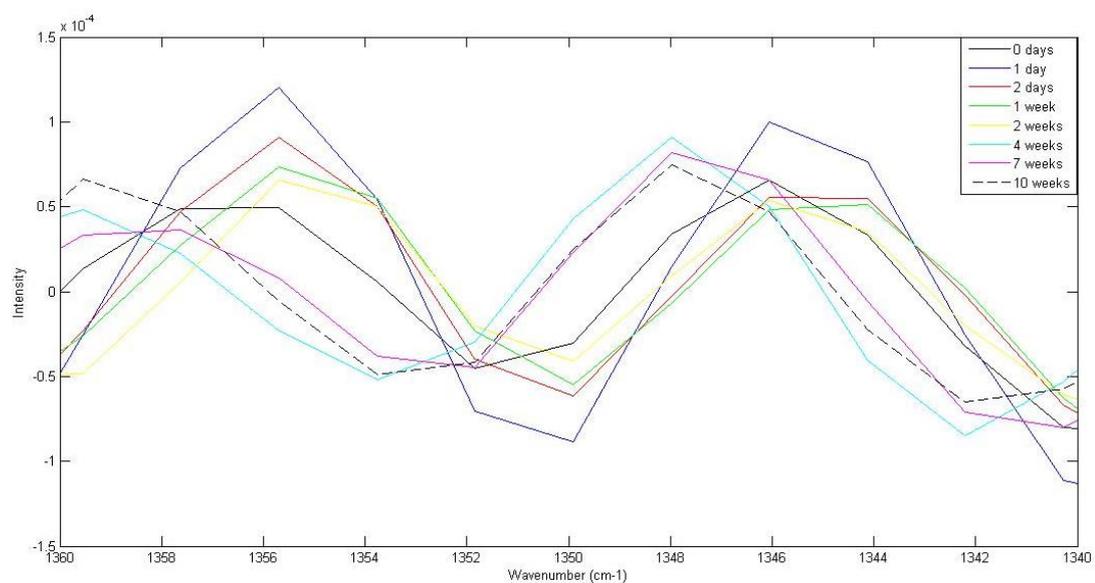


Figure 72: Second derivatised spectrum of Wilko pink ink over the wavenumber range of 1340 cm^{-1} to 1360 cm^{-1} .

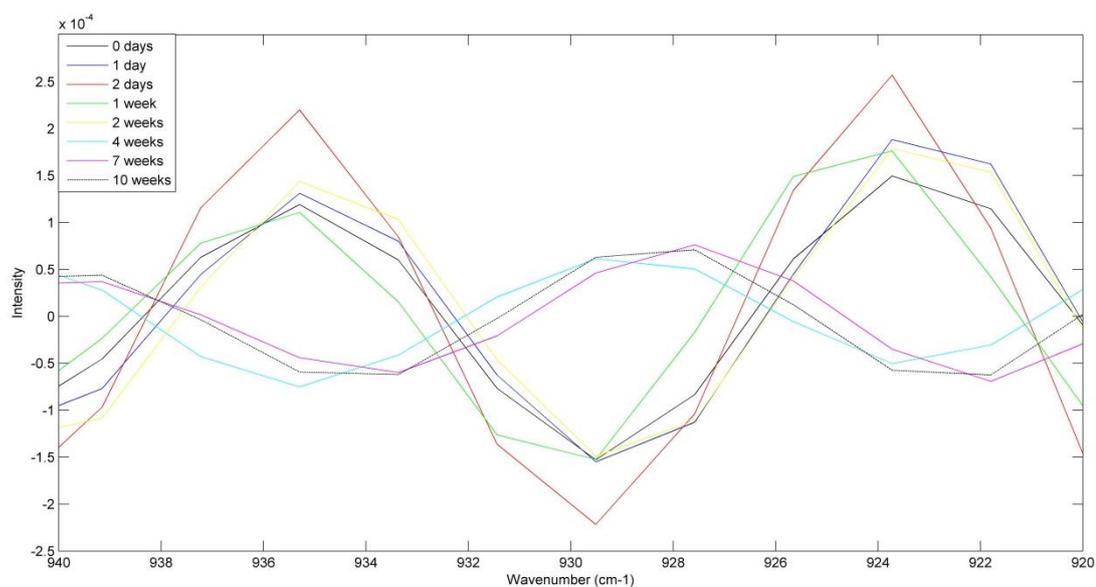


Figure 73: Second derivatised spectrum of Wilko purple ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

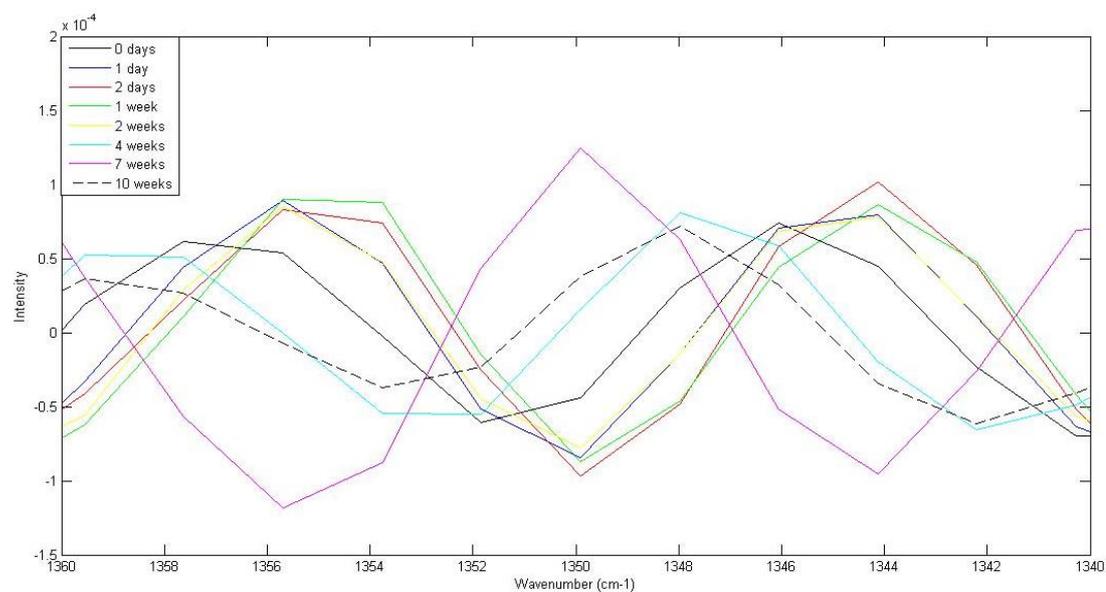


Figure 74: Second derivatised spectrum of Wilko purple ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

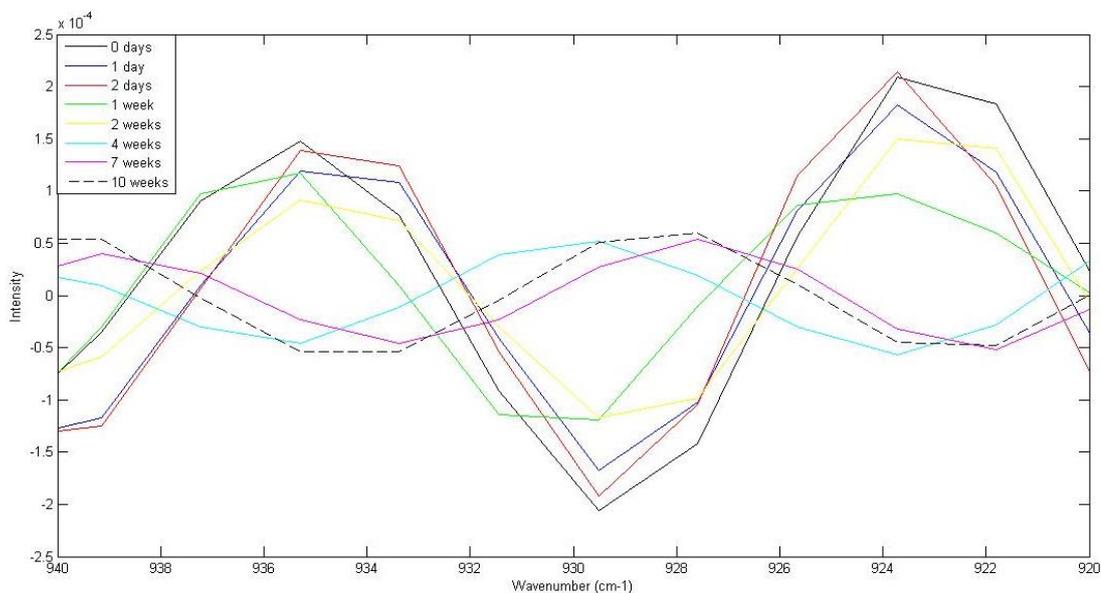


Figure 75: Second derivatised spectrum of Wilko yellow ink over the wavenumber range of 920cm^{-1} to 940cm^{-1} .

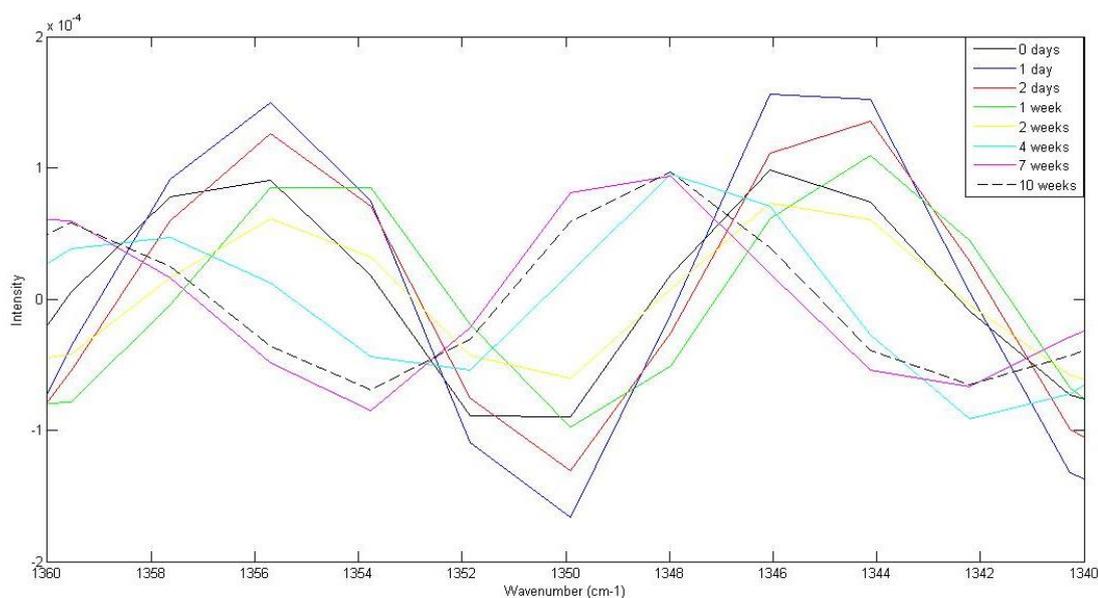


Figure 76: Second derivatised spectrum of Wilko yellow ink over the wavenumber range of 1340cm^{-1} to 1360cm^{-1} .

