ABSTRACT

YAWEN, WANG. Using Mass Spectrometry to Study the Biodegradation in Soil of Cotton Fabrics with Wrinkle-free Finishing (Under the direction of Dr. Nelson Vinueza Benitez).

People prefer high quality and functional clothes in contemporary fashion. However, achieving this functionality can require chemicals and textile auxiliaries that may cause pollution when the textiles are disposed. The current methods for disposing fabrics are landfilling and incineration. An alternate method that could be used for biodegradable materials is composting. As a natural fiber, cotton is bio-degradable, however, once it is treated with wrinkle-free finishing the biodegradability may be impacted and the fate of the finishing chemicals is unknown. The goal of this study was to determine the presence and amount of wrinkle-free finishing chemicals on cotton fabrics after exposure to composting conditions.

This study uses high-resolution and low-resolution mass spectrometry to measure the products of bio-degradation of cotton fabrics with wrinkle-free finishing. After composting for 90 days, the fabric residuals from two woven cotton fabrics treated with Permafresh 600 or Arkofix NZF were extracted using a solvent and analyzed to detect non-covalently bound chemicals. Covalently bound chemicals released from the composted fabrics by acid, alkaline or enzymatic treatment were also analyzed. This work resulted in a new tandem mass spectrometry (MS/MS) method for quantifying dimethyloldihydroxyethyleneurea (DMDHEU) and glycolated DMDHEU, wrinkle-free finishing chemicals, which were shown to be released from fibers after chemical and enzymatic treatment. This method showed that the acid treatment released more DMDHEU from the composted fabrics compared to the alkaline treatment. Furthermore, the method enabled us to detect the reaction products of chemical auxiliaries with glucose and cellobiose. These methods and findings can help future environmental assessment of the impact of textile disposal.

Using Mass Spectrometry to Study the Biodegradation in Soil of Cotton Fabrics with Wrinkle-Free Finishing

by
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APPROVED BY:

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DEDICATION

I would like to extend my deepest appreciation and dedicate this thesis to my parents, Hongjun Wang and Yonghong Tian.

BIOGRAPHY

Yawen Wang was born in Urumqi, Xinjiang Province, China on August 28, 1996. She was accepted by Jiangnan University in the year of 2014. During her academic years, she has acquired the knowledge of dyeing and finishing systematically. Yawen took a variety of courses, the course selection benefits her a lot for helping her in applying her knowledge to addressing professional problems. Yawen acquired her bachelor's degree in textile chemistry from Jiangnan University in 2018. These experiences stimulated her to reach a higher level of study. She applied the Master degree at North Carolina State University and studied the degradation of cotton fabrics with chemical finishing under the leadership of Dr. Nelson Vinueza.

ACKNOWLEDGMENTS

My deepest gratitude goes first and foremost to Dr. Nelson Vinueza, my advisor, for his constant encouragement and guidance, who gave me great help by providing me with necessary materials, advice of great value and inspiration of new ideas. He has walked me through all the stages of writing of this thesis. Without his consistent and illuminating instruction, this thesis could not have reached its present form.

Second, I would like to express my heartfelt thanks to our group members, Emily Lichtenberger, Xinyi Sui, Chengcheng Feng, and Ciera Cipriani. They graciously made considerable comments and sound suggestions to the outline of this paper.

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CHAPTER 1

1. Introduction

More than 15 million tons of used textile waste is created each year in the United States, and the amount has doubled over the last 20 years. Of this amount, 17 percent of waste clothes were recycled, 20 percent of them were combusted for energy recovery, more than 60 percent of textile waste was sent to landfill. On average, nationally, it costs cities $45 per ton to dispose of old clothing.*(1)* Composting would seem to be a very environmentally friendly method to eliminate these waste textiles, because it will provide an environmental benefit and creates jobs.

Nowadays, people prefer more function in their clothes and do not want to spend too much time doing laundry. Wrinkle-free chemical auxiliaries are therefore preferred. Dimethyloldihydroxyethyleneurea (DMDHEU), Glycolated DMDHEU, and dimethyldihydroxyethyleneurea (DMUG) are the three most common commercial products for permanent press finishing. These chemicals supply superior performance for the clothes and textiles during use. However, when the clothes are disposed of by society, these finishing chemicals have the potential to produce negative effects that lead to pollution on the environment.*(2)* This research focuses on the identification of the degradation products of cotton fabrics with anti-wrinkle finishing after they have been placed in soil ("degraded fabrics"). Control fabrics that were not placed in the soil ("undegraded fabrics") were also evaluated. Determining the composition and amount of chemicals on the fabrics and in the fabrics was the primary purpose of the study.

This project was divided into four phases, one for each objective. In the first phase, solvent extraction was carried out to remove non-covalently bound chemicals from fabrics in order to determine what is on the fabrics. Second, enzymatic treatment was used to release covalently

bound chemicals from both degraded and undegraded fabrics. Third, acid and alkaline treatments were used to release covalently bound chemicals from undegraded fabrics. The main goal of these experiments was to determine the degradation products released from the fabrics. In the final phase, calibration curves for Permafresh 600 were established to quantify the concentration of dimethyloldihydroxyethyleneurea (DMDHEU) released by the different chemical or enzymatic treatments. The degradation products were monitored by Liquid Chromatography-Mass Spectrometry (LC-MS). For future work, it will be important to analyze the compost soil directly for the presence of wrinkle-free chemicals.

CHAPTER 2

2. Literature Review

2.1. Mass spectrometry

2.1.1. History of Mass Spectrometry

Mass spectrometry could be traced back to experiments performed over a century ago. At the end of the 19th century, scientists began experimenting with vacuum glass tubes to gain some insight into the properties of electricity.*(3)* The first instrument providing mass spectra comparable to today's was constructed by Sir Joseph John (J.J.) Thomson. In 1897, Thomson concluded that cathode rays were particles with a negative charge and much smaller in size than an atom. Before this, many thought atoms were the fundamental and smallest blocks of matter. Thomson was awarded the Nobel Prize in Physics for this work, and the negative particles were later renamed electrons.

Earlier, Eugen Goldstein, a German scientist, discovered that gases in cathode-ray tubes also produced radiation very different from that of cathode ray tubes (Figure 1). In 1898, Wilhelm (Willi) Wien used powerful electromagnets and found that canal rays deflected in a direction opposite of cathodes rays.*(3)* This implied they had an opposite charge or positive charge. Thomson decided to use a device similar to Wien but allowed the positive rays to hit a screen coated with a material that fluoresced when hit. This permitted the deflection induced by the electrical and magnetic fields to be recorded. According to this method, he was able to identify positive ions from hydrogen and helium.*(4)*

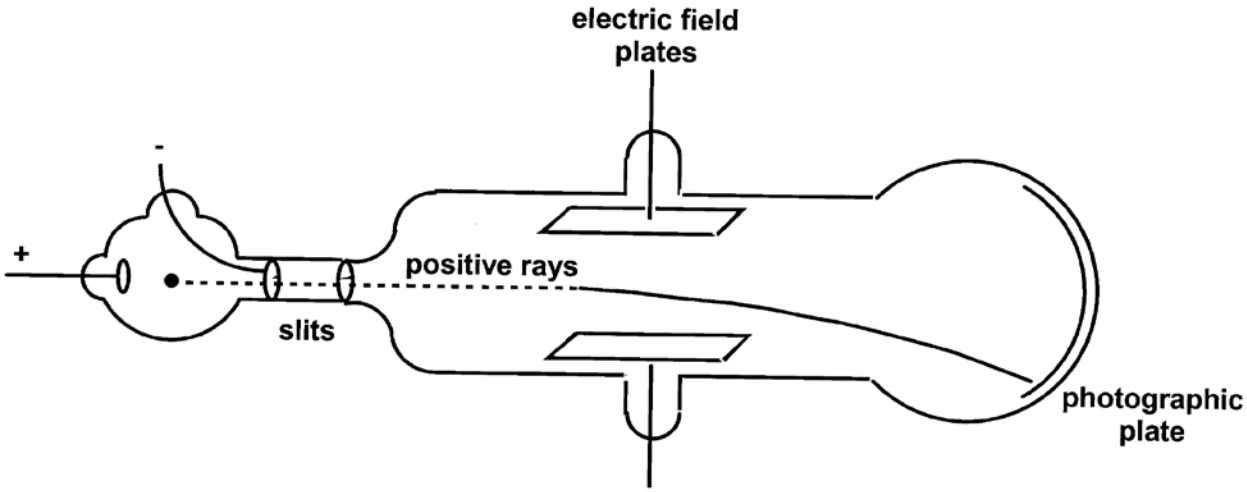


Figure 1 Representation of the cathode ray tube showing the deflection of positive rays (ions)*(3)*