Appendix F

Appendix F contains a collection of group scatter plots for each of the inks being analysed. The scatter plots compared the most discriminative feature from the second derivatised spectra over the time periods analysed during the aging study.

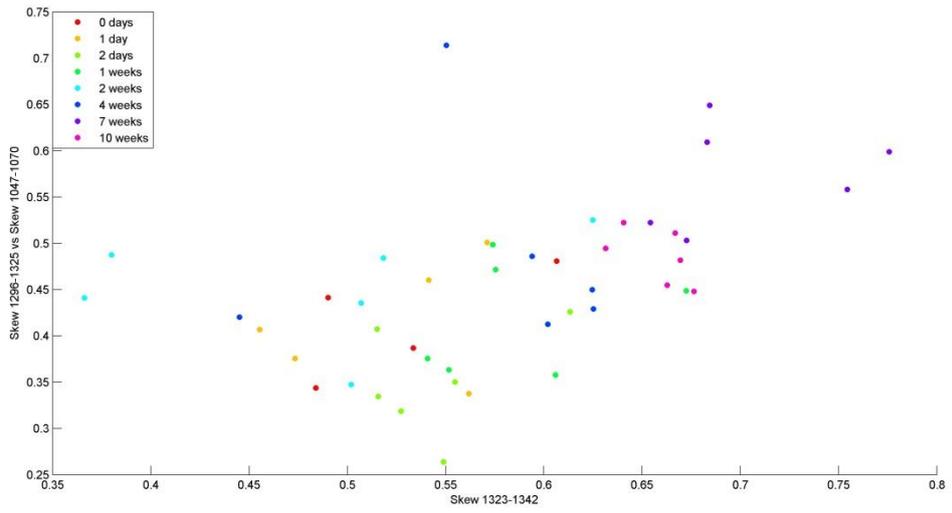


Figure 1: Group scatter plot for Club black ink.

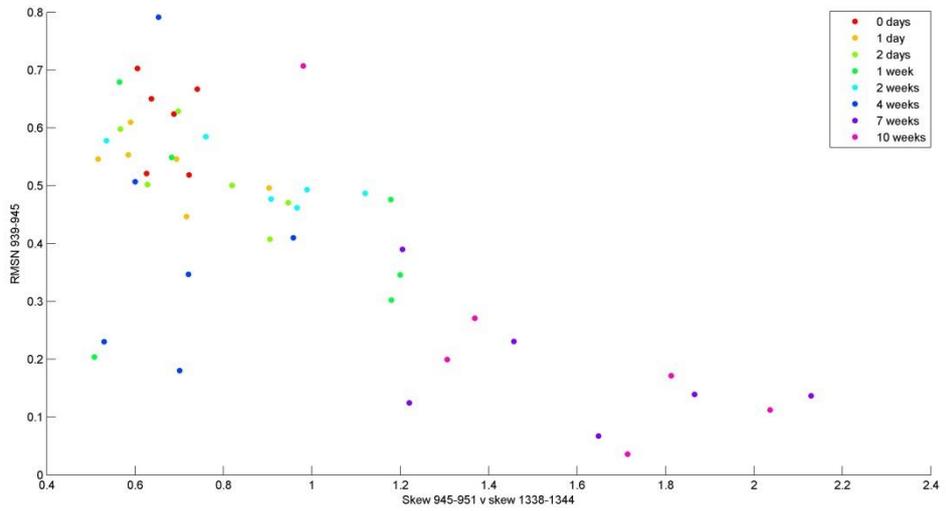


Figure 2: Group scatter plot for Club blue ink.

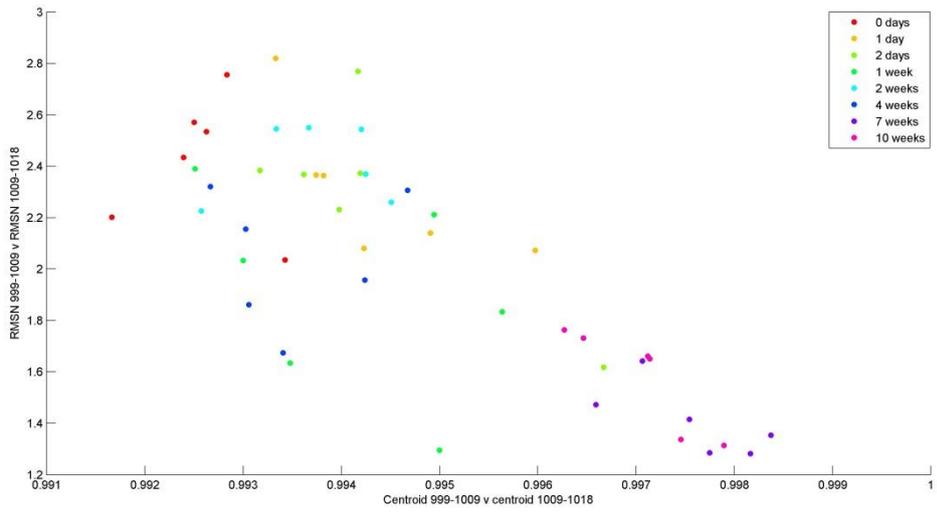


Figure 3: Group scatter plot for Club green ink.

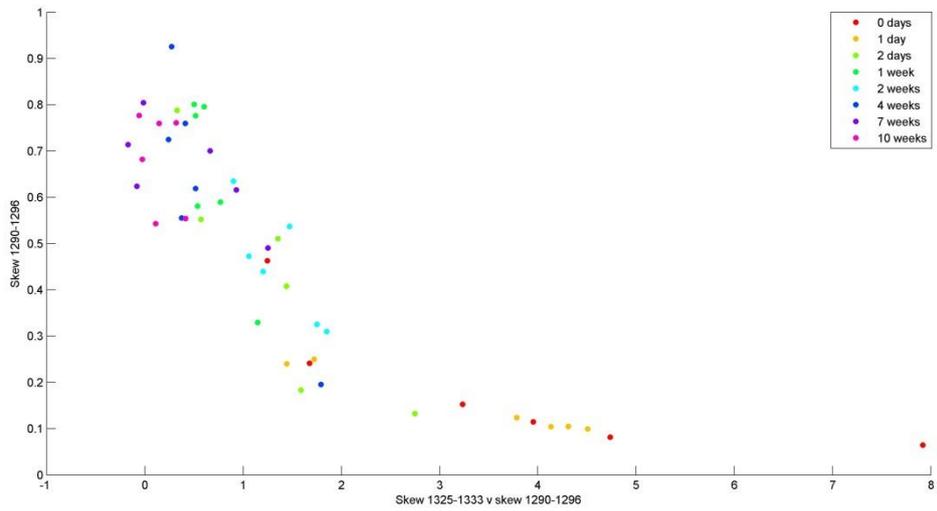


Figure 4: Group scatter plot for Club red ink.

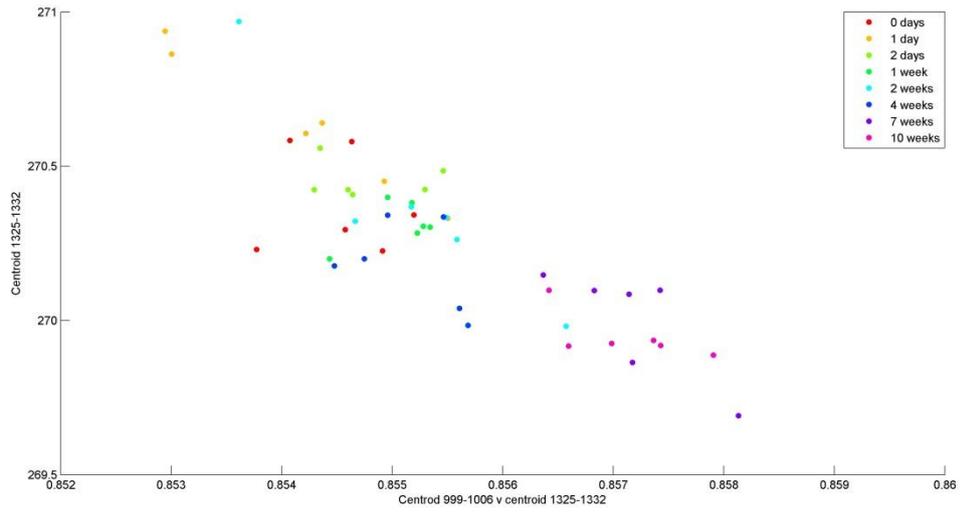


Figure 5: Group scatter plot for Papermate black ink.

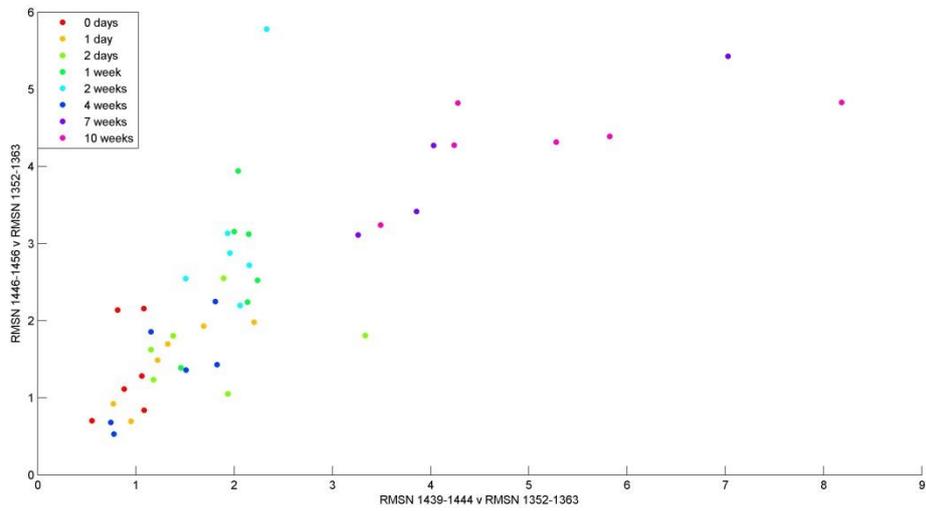


Figure 6: Group scatter plot for Papermate blue ink.