First with hydrogen, and later with other atoms and molecules of carbon, nitrogen, and oxygen, Thomson discovered that each charged particle followed its parabolic path based upon the position of their detection on the photographic film from Figure 2. In other words, unless two particles have the same velocity and charge to mass ratio, they will not hit the plate at the same position.*(4)* He concluded that the positive rays consisted of charged atoms or molecules, known today as ions. This was the birth of the field of mass spectrometry.

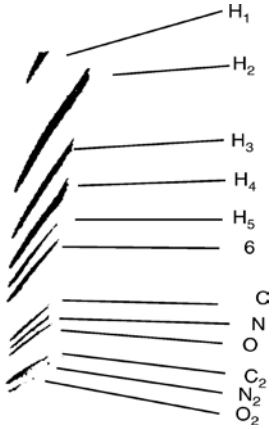


Figure 2 Parabolic paths of ionized forms of atoms and small molecules within a cathode ray tube*(3)*

When Thompson discovered the electrons, he also used one of the simplest mass spectrometers to bend the path of the cathode rays (electrons) and determine their mass-to-charge ratio. In 1919, Aston made the first isotope measurements enhancing the ability of this new technique. In 1918 and 1919, Arthur Jeffrey Dempster and F. W. Aston discovered additional techniques by improving the resolving power of mass spectrometry. Since then, there were plenty of developments in the field of mass spectrometry.*(5)* For instance, the introduction of samples into the ionization source was one of the key developments to connect the mass spectrometer to other instruments like gas and liquid chromatography. Other improvements in ionization sources and mass analyzers included the development of, for example, double focusing magnetic sector mass filters by Mattauch and Herzog in 1934, a time-of-flight mass analyzer by Stephens in 1946 and an ion cyclotron resonance (ICR) mass analyzer by Hipple and Thomas in 1949. Steinwedel started to develop the quadrupole mass analyzers in 1953, and the ion trap mass analyzer was created by Paul and Dehmelt in the 1960s. *(5)*

2.1.2. Components of Mass Spectrometry

Mass spectrometry works by (1) ionizing each analyte as it leaves the GC, LC system, or is injected directly into the ionization source, then by (2) accelerating and focusing the ionized compound and its fragments into the mass spectrometer, followed by (3) separating the fragments in the mass spectrometer according to the mass-charge ratio (m/z), and (4) detecting the fragments when they leave the mass analyzer. The signals are then sent to the data system and shown on the screen.*(5)* As Figure 3 shows, the main components of mass spectrometry are sample introduction, an ionization source, the mass analyzer and detection system which interacts with the data system.

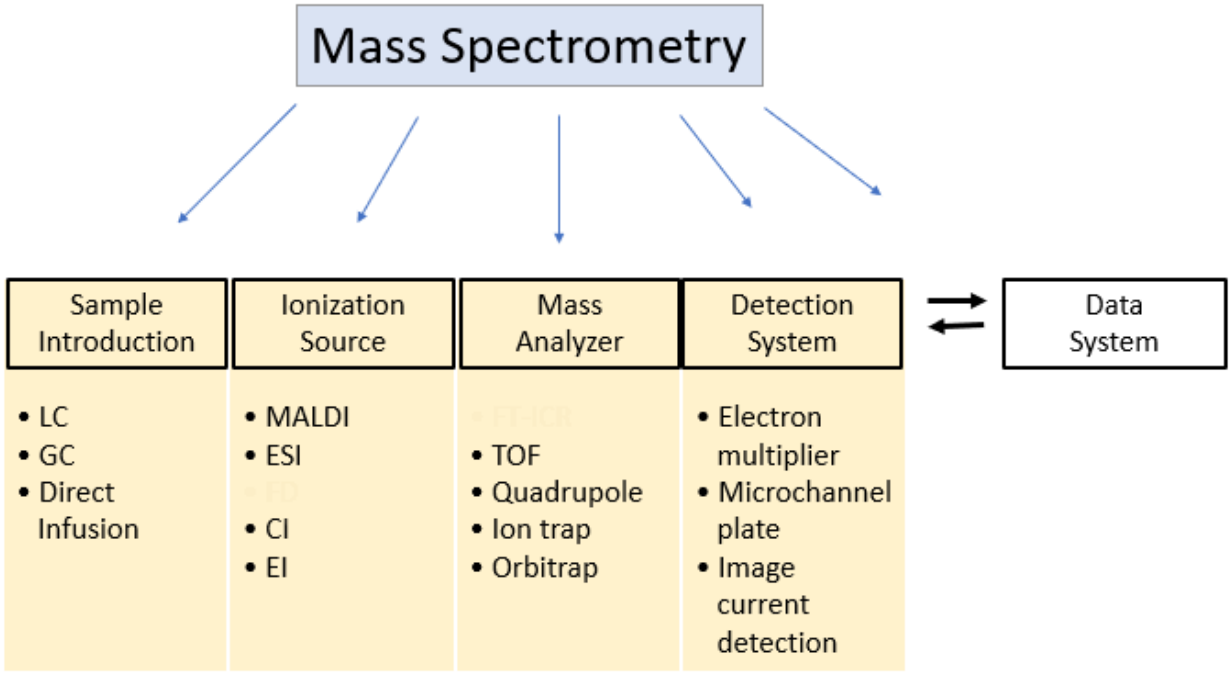


Figure 3 Components of mass spectrometry

For sample introduction, chromatography is an analytical technique used to separate mixtures of compounds, which are dissolved in the liquid or gas mobile phase. The mobile phase carries the mixture through a structure holding another material named the stationary phase.*(6)* The interaction of the analyte of interest with the mobile phase and the stationary phase is based on the partition coefficient of the analyte and the two phases in equilibrium. Structural differences in a compound result in differential retention on the stationary phase which affects the separation.*(7)* In other words, separation is based on differential partitioning between the mobile and stationary phases. Gas chromatography (GC) and liquid chromatography (LC) are two significant and common chromatography techniques commonly used nowadays for separation and analysis of chemical compounds.

The ionization source is where neutral molecules gain charge (positive or negative) prior to their manipulation by electric and/or magnetic fields inside the mass spectrometer. Ionization is one of the most important steps in mass spectrometry (MS) since the analyte of interest needs to

gain a charge (positive or negative), if this does not happen the MS analysis cannot be performed. Electron impact (EI) was one of the first ionization methods developed for mass spectrometry, which uses energetic electrons reacting with gas or solid phase atoms or molecules in order to achieve ionization. EI is commonly used in combination with GC and can be found in older mass spectrometers.

Nowadays, it is more common to find electrospray ionization (ESI) sources in commercial mass spectrometers. ESI is considered the softest ionization technique compared to EI, chemical ionization (CI) and matrix-assisted laser desorption ionization (MALDI). For this reason, ESI can be used for a diversity of chemicals and biological samples (e.g., proteins and tissues). However, what makes ESI the source of choice for many users is its ability to ionize liquid samples coming from an LC system or a syringe pump.