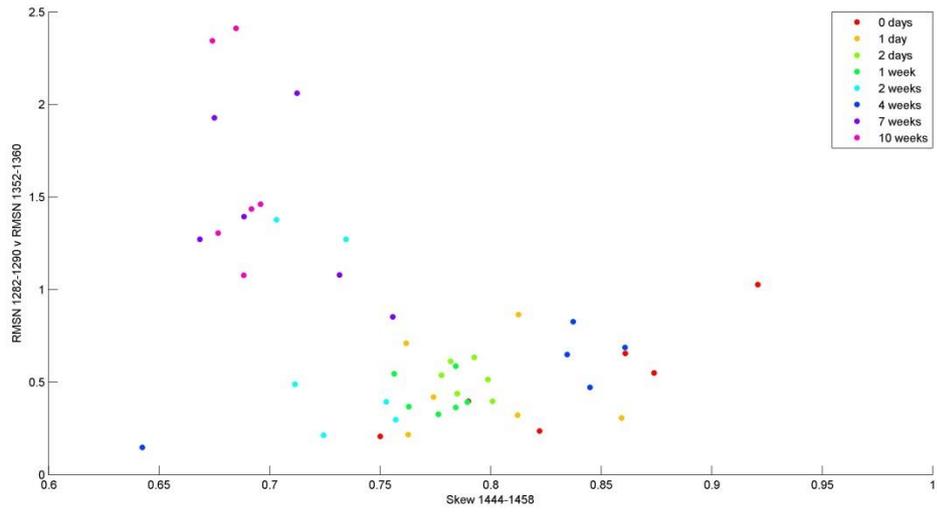


Figure 7: Group scatter plot for Papermate green ink.

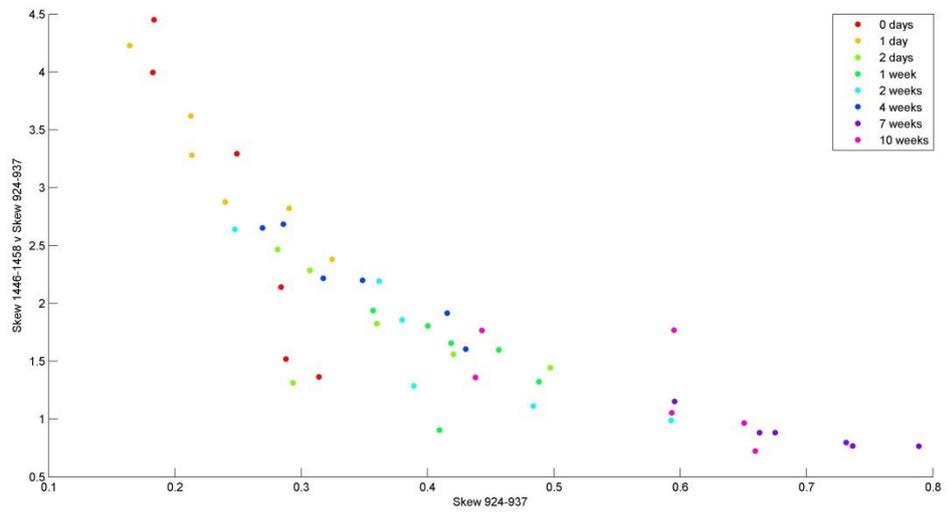


Figure 8: Group scatter plot for Papermate red ink.

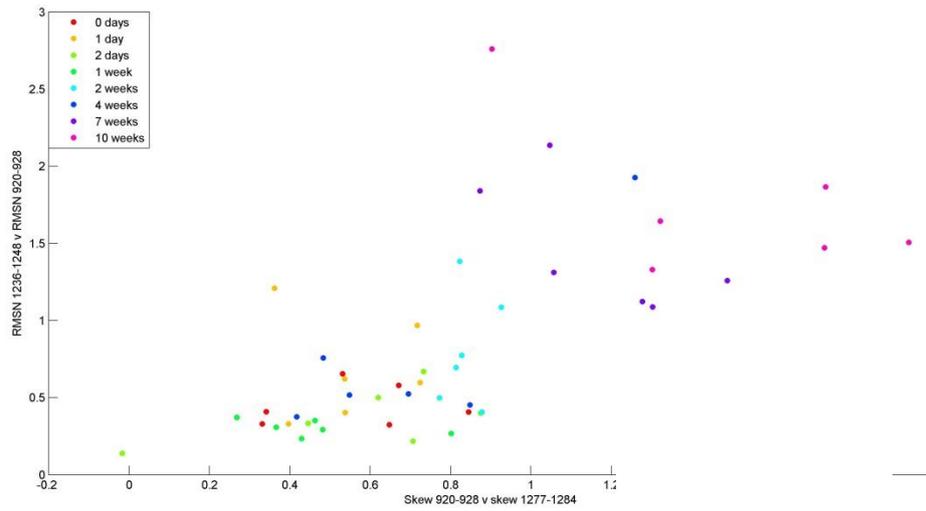


Figure 9: Group scatter plot for Uni-ball Signo black ink

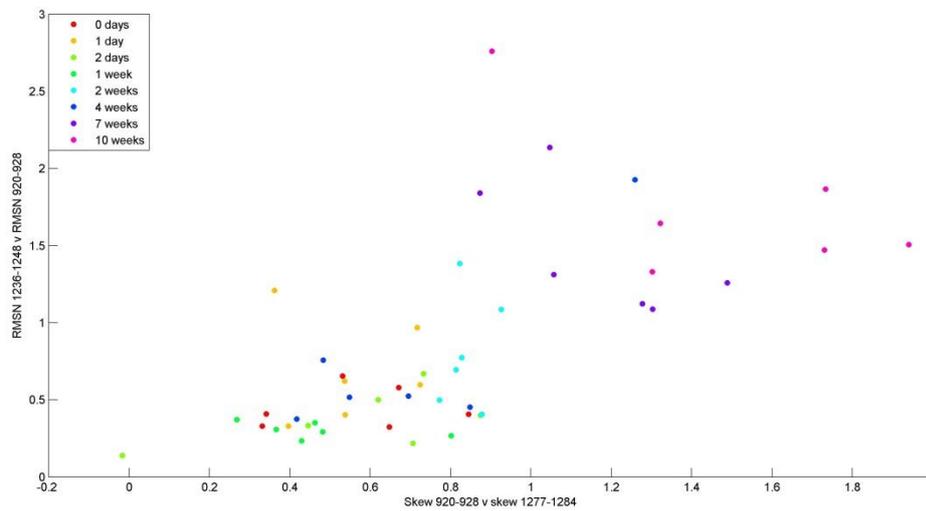


Figure 10: Group scatter plot for Uni-ball Signo blue ink.

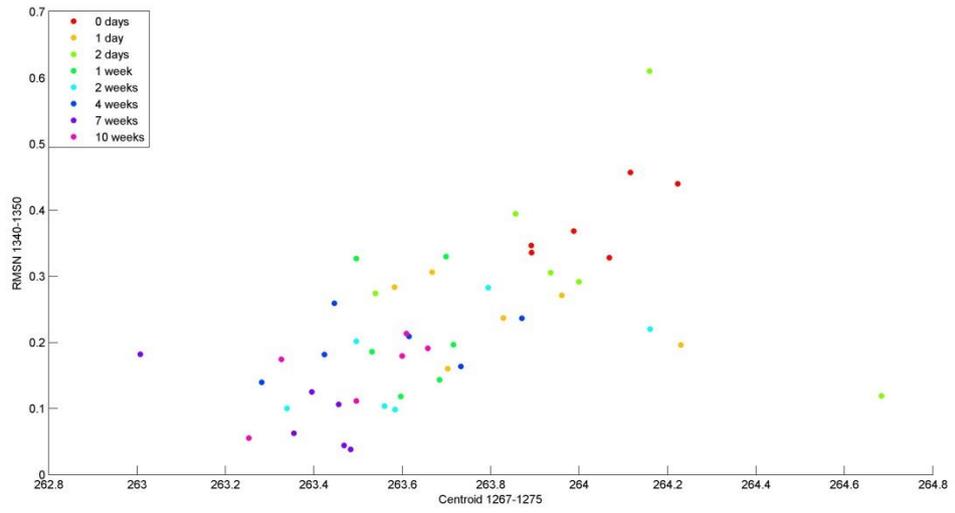


Figure 11: Group scatter plot for Uni-ball Signo green ink.

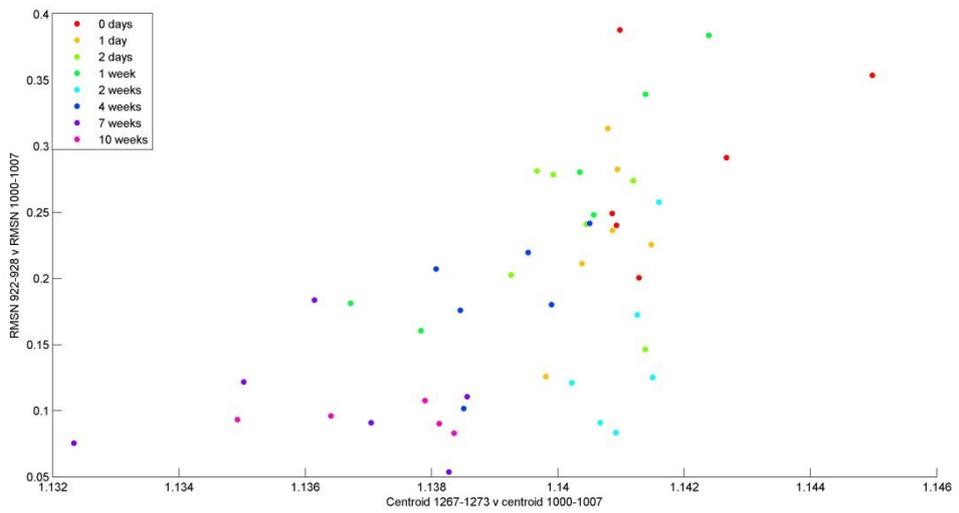


Figure 12: Group scatter plot for Uni-ball Signo light blue ink.

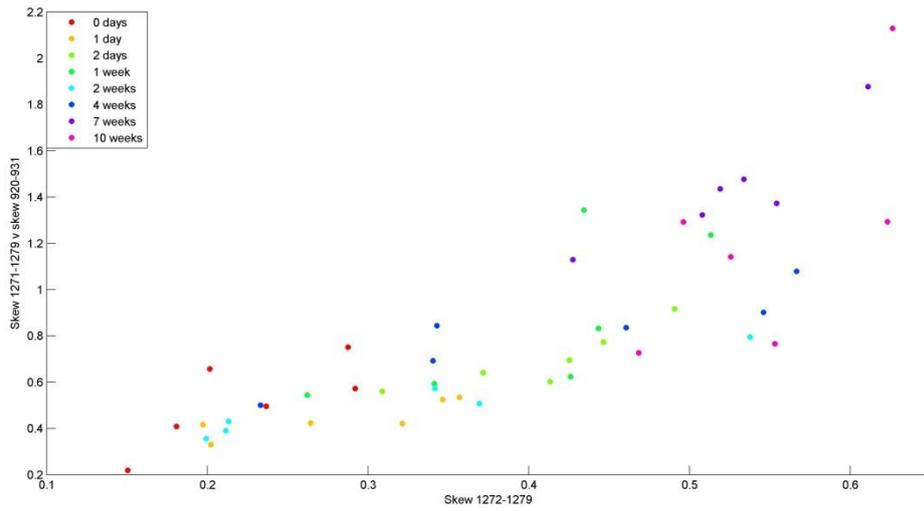


Figure 13: Group scatter plot for Uni-ball Signo orange ink.