The mass analyzer separates molecular ions and their fragments through ion velocity, mass or mass-to-charge ratio. Many different mass analyzers can be used in gas chromatography and liquid chromatography, but not all of them are commercial.*(8)* Mass analyzer can be classified as scanning or pulsed types. For example, linear quadrupole ion trap (LIT) is a scanning mass analyzer, because it stores ions inside the quadrupoles and activates ions with collision of residual gas, also it transmits a single selected m/z to the detector and the complete mass spectrum is obtained by scanning the analyzer so that different mass-to-charge ratio ions are detected.*(9)* Time-of-flight is a pulsed mass analyzer because the instrument collects an entire mass spectrum from a single pulse of ions, then the ions' mass-to-charge ratio (m/z) is determined via a time of flight measurement.*(10)*

Today, two common mass spectrometer detectors are the electron multiplier and the microchannel plates. The electron multiplier basic operating process is called secondary electron

emission. This means that when a charged particle (ion or electron) strikes a surface it causes secondary electrons to be released from atoms in the surface layer. The number of secondary electrons released depends on the type of incident primary particle, its energy, and characteristic of the incident surface.*(11)* In mass spectrometry, electron multipliers are often used as a detector of ions that have been separated by a mass analyzer of some sort.*(11)* It is suitable for quadrupole mass analyzers. A microchannel plate (Figure 4) can be thought of as a combination of millions of miniature electron multipliers. It also amplifies the intensity of single particles by multiplication of electrons through secondary emission, and its multiple channels provide special resolution*(12)* and are always used in combination with time-of-flight mass analyzer.

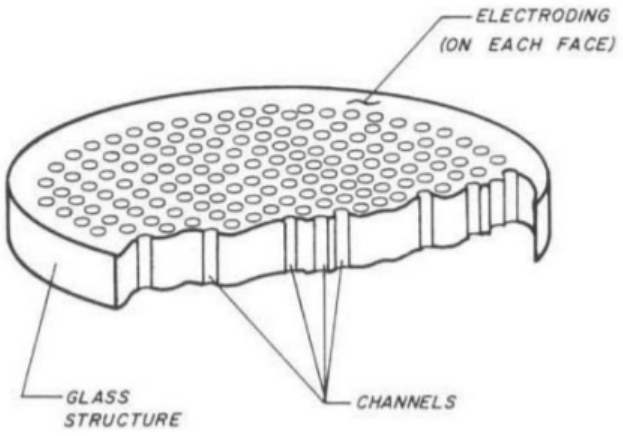


Figure 4 A microchannel plate*(13)*

2.1.3. Electrospray Ionization

Electrospray ionization (ESI), a mass spectrometry technique first introduced in 1968, uses high voltage to produce ions, in which a liquid is subjected to high pressure to produce an aerosol. It is particularly useful in generating ions from macromolecules because it overcomes the tendency of these molecules to break up when ionized. “Ionization” in ESI is referred to as soft ionization and commonly forms a protonated molecule in positive ion mode or a deprotonated ion in negative mode. ESI differs from other ionization processes in that it may generate multiply charged ions,

effectively extending the analyzer's mass range to 100,000 Da observed in proteins and related peptides.*(14), (15)*

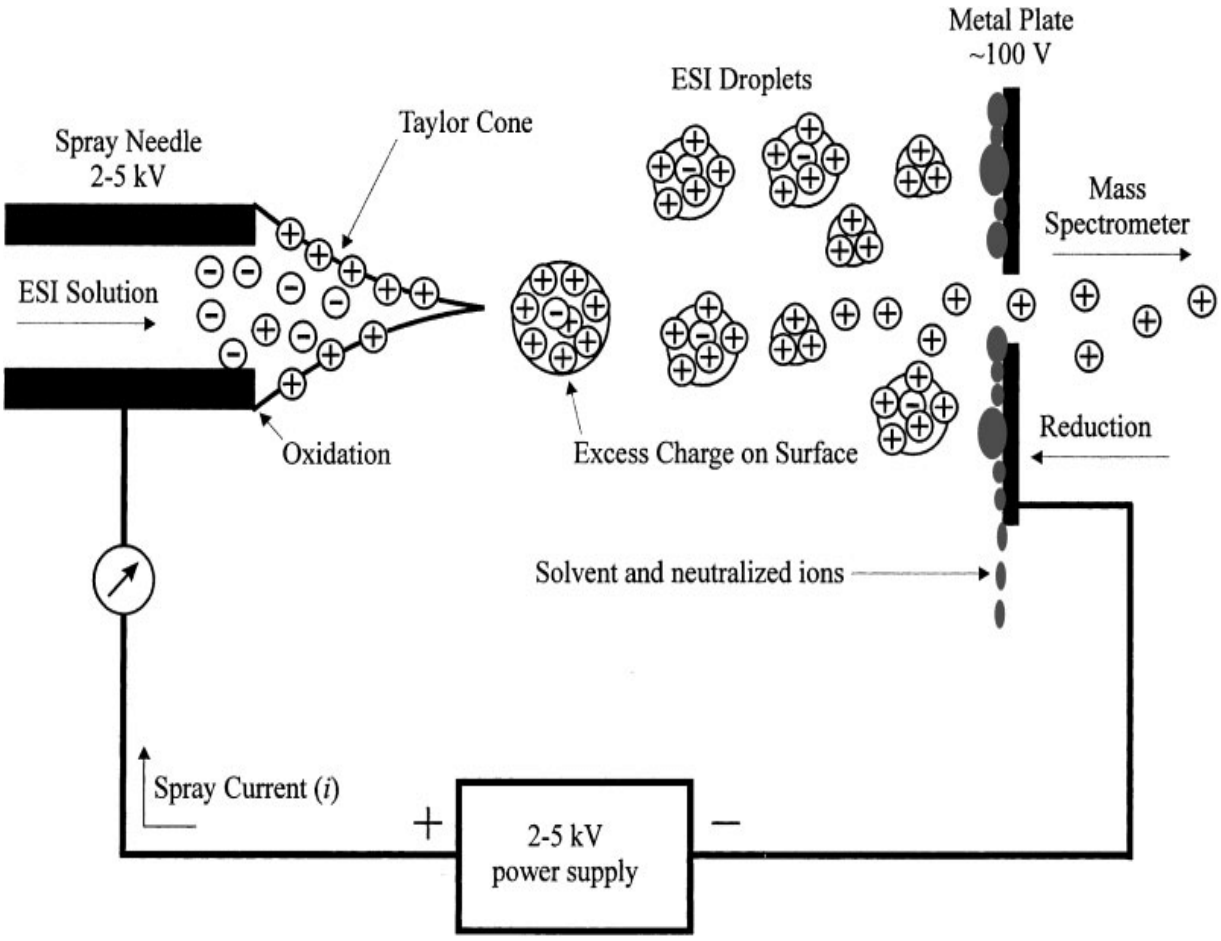


Figure 5 Schematic representation of electrospray ionization (ESI) process*(16)*

As presented in Figure 5, the analyte(s) of interest enters the mass spectrometer through a capillary with a positive applied voltage. The collector, typically a mass spectrometer, is also charged but with a negative charge. As positive charge builds at the tip of the capillary, the analyte is attracted by the negative charge on the collector and forms a cone of analyte protruding from the tip of the capillary. This is called a Taylor cone. Due to the repulsive interactions between the positive charges amassing in the analyte, the Taylor cone grows and pushes further out of the capillary until the coulombic repulsion of charges overcomes the surface tension of the analyte.

When this limit is surpassed, droplets explode from the Taylor cone and spray towards the collector for the MS analysis.*(17)*,*(18)* There are two main theories for ion formation in ESI shown in Figure 6. The first model is the Ion Evaporation Model, where the droplet reaches a certain radius, and the field strength at the surface of the droplet becomes large enough to facilitate the field desorption of solvated ions. The second model is the Charge Residue Model, where the droplets undergo an evaporation and fission cycle that ultimately produces offspring droplets that contain an average of one or fewer analytes.*(19)* The second model is more understood by the scientific community, because the droplets carry positive charges and move from left to the right. During the desolvation stage of the ionization, droplets are dried through a flow of N_2 gas. Then, the droplets start shrinking due to the surface tension of the liquid which cannot sustain the charge accumulation reaching the Rayleigh limit. Above the Rayleigh limit, the droplets are torn apart to form small charge droplets containing molecules of the analyte which are known as Rayleigh fission. Later, desolvation is complete and the charge is transferred to the ionized particles becoming gaseous molecules and entering the mass spectrometer.*(5)*

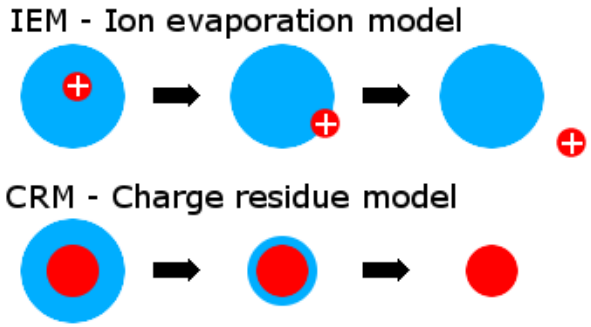


Figure 6 The model of two ion production theories*(5)*

2.1.4. Time-of-Flight Mass Spectrometry

Time-of-flight (TOF) mass spectrometry (MS) is a technique in which the mass analyzer measures the mass-to-charge ratio by determining the time it takes for the ions to pass through the

"field-free" drift tube. Field-free means there is no electronic or magnetic field affecting the ions.*(8)*

$$E_{el} = qU = ezU = \frac{1}{2} m_i v^2 = KE \quad (1)$$

$$\frac{m_i}{z} = \frac{2eU}{v^2} \quad (2)$$

$$v = \sqrt{\frac{2zeU}{m_i}} = \frac{\Delta x}{t} \quad (3)$$

The TOF MS follows three principles explained with three equations. An ion "packet", produced by a laser pulse, or by chopping a continuous ion beam into discrete pulses, which is separated according to their m/z ratio. This is accomplished by giving all the ions the same kinetic energy (KE) and allowing them to start their journey to fly for a fixed distance and then one measures their arrival time.*(20)* According to equations (1) to (3), the flight time for each ion is unique and it is determined by the kinetic energy (KE) to which an ion is accelerated (v) with the same voltage, the distance (Δx) that has been traveled and its mass-to-charge ratio. TOF MS is just a fancy clock, the longer the flight time, the larger the mass-to-charge ratio. Because TOF MS ensures that all ions start the "flight" at the same time, energy, and distance, the lighter ions will have higher velocities and will arrive at the detector earlier than the heavier ions (Figure 7). *(8), (21)*

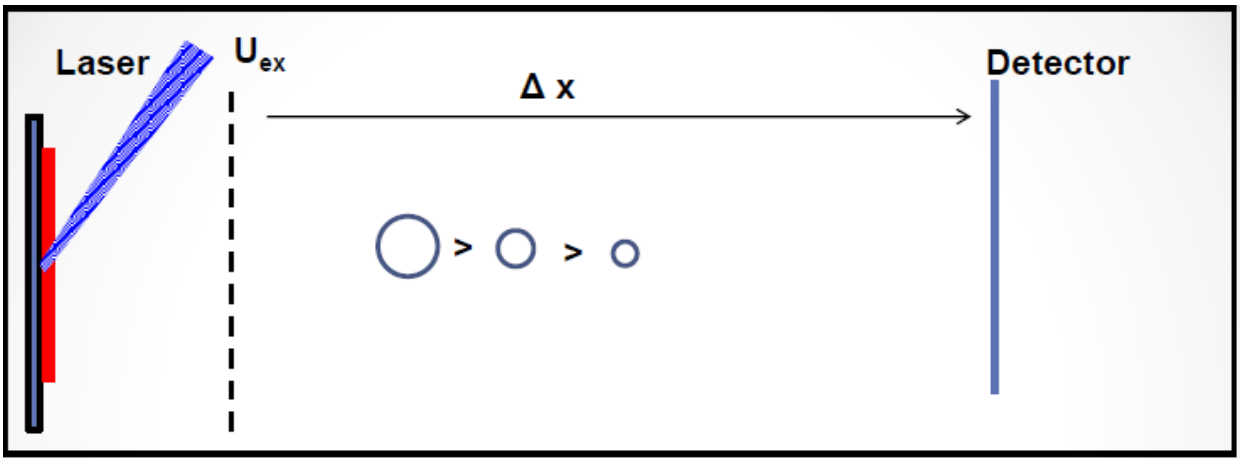


Figure 7 Schematic diagram of TOF MS*(22)*

The first generation of times-of-flight was the Linear TOF, which was not very popular due to its limited resolving power (R=500) caused by initial spreads in the time, space and kinetic energy distributions of the ions. In the late '80s-'90s, there was a return to TOF MS due to the invention of reflectrons which increased their resolving power. In Figure 8, the two ions have the same m/z but different initial kinetic energy (E_1>E_2) in the TOF analyzer. Without reflectrons, the two ions will arrive at the detector at different time. If reflectrons are used, the higher KE ion penetrates the reflectron further to compensate the extra momentum of the ion. Finally, the reflectron balances the influence caused by different initial KE, and the two ions with the same m/z value will enter the detector at the same time improving resolution. With the whole process, the resolving power can be as high as 10000 to 25000, and the m/z accuracy is 0.001.*(10)*

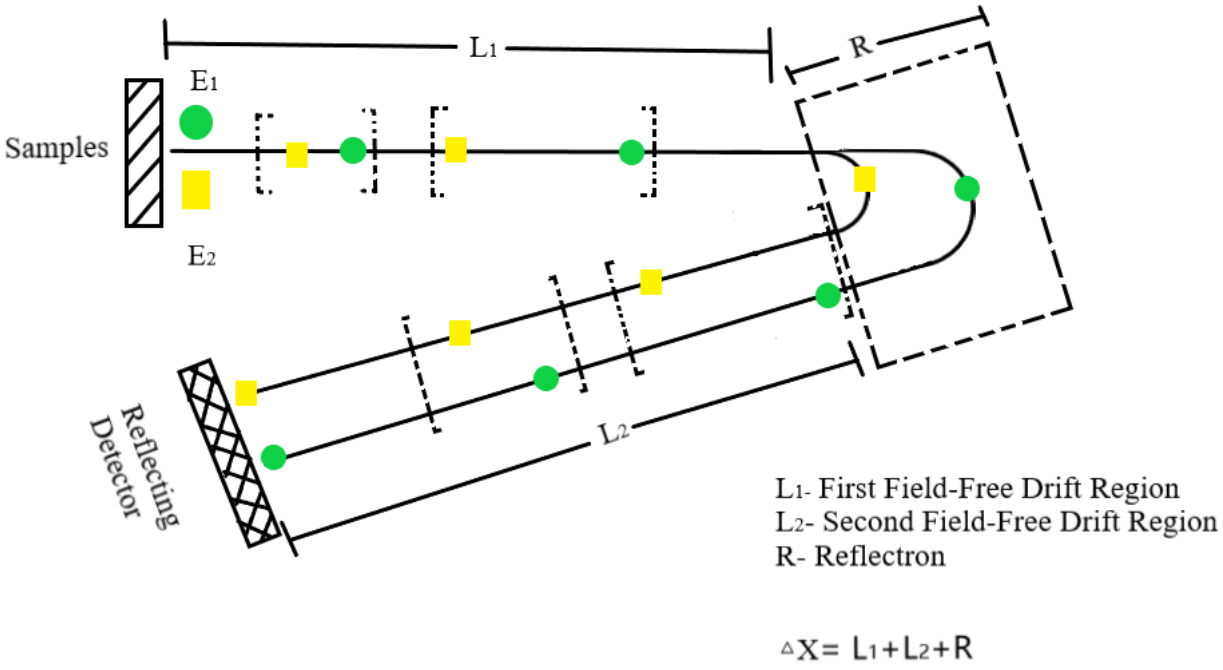


Figure 8 Reflectrons

2.1.5. Linear Ion Trap Mass spectrometry

Ion Trap MS manipulates ions radially by two-dimensional radio frequency (RF) fields and stopping potentials applied to the end electrodes along the central axis (Figure 9). There are a set of quadrupole rods used for blocking ions rapidly and an electrostatic potential is established at the end electrode to limit the axial direction of the ions.