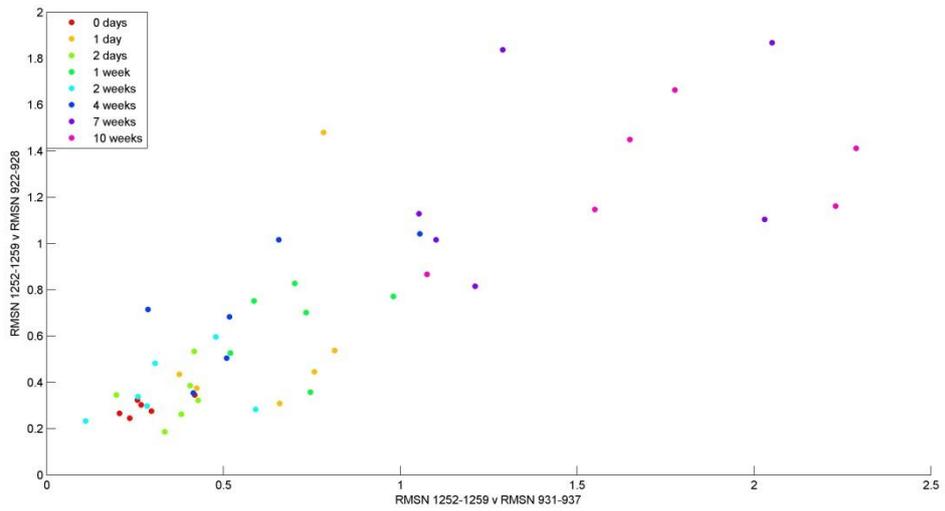


Figure 14: Group scatter plot for Uni-ball Signo pink ink.

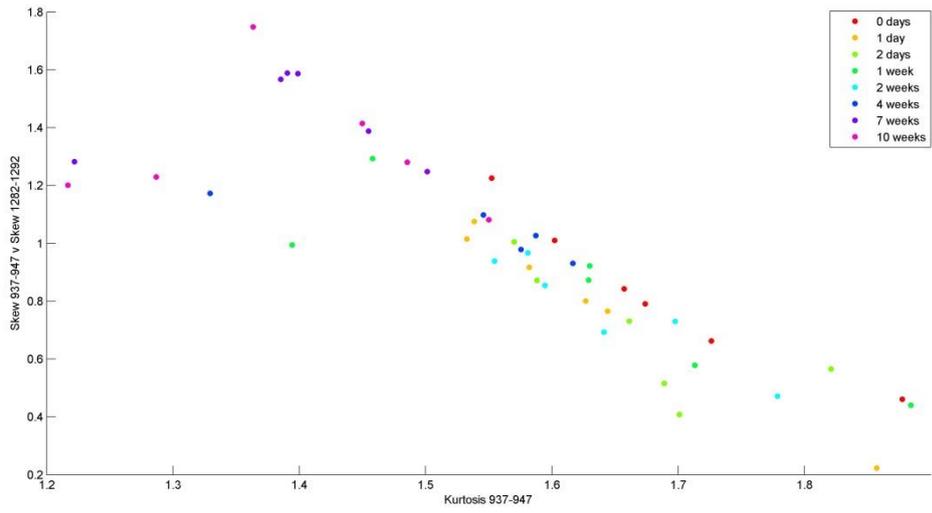


Figure 15: Group scatter plot for Uni-ball Signo purple ink.

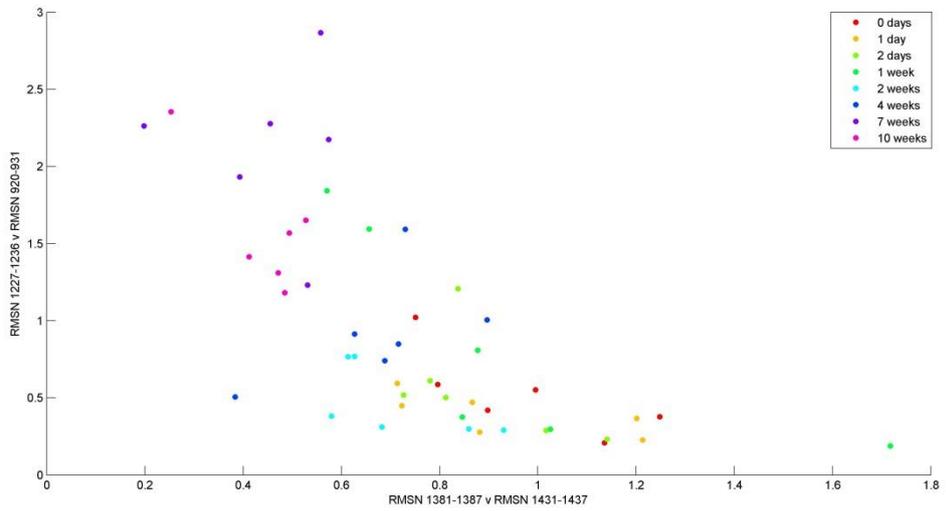


Figure 16: Group scatter plot for Uni-ball Signo red ink.

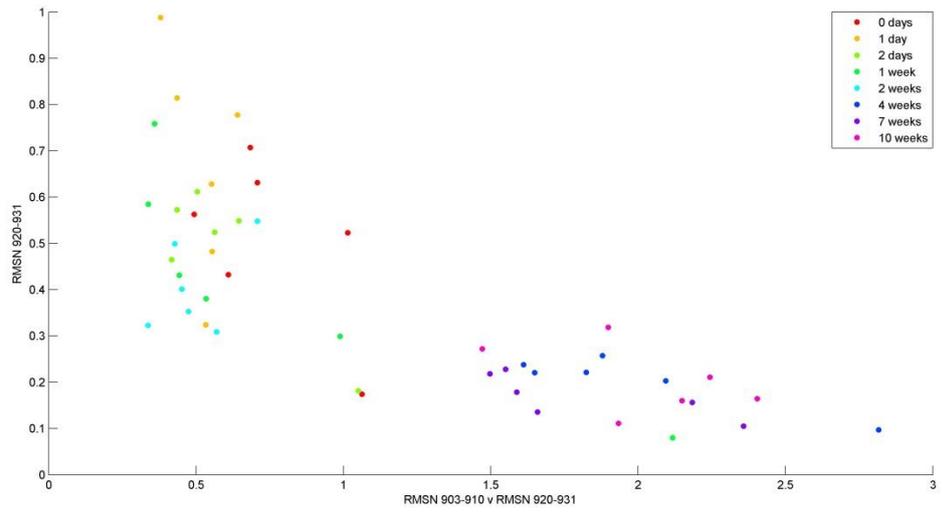


Figure 17: Group scatter plot for Wilko green ink.

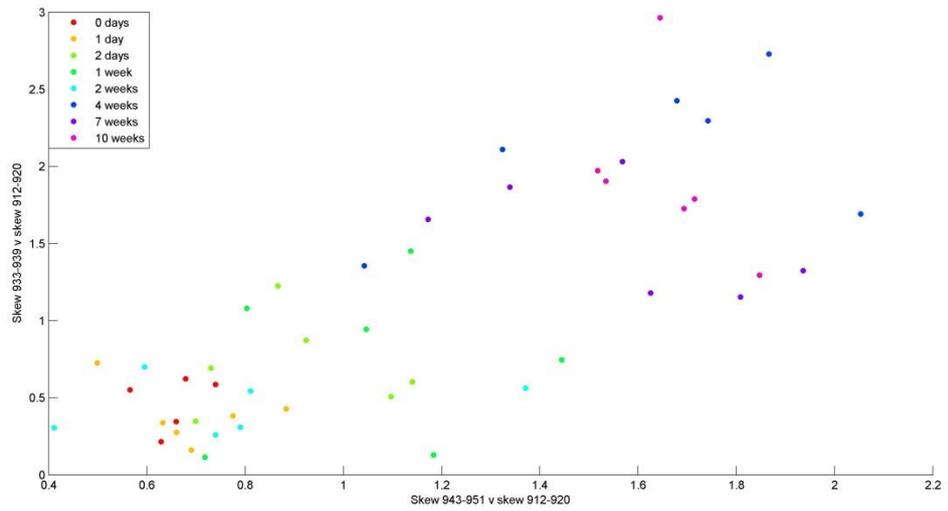


Figure 18: Group scatter plot for Wilko orange ink.

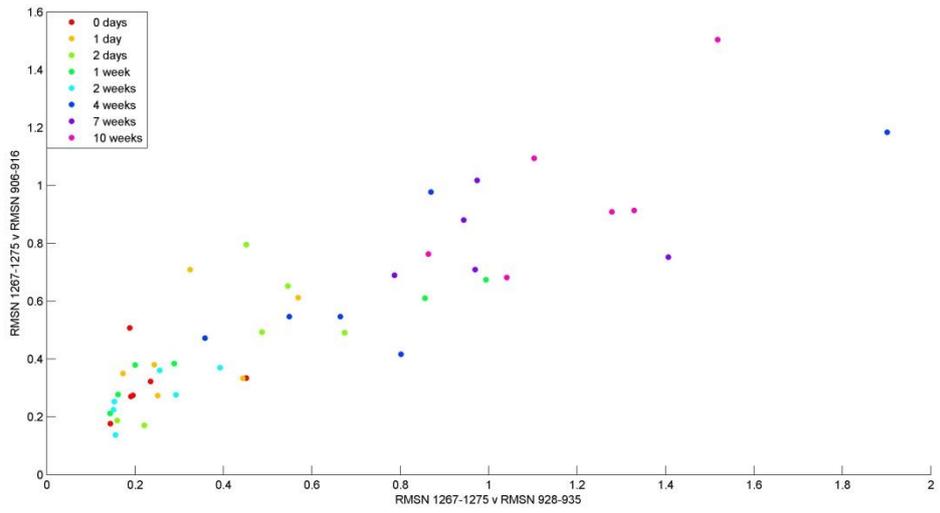


Figure 19: Group scatter plot for Wilko pink ink.

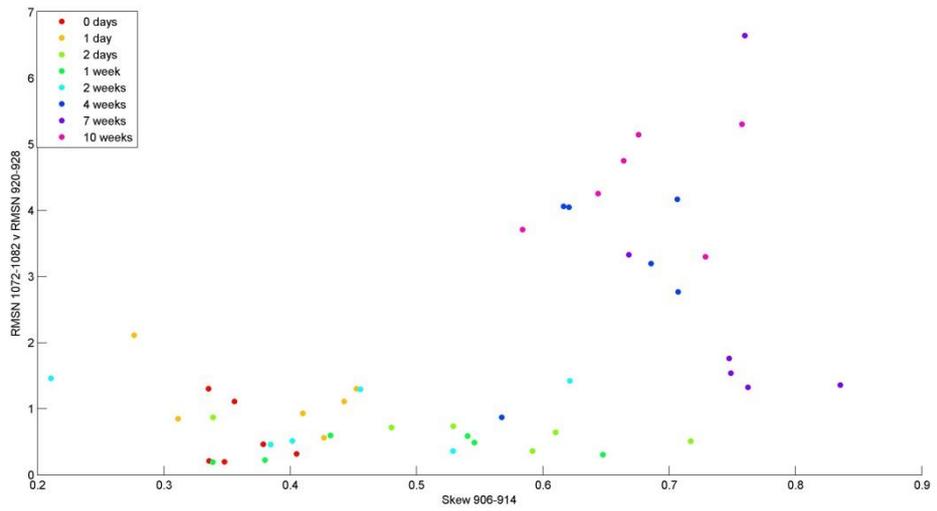


Figure 20: Group scatter plot for Wilko purple ink.