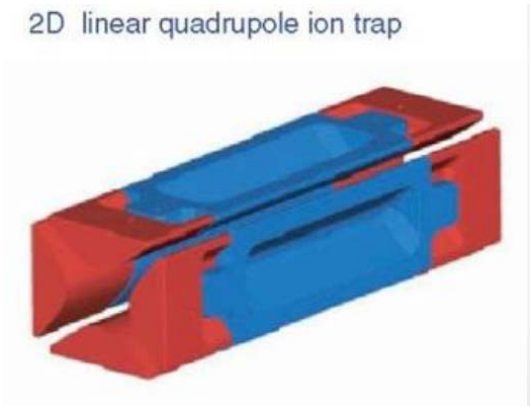


Figure 9 2D Linear Ion Trap*(23)*

Quadrupoles in the linear ion trap (LIT) are the only devices capable of mass-selective operation. Higher-order RF ion guides or higher-order LIT can only guide, accumulate, store and release ions for m/z analysis. The ion trap MS stores ions inside the quadrupoles and active the ions with the collision of residual gas (commonly helium). LIT can accumulate ions to provide ion packages for other analyzer stages. However, it is not adequate for highly accurate mass measurements. Usually, ion traps are always combined with TOF, FT-ICR, and triple quadrupole mass analyzers.*(24)*

2.1.6. Tandem Mass spectrometry

Except for electron ionization, all the ionization methods described before are used to generate protonated or deprotonated molecules which are helpful for getting molecular weight information, but not for structure elucidation. Tandem mass spectrometry is designed to determine the structure of a known or unknown chemical compound. The most common mass spectrometer used for tandem mass spectrometry is the triple quadrupole (QqQ) mass spectrometer (Figure 10). The first quadrupole, Q1, is a mass filter which is used to transmit the selected ions with a particular m/z into the dissociation region at any time. The second part, q2, is called “collision cell” which induces fragmentation of molecular ions in the gas phase. The molecular ion usually is accelerated and then allowed to collide with neutral gas molecules (e.g., helium, nitrogen or argon). During the collision, the kinetic energy is converted to internal energy resulting in bond cleavage. The third quadrupole is also a mass filter named “Q3” which scans and detects the fragments and dissociated products which pass to the detector. The first and third quadrupoles are operated using a combination of RF and DC voltages, and the second quadrupole (q2) is only operated with an RF voltage.*(3)*

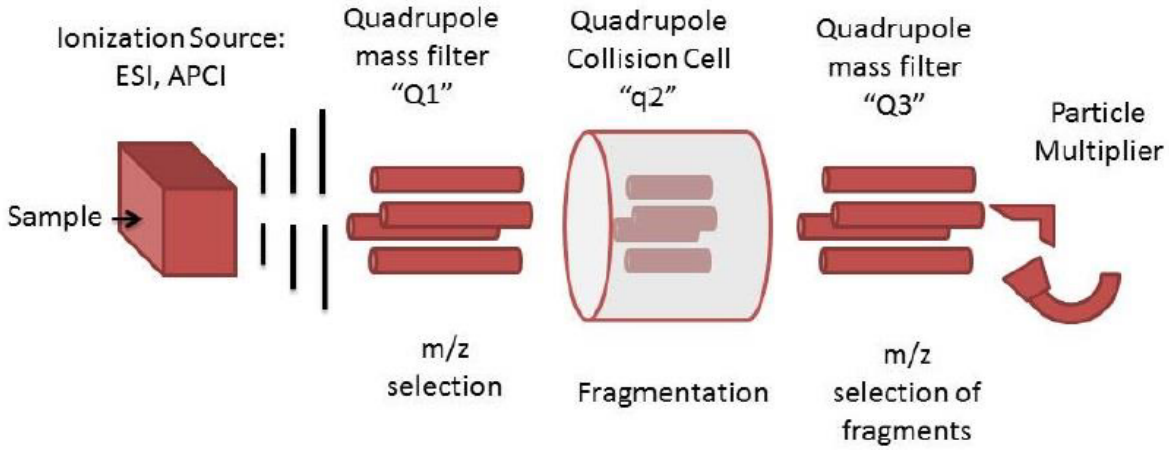


Figure 10 Schematic diagram of tandem mass spectrometry*(25)*

Tandem mass spectrometry has four scan modes due to the different function of the three quadrupoles. First is the product scan, The Q1 selects fixed ions with a particular m/z, and q2 performs collision-induced dissociation (CID), so that Q3 can scan the entire m/z range. Second is called precursor mode when Q1 scans all the ions and q2 performs CID, and Q3 selects a fixed product fragments to be detected. The third is called neutral loss scan, where Q1 scans with the product ions' m/z and q2 performs CID, Q3 scans the mass-to-charge ratio which is the product mass minus the neutral molecule mass. The last is also known as select reaction monitoring (SRM). The Q1 fixes the precursor ions mass-to-charge ratio, q2 performs CID and Q3 detect the fragment ions mass-to-charge ratio. Tandem quadrupole mass spectrometry can be applied to many quantitative studies to determine whether or not a substance is in the analyte and in what specific concentration. This application is great for fields of drug metabolism, environmental studies, and biological analyses.*(3)*

2.1.7. Liquid chromatography-mass spectrometry

The combination of liquid chromatography (LC) and MS started in the early 1970s. The combination of a separation technique and mass spectrometry makes a unique combination for the analysis of complex mixtures. This technology has been extensively reviewed since the mid-1970s. *(26)*

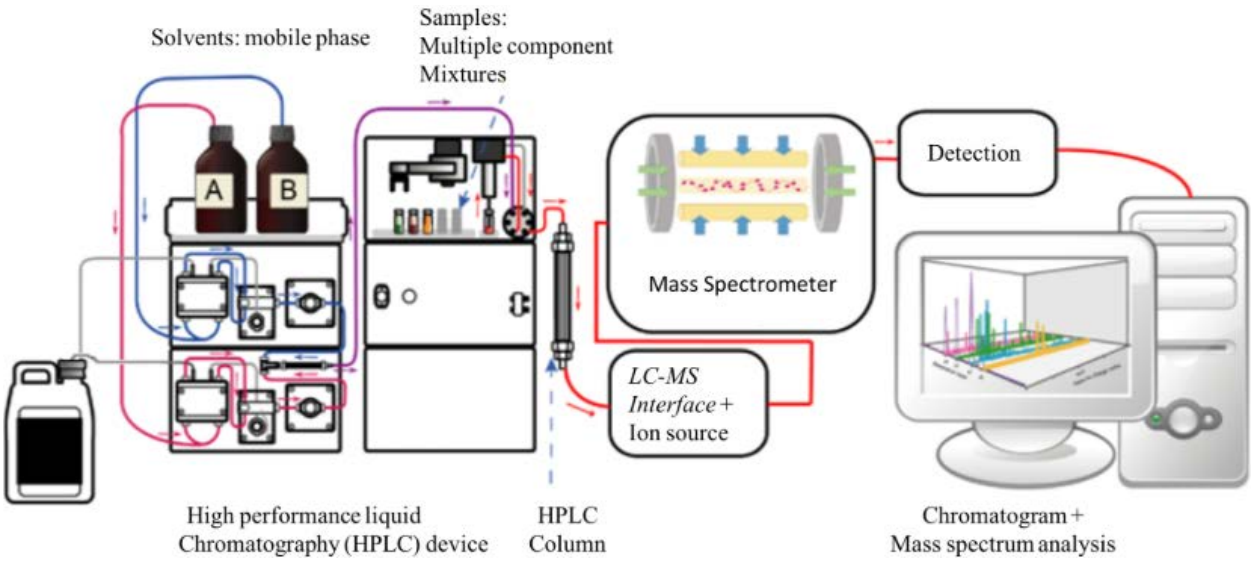


Figure 11 Diagram of an LC-MS system*(15)*

Initially, liquid chromatography was largely inefficient due to the flow rate of the solvent was dependent on gravity. The separation took hours even several days to complete. The coupling of MS and LC is self-evident, but because of the relative incompatibility of the continuous liquid stream and MS ion sources, the field was not developed for many years.

In the 1960s, researchers found LC could be operated in the high-efficiency mode by reducing the packing-particle diameter substantially below 150 μm and using pressure to increase the mobile phase velocity. That's the beginning story of High Performance Liquid Chromatography (HPLC). HPLC is the same as the other chromatography methods, it used to

separate, identify, and quantify each component in a mixture. For HPLC, the mobile phase is the liquid and the stationary phase is the column packing.

HPLC relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Each molecule interacts with the adsorbent material differently, leading to the separation of the component as they flow out of the column. Sometimes, HPLC-MS is used without a column, because the samples do not need to be separated. This is performed by removing the column and reconnecting them with a small metal or plastic tube that depends on the materials at the junction. This situation is often called by-pass or direct injection.*(26)*

Nowadays, many mass spectrometers have high mass accuracy and sensitivity which are now viable replacements for many immunoassays and in combination with HPLC has the ability to process multiple analytes at a minimal incremental cost in a single analysis run. According to Figure 11, different samples are set into small HPLC vials, and then the needle on the top left of the picture withdraws an aliquot of the solution and injects it into the HPLC column system to be separated, and then it is send into the ionization source of the mass spectrometer to be characterized. This may simplify laboratory settings and provide additional useful information like retention times of analytes. Applications that can detect hundreds of analytes in a single run have been proven, and the analyst's imagination and originality largely limit the possibility of reuse. LC-MS analysis may be one of the most useful in clinical laboratories. When used for multiplexing and screening type analysis, the large amount of information obtained justifies the cost of purchasing and operating instruments.*(15)*

2.2.Antiwrinkle finishing with cotton fabrics

Wrinkle-free means finishing applied to cellulose and cellulose blend fabrics to overcome certain fiber deficiencies such as wrinkling or shrinkage. Thicker fibers, hydrophilic fibers, high twist yarns, and tighter construction fabrics wrinkle more.*(27)* A high-performance level of wrinkle-resistant is also called durable press, easy care, permanent press, and wash and wear. The fabrics wrinkle when the hydrogen bonds are broke and the fibers are less rigid with respect to each other, so they can shift into new positions. As the fabric cools, new hydrogen bonds form, locking the fibers into a new shape. Cotton is a soft, fluffy staple fiber composed mostly by cellulose. Cellulose is a natural organic polymer with a semi-crystalline structure. Cellulose is derived from D-glucose units, which condense through β (1→4)-glycosidic bonds. Cellulose is a straight chain polymer (Figure 12). Hydrogen (H) bonds hold the chains firmly together side-by-side. High tensile strength and modulus are achieved by intra-molecular bonds between chains with multiple hydroxyl groups and oxygen atoms on the same or the neighboring chain.*(28)* Figure 13 shows that the connection of two polymer chains can easily move due to their chemical environment, or because they contain absorbed moisture which lubricates the polymer chains. Once the hydrogen bond between two chains breaks, it will reform quickly in another position, and the wrinkle occurs.

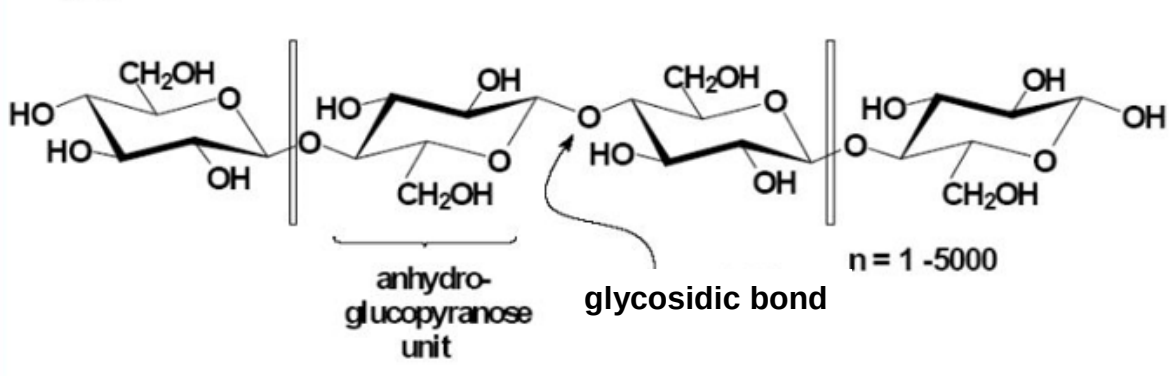


Figure 12 Chemical structure of cellulose*(29)*

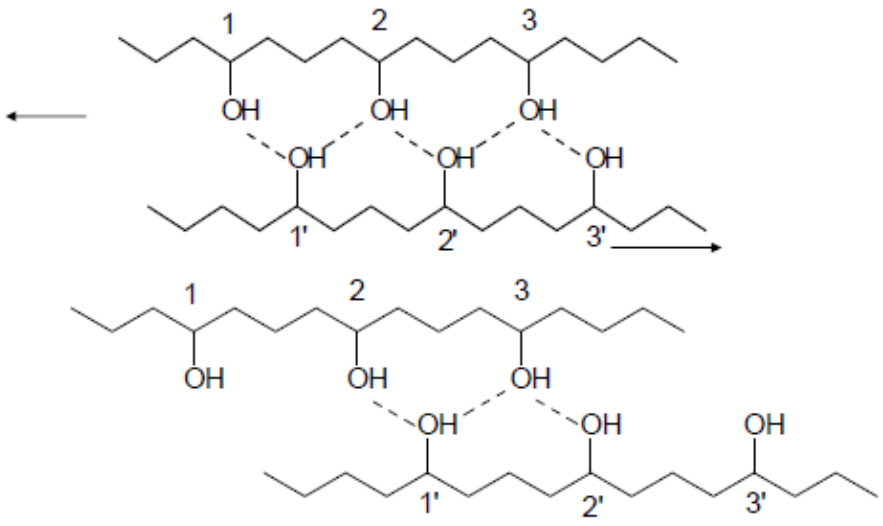


Figure 13 Mechanism of wrinkle formation

In fact, there is a way to prevent wrinkling by crosslinking the polymer chains, adding other chemicals to crosslink two polymer chains and form a permanent chemical bond. Chemical cross-links prevent the rearrangement of hydrogen bonds that can lead to wrinkling.

2.2.1. DMDHEU

Dimethyloldihydroxyethyleneurea (DMDHEU) also named Permafresh 600, a faint yellow viscous liquid, is a derivative of dimethylolethylene urea (DMEU) because DMEU easily hydrolyzes. DMEU can release formaldehyde (Figure 14) but only contains two hydroxyls that can react with the cotton cellulose chains. In Figure 15, DMDHEU presents four reaction sites that can crosslink with cotton cellulose chains. In a comparison between DMEU and DMDHEU, the later has better laundry durability and lower reactivity, resulting in longer shelf and pad bath life. However, DMDHEU also has the potential to release more formaldehyde. Therefore, double glycolate DMDHEU (Figure 15) was introduced to the textile industry. Diethylene glycol is added between the nitrogen and methylol bond. This approach greatly reduces the release of

formaldehyde compared to DMDHEU. Nowadays, glycolated DMDHEU plays an increasingly important role in the permanent press market.