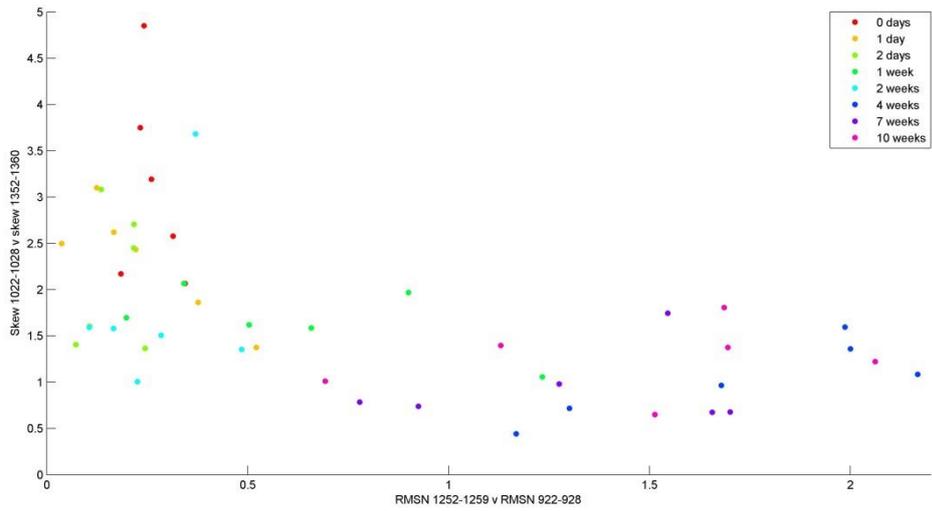


Figure 21: Group scatter plot for Wilko yellow ink.

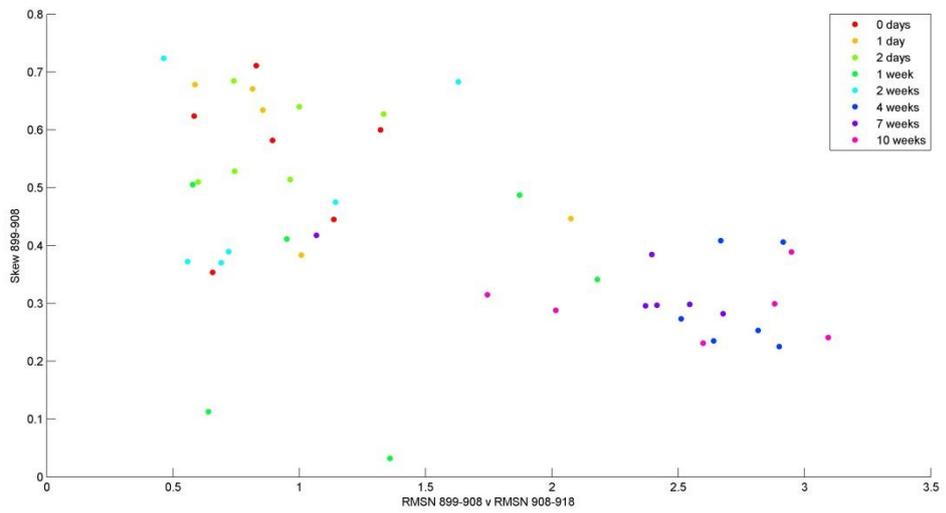


Figure 22: Group scatter plot for WHSmith black ink.

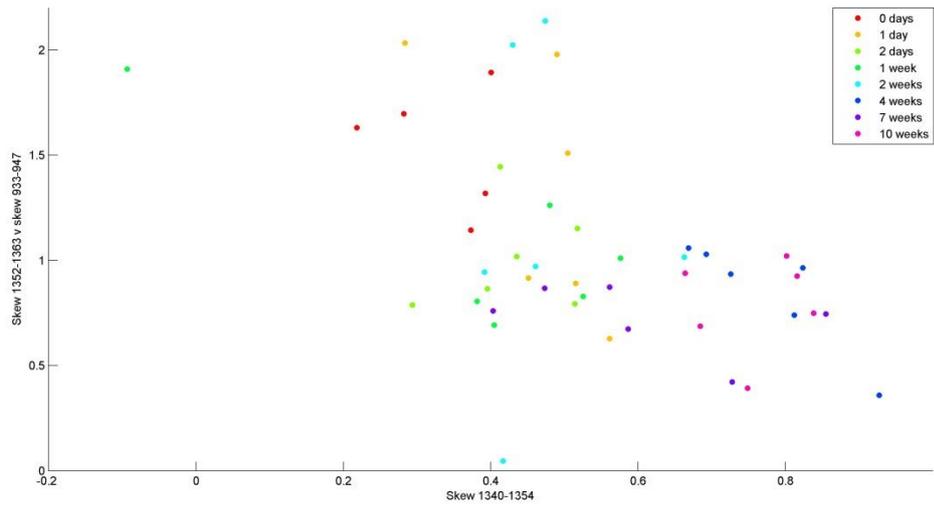


Figure 23: Group scatter plot for WHSmith blue ink.

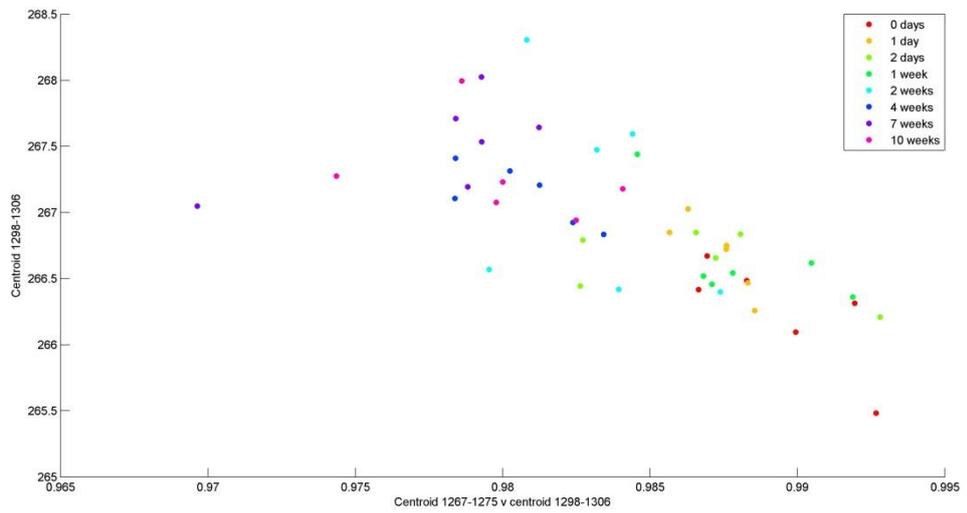


Figure 24: Group scatter plot for WHSmith brown ink.

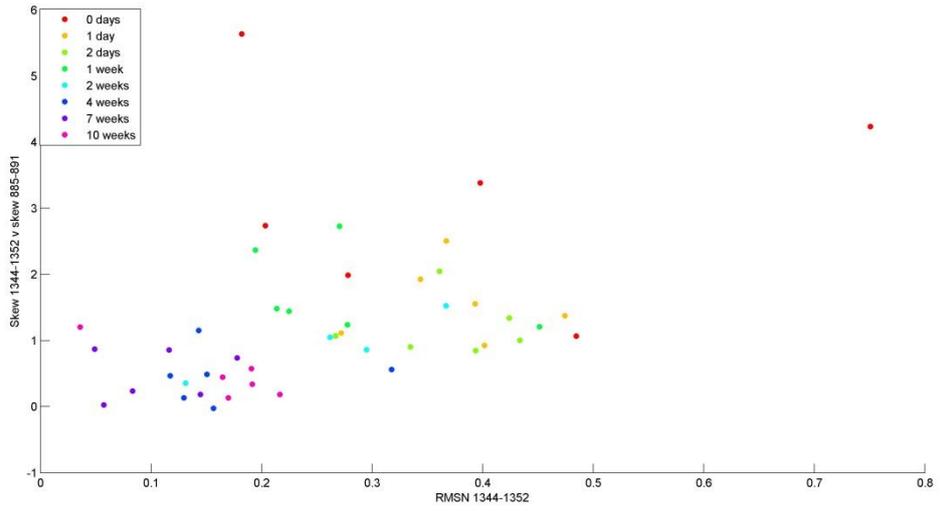


Figure 25: Group scatter plot for WHSmith gold ink.

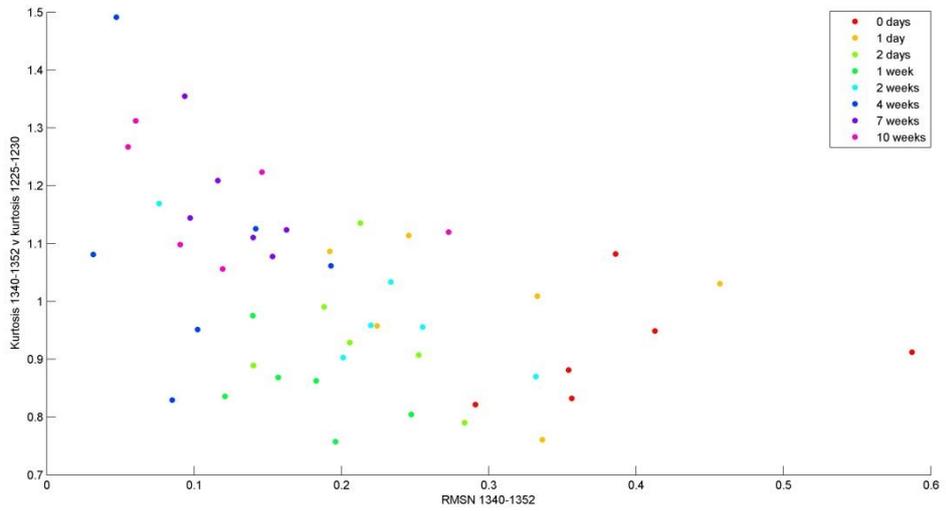


Figure 26: Group scatter plot for WHSmith green ink.