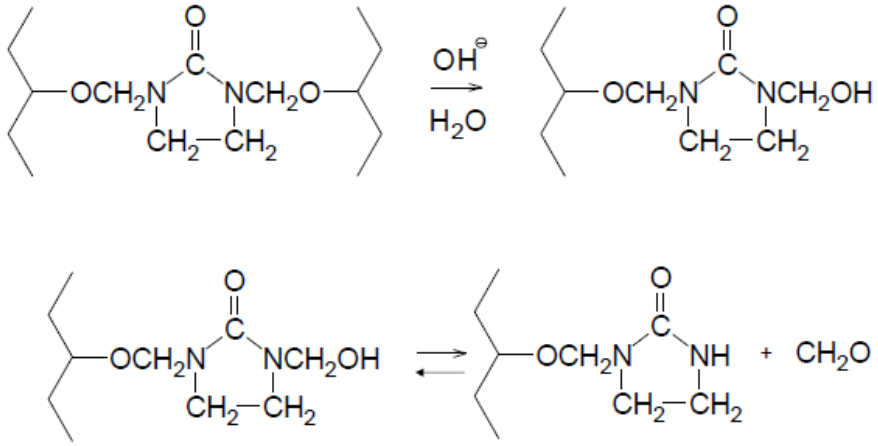


Figure 14 Hydrolysis of DMEU crosslinks

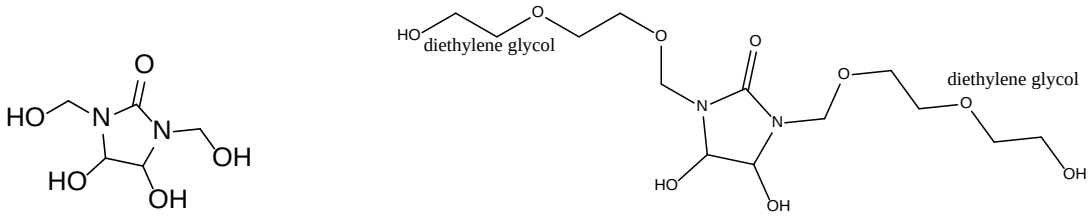


Figure 15 Structure of DMDHEU (Left) and double glycolate DMDHEU(Right)

2.2.2. DMUG

Dimethyldihydroxyethyleneurea (DMUG) also called Arkofix NZF (Figure 16) is a chemical that is derived from dimethyl urea and glyoxal. It is a faint yellow liquid that is used to treat cellulose-based heavy fabrics to inhibit wrinkle formation. DMUG is another option because of its low free formaldehyde release. However, it is expensive and not as efficient as DMDHEU because it only contains two reactive sites to interact with the cotton cellulose chains. *(30)*

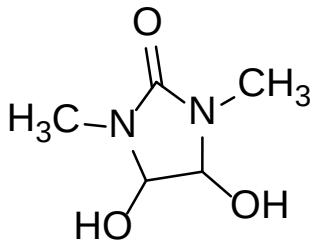


Figure 16 Structure of DMUG

2.3. Degradation of wrinkle-free finished fabrics

2.3.1. Chemical reaction on cotton fabrics

From yarns to fabrics, chemicals play a necessary role in textile processing. For example, yarn manufacture, fabric formation, yarn or fabric preparation use chemicals that help in the fabrication process. Coloration gives clothes diversity and fabric finishing gives clothes protection, provides comfort and maintains many desirable functional properties. However, the chemicals in use in the finishing process can cause water pollution or health issues. Nevertheless, the advantages are considered to far outweigh the disadvantages because chemicals can give fabrics a variety of important features.

2.3.2. Effect of alkaline on cellulose

Some wet processes for cotton fabrics, such as desizing, souring, and mercerization, demand an alkali solution with different concentrations. Besides, cotton is frequently treated with hot alkali in the preparatory process of mercerization prior to dyeing, as well as in the preparation of pure cellulose for research purposes. The chemical structure of cotton cellulose macromolecules is made up of β-D glucose residues linked with each other by 1,4 glycosidic bonds. The two end glucose residues of the polymers have different groups; one end (left of Figure 12) has four free hydroxyl groups, the other end (right of Figure 12) has three free hydroxyl groups and a hemiacetal group. The stability of the glycosidic bonds within cellulose chains to alkali is high, but it easily

hydrolyzes under acidic conditions. The degradation mechanism of cellulose for alkali is different compared to acid, but it is generally believed that alkali can only interact with the hydroxyl groups on the cellulose. For this reason, there have been two different theories to explain the chemical behavior of the cellulose with alkali. *(31)* For the first theory, cellulose is considered a weak acid, and it will have a similar neutralization reaction with a base to produce alkyl sodium compounds. In the second theory, the base and the hydroxyl groups of cellulose are combined to form molecular compounds, namely, the molecular combination theory. Both theories are thought to be possible. However, the product of alkali and cellulose is called alkali cellulose, which is an unstable compound. After washing, it can return to the original molecular structure of cellulose, but the microstructure of the fiber has changed. This means that the crystallization area has decreased, and the amorphous area has increased. The crystallinity of natural cotton fiber is 70%. After mercerization with high concentrations of sodium hydroxide (NaOH), the crystallinity is reduced to 50%-60%, which indicates that the alkali solution makes the fiber swell and decreases the crystallinity. This effect is of great practical significance and is an essential step in cotton fiber dyeing and finishing processes. *(31)*

2.3.3. Effect of acid on cellulose

The cellulose fiber treated with acid often shows a hand feeling of stiffness, reduced strength, and in some cases the fiber can be carbonized. This is because of the catalytic effect of the acid that hydrolyzes the glycosidic bonds of cellulose (Figure 17). After hydrolysis, a mixture of products with different degrees of polymerization is formed, which is called hydrolyzed cellulose. The chemical composition of hydrolyzed cellulose is no different from that of raw cellulose, except that the degree of polymerization is lower and cellulose molecular weight has greater polydispersity. If hydrolyzed cellulose continues to react with acid, the degree of

polymerization decreases below 50%, which is commonly called cellulose dextrin. If the cellulose glycoside bonds are completely hydrolyzed and broken, the product is glucose. *(31)*

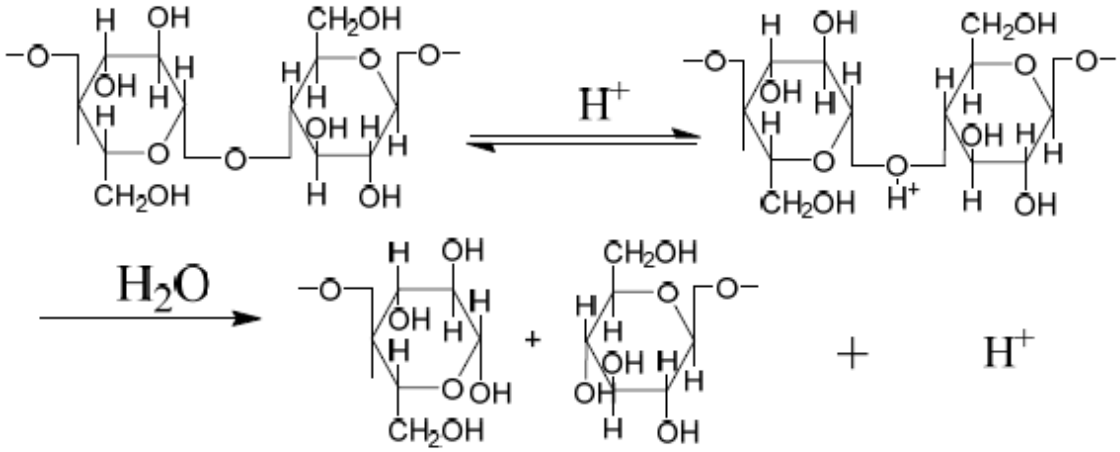


Figure 17 Cellulose hydrolysis by acid media*(31)*

The main factors affecting cellulose hydrolysis are the strength of the acid, the reaction temperature and the reaction time. In real production, if acid is properly used, no deep damage to the fiber will occur. The general rule of acid-cellulose interaction is that the stronger the acidity, the stronger the catalytic capacity and the faster the hydrolysis. Strong inorganic acids such as hydrochloric acid, sulfuric acid, and nitric acid can hydrolyze cellulose quickly. Weak acids such as phosphoric acid and boric acid have a poor catalytic capacity. Organic acids such as acetic acid are milder. Although acids are harmful to cellulose fibers, they have many practical uses. For example, fabric bleached with chlorine bleach is treated with dilute acid, which can further enhance the bleaching effect and neutralize the remaining alkali on the fabric with acid.*(31)*