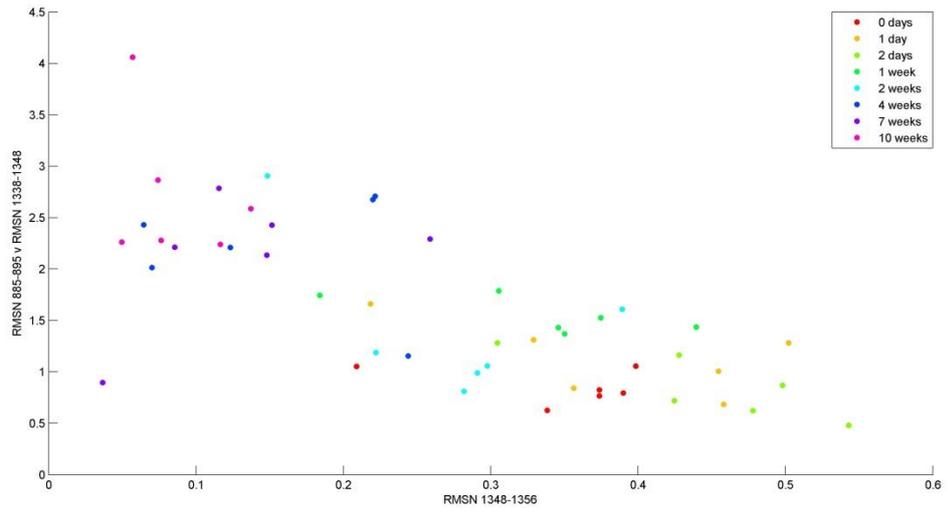


Figure 27: Group scatter plot for WHSmith light blue ink.

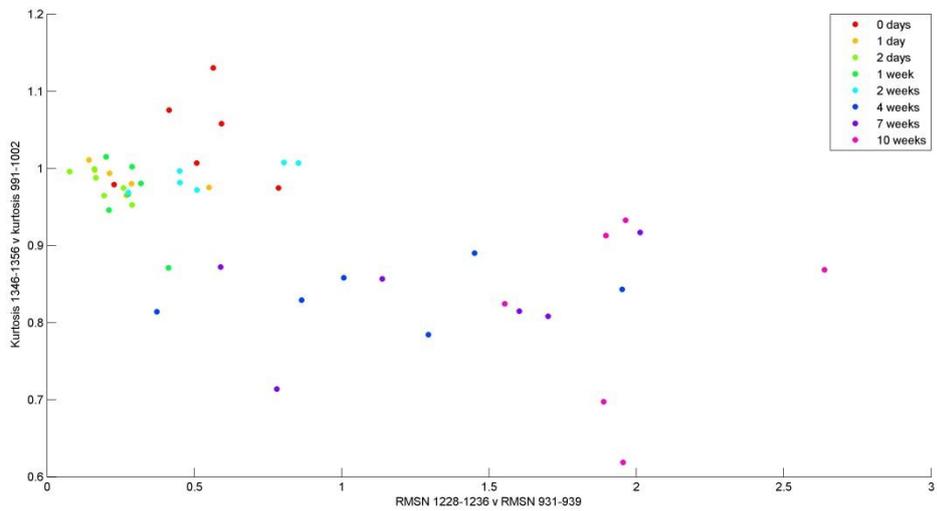


Figure 28: Group scatter plot for WHSmith lime ink.

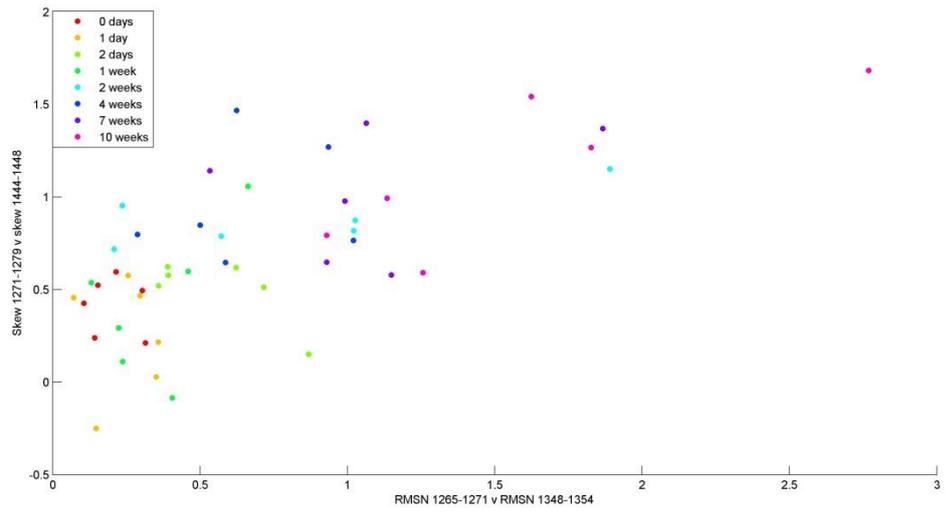


Figure 29: Group scatter plot for WHSmith mauve ink.

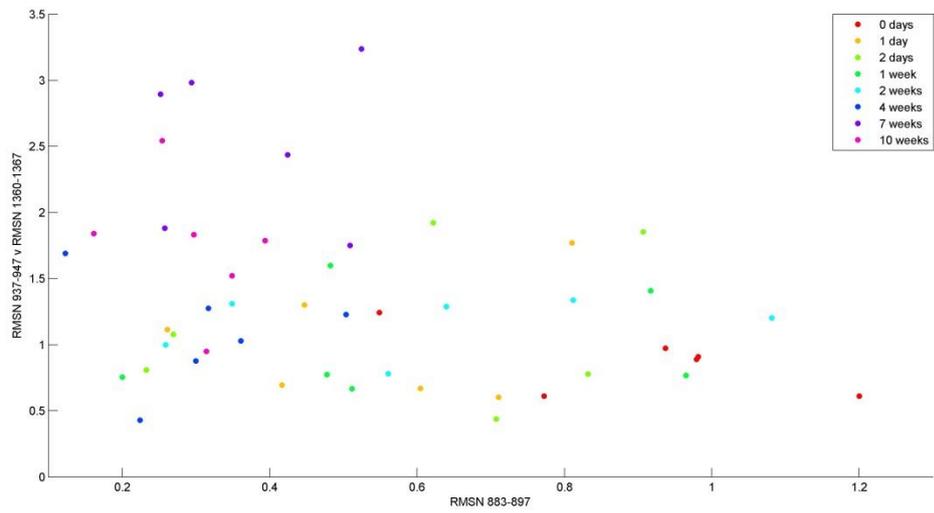


Figure 30: Group scatter plot for WHSmith orange ink.

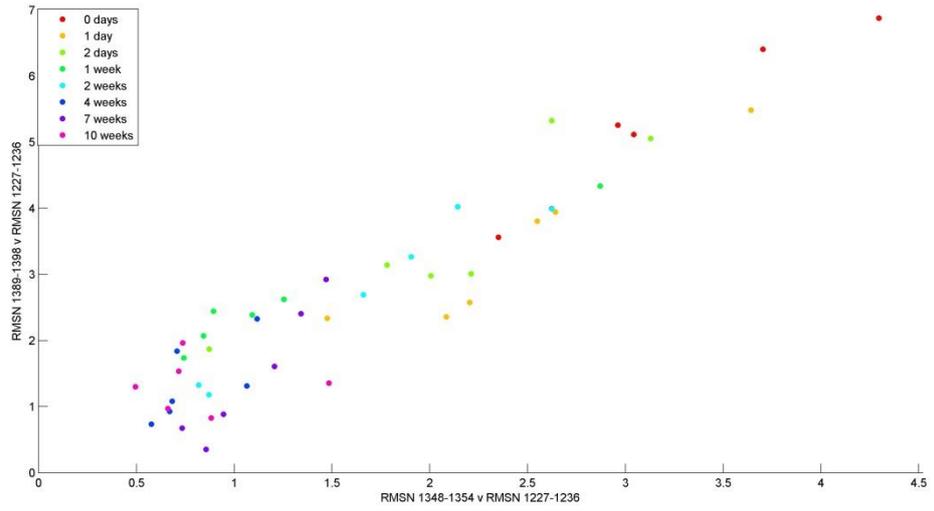


Figure 31: Group scatter plot for WHSmith peach ink.

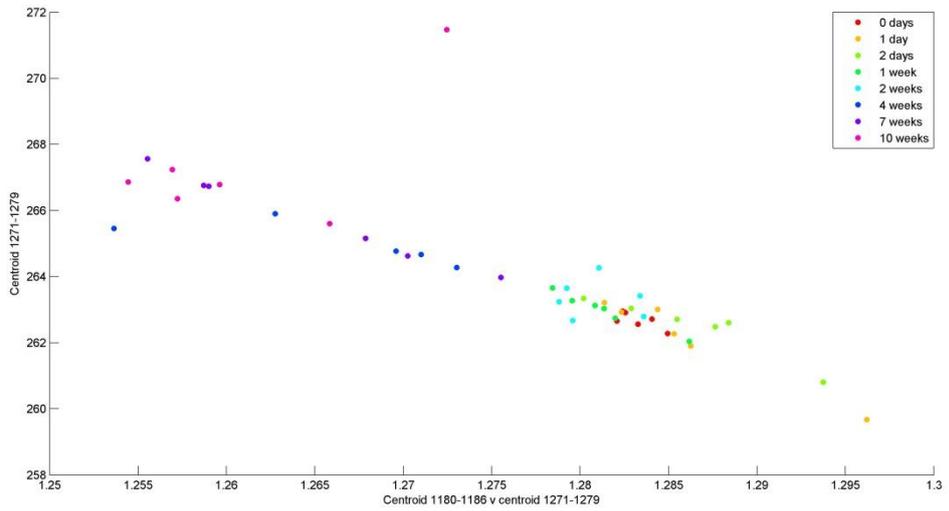


Figure 32: Group scatter plot for WHSmith pink ink.

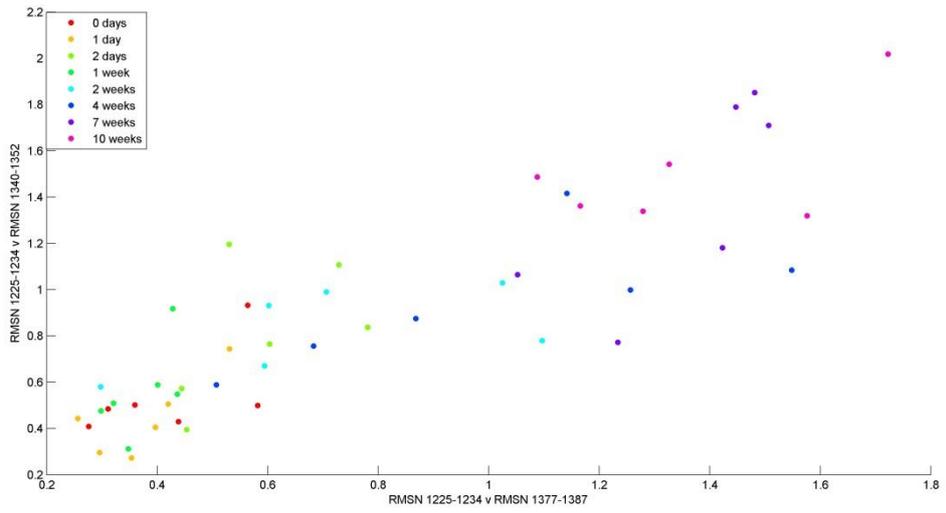


Figure 33: Group scatter plot for WHSmith purple ink.

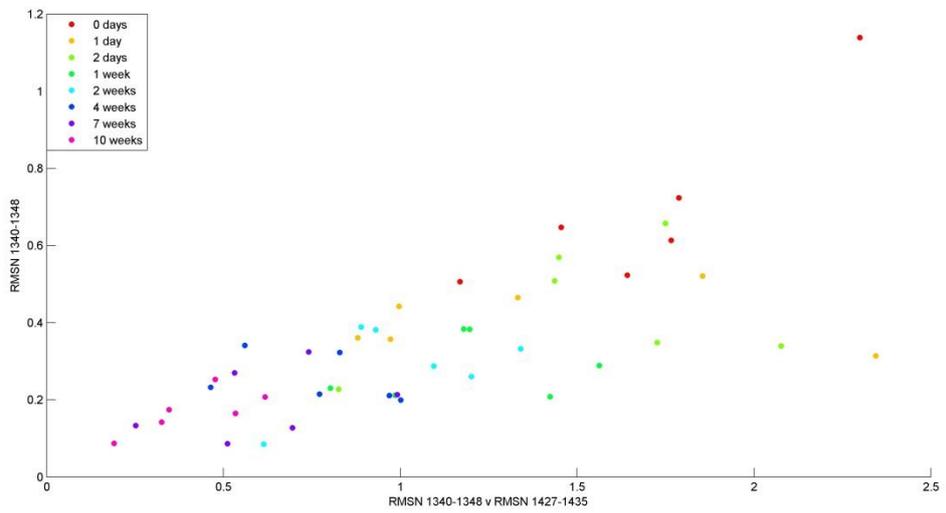


Figure 34: Group scatter plot for WHSmith silver ink.

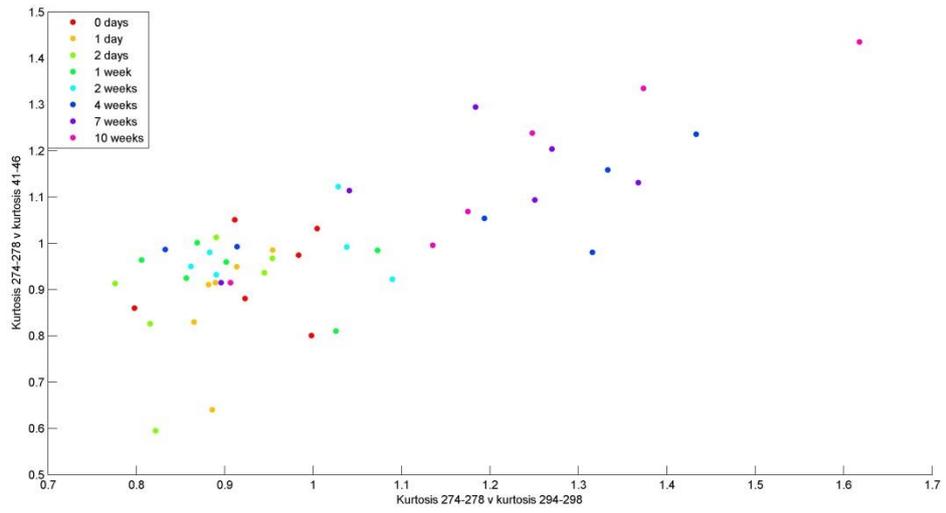


Figure 35: Group scatter plot for WHSmith violet ink.

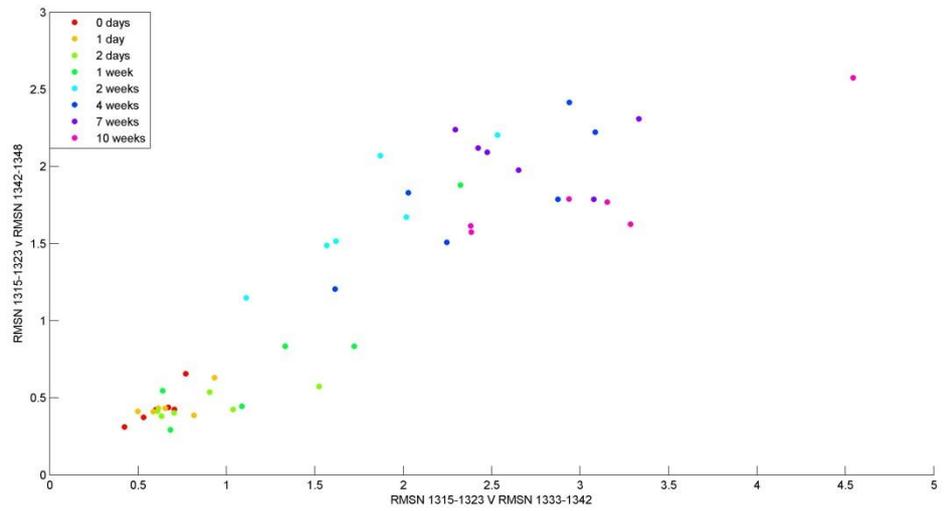


Figure 36: Group scatter plot for WHSmith yellow ink.

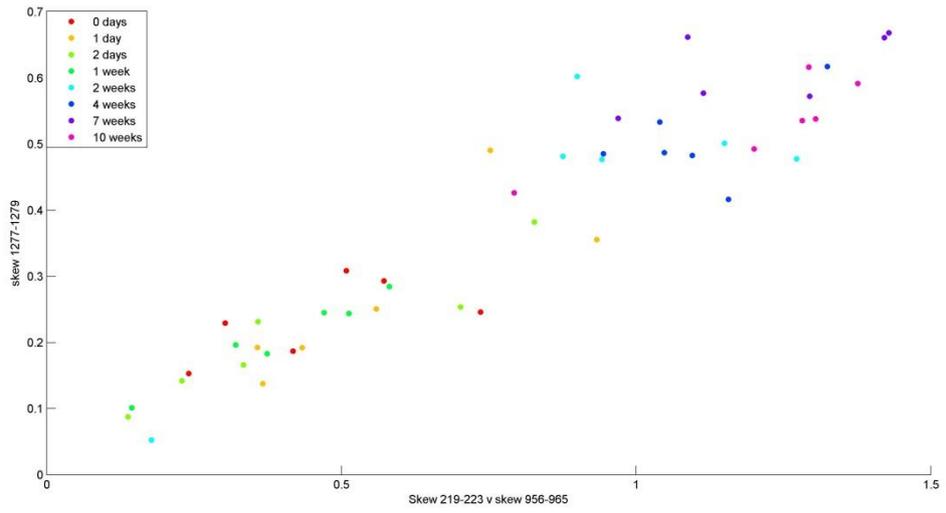


Figure 37: Group scatter plot for WHSmith glitter black ink.

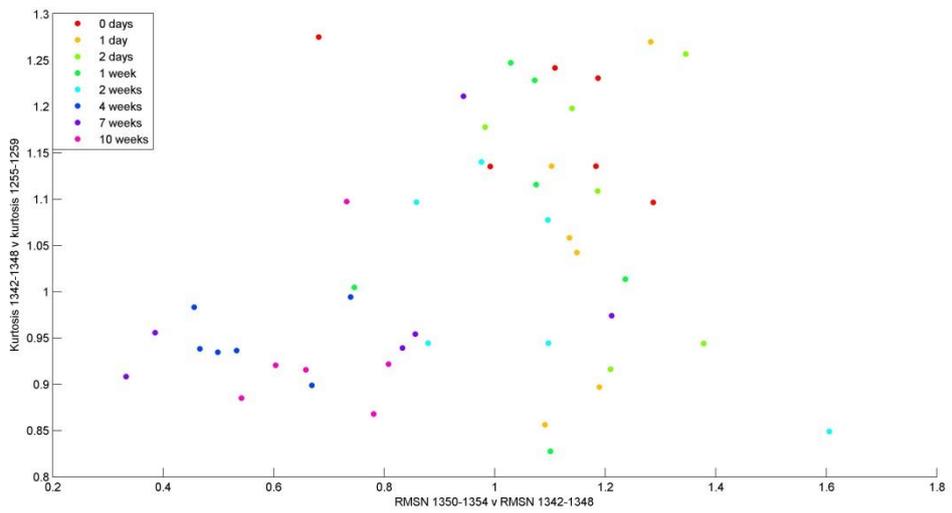


Figure 38: Group scatter plot for WHSmith glitter blue ink.

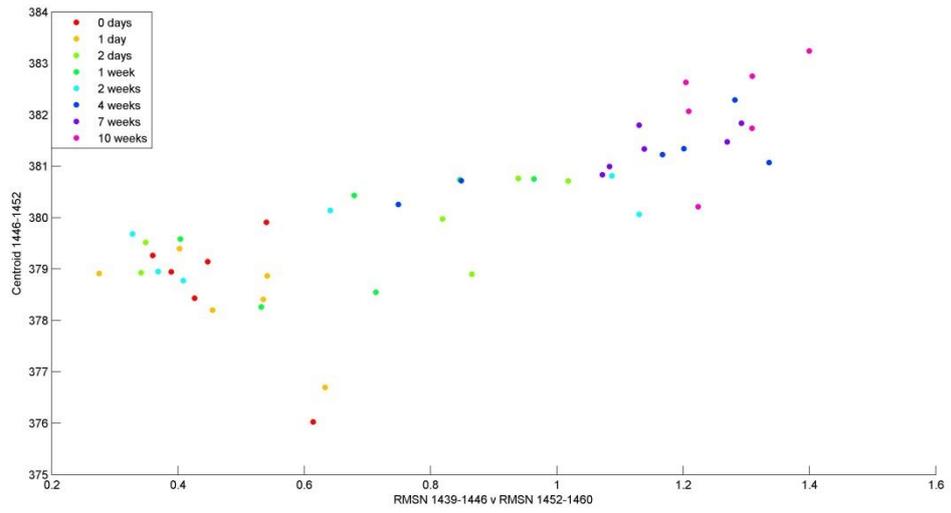


Figure 39: Group scatter plot for WHSmith glitter green ink.

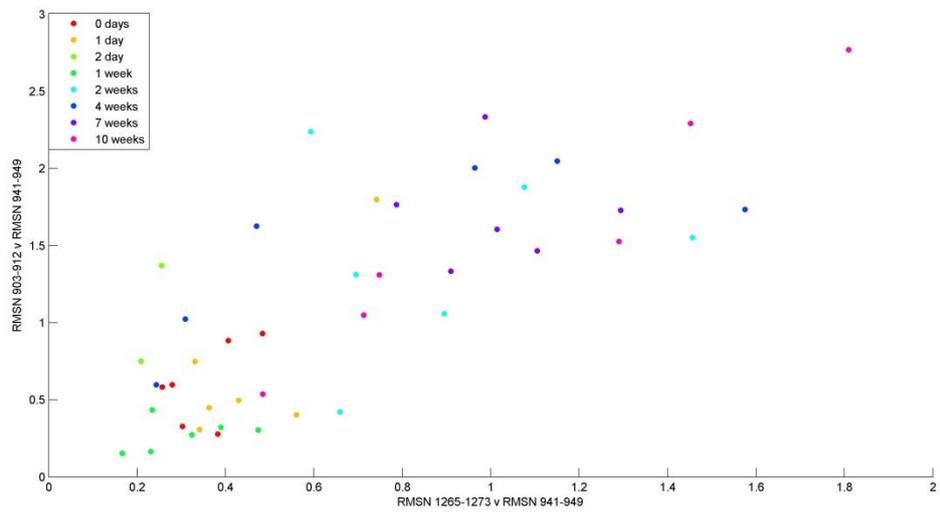


Figure 40: Group scatter plot for WHSmith glitter gold ink.

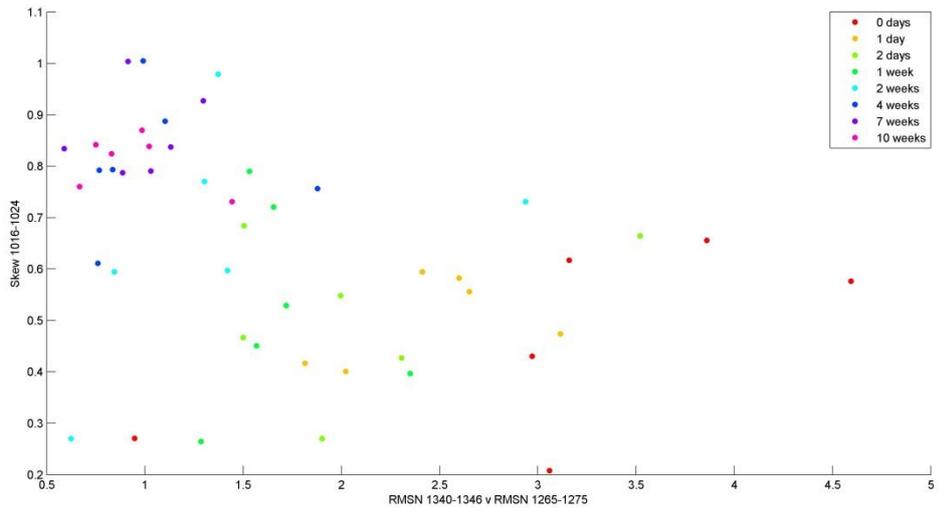


Figure 41: Group scatter plot for WHSmith glitter light blue ink.

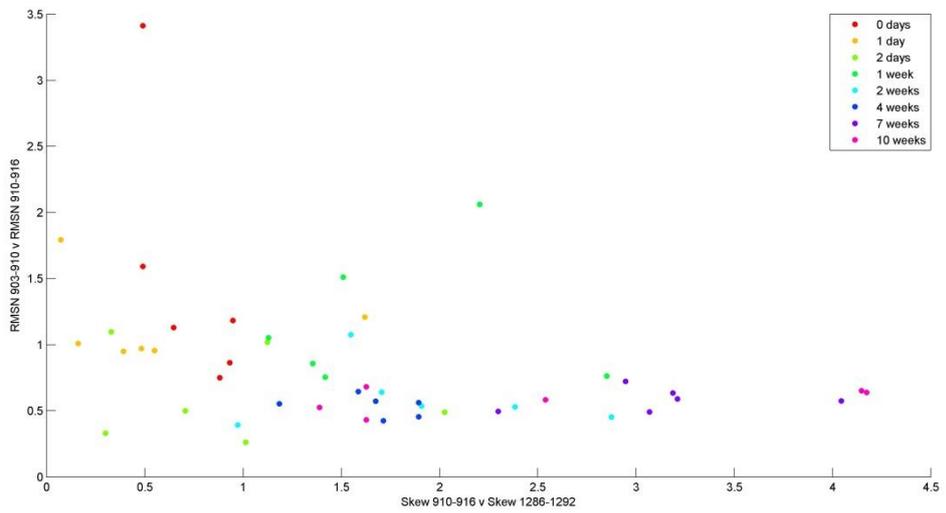


Figure 42: Group scatter plot for WHSmith glitter orange ink.

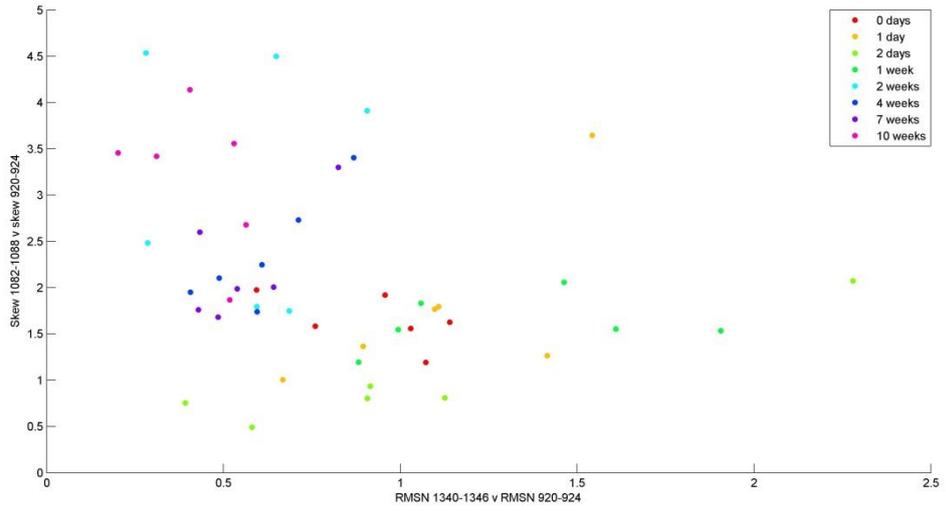


Figure 43: Group scatter plot for WHSmith glitter pink ink.

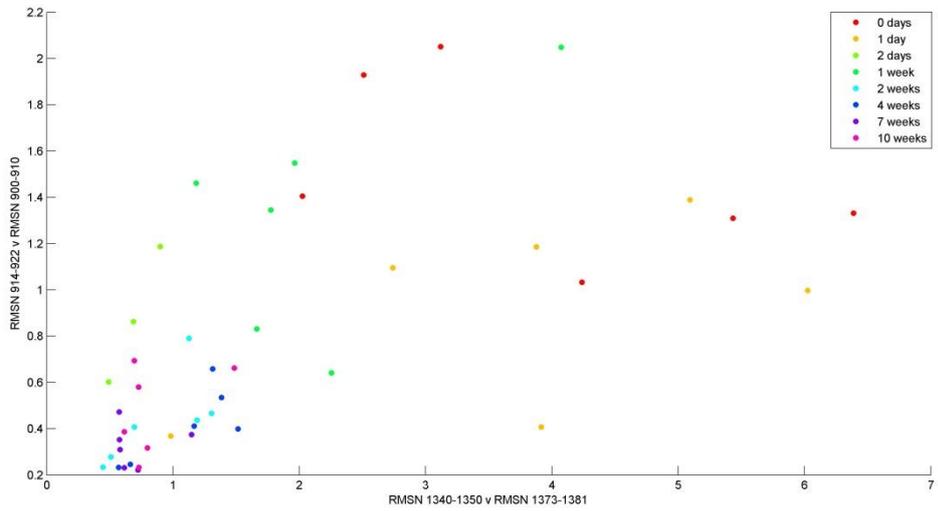


Figure 44: Group scatter plot for WHSmith glitter purple ink.

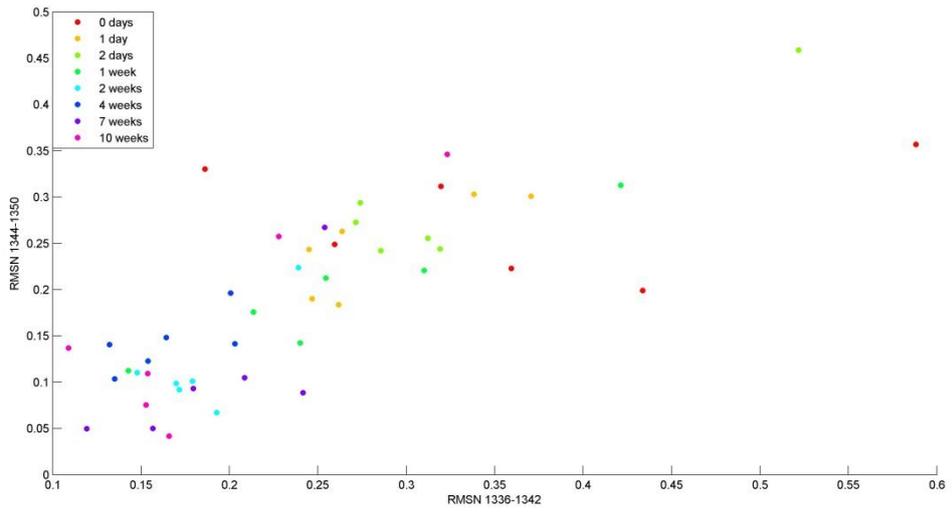


Figure 45: Group scatter plot for WHSmith glitter red ink.

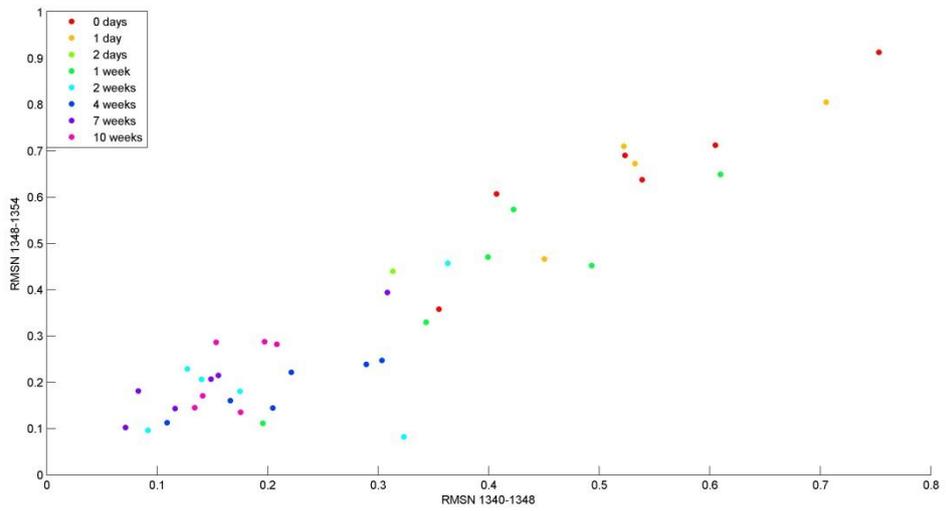


Figure 46: Group scatter plot for WHSmith glitter silver ink.