2.3.4. Enzymatic treatment of cotton fabrics

Enzymes have been used for a long time in processes like amylase desizing of starch from fabrics and the natural retting of lignocellulosic fibers using hemicellulases. Other enzyme-based effects and processes have been introduced, like the aged look in denim abrasion or “bio-stoning”

of indigo dyed fabrics, pill-free cotton fabric surfaces, the elimination of residual hydrogen peroxide after bleaching, and others.*(32)*

The enzyme used to treat cotton is called cellulase, which hydrolyzes the β-1,4-linkages in cellulose as shown in figure 18, resulting in cleavage of the cellulose polymer chain. In the textile process, cellulase can be beneficial to modify the surface of cellulosic fibers and fabrics so as to achieve a desired hand or surface effect.

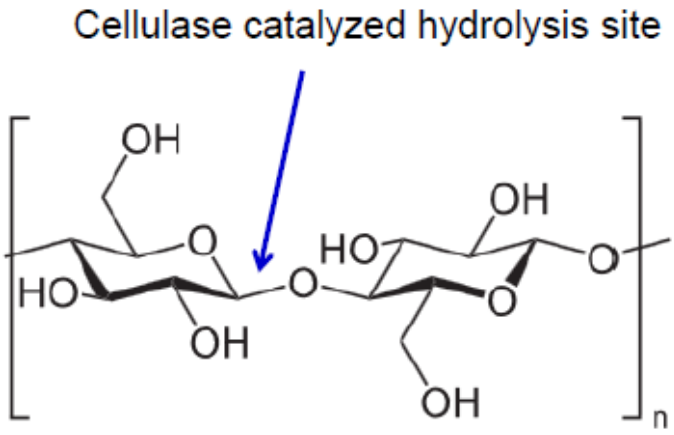


Figure 18 Cellulase catalyzed hydrolysis site

Multi-component based products of cellulase are needed to completely hydrolyze cotton to glucose and contain a mix of different cellulases with different modes of action. Endoglucanases (EG) ("endocellulases") attack internal bonds of amorphous cellulose polymer randomly. Cellobiohydrolases (CBH) ("exocellulases") degrade amorphous and crystalline cellulose by a progressive mechanism starting from the chain ends. Some CBHs degrade cellulose from the reducing chain end. Other CBHs degrade cellulose from the non-reducing chain end. Lastly, β-glucosidases (BG) ("cellobiases") hydrolyze cellobiose to glucose. In line with Figure 19, the cellobiose (substrate) and water move to the BG's active site where enzyme catalyzes the reaction between the substrate and water. Then the enzyme is able to release the products.

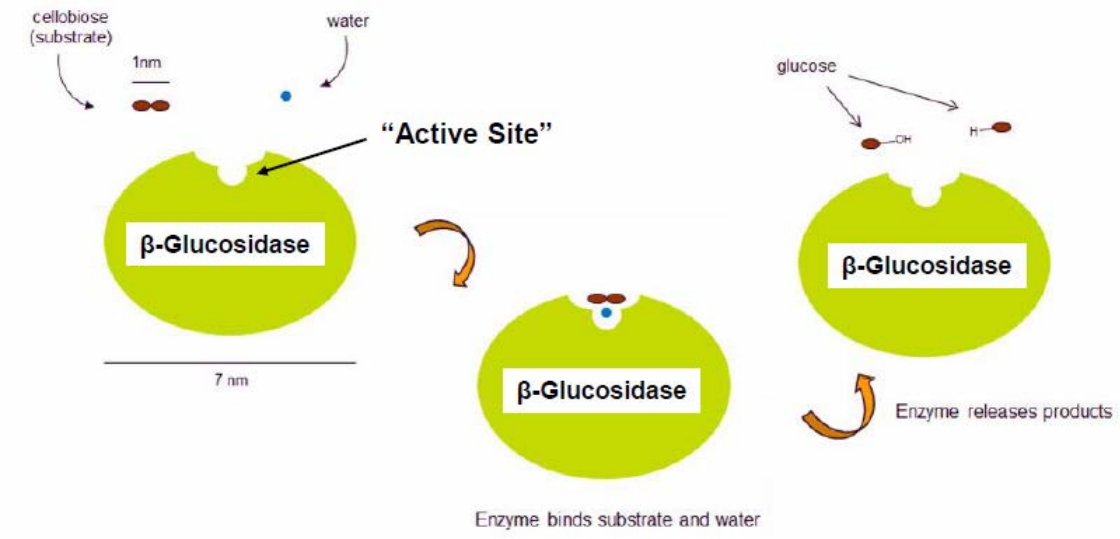


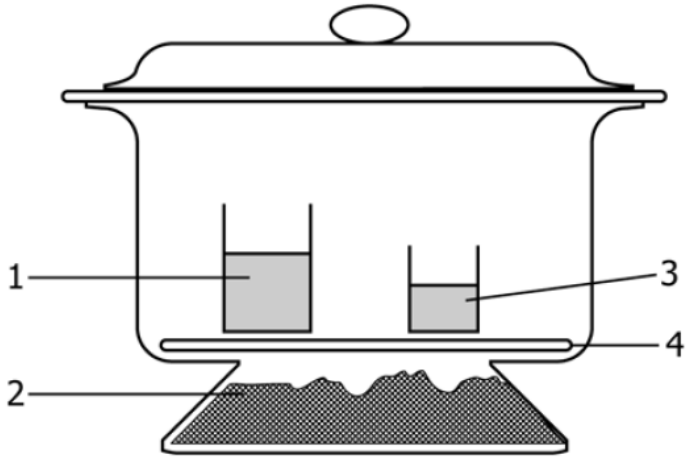
Figure 19 Hydrolyze cellobiose to glucose*(33)*

2.4. Compost of cotton fabrics

Around 20 pieces of clothing per person are manufactured, sold and worn each year.*(34)* The growth of the multi-trillion-dollar apparel industry has been fed by "fast fashion," which makes clothing cheaply and quickly at a low price. People already shop too much and wear clothes too little. The average American discards about 70 pounds of clothing per year; of which only 10 pounds are donated. The remaining 60 pounds need to be disposed of.*(1)* Furthermore, one company admitted to destroying unsold clothes instead of selling them off cheaply, in order to protect the brand's exclusivity and value. It added that it had captured the energy from the incinerating the clothes to try and make the process more environmentally friendly.*(34)*

Therefore, composting is a new way of disposing of textiles and clothing, and it only needs little air, water, sunlight, and micro-organisms. Cotton Incorporated's CottonWorks™ program employs a standard method ASTM D5988-03 which is an efficient technique to compost cotton in soil. For our studies, scoured and bleached 100% cotton jersey no finish (Sample 1), softener only (Sample 2) and resin plus softener (Sample 3) were selected. The fabrics degradation in soil was performed at Cornell University. The soil used in this study strictly complied with ASTM D5899-

03’s standard method. The standard method measures the generation of CO_2 by titrating with $Ba(OH)_2$. During composting, the weight loss of the fabric is measured. This experiment also requires the use of distilled water to ensure humid conditions. In addition, the fabrics are kept in the dark for 90 days at a temperature of 21±2°C (Figure 20). The results obtained from Cornell University showed that Sample 2 almost 80% weight loss, Sample 1 had 55% weight loss and Sample 3 had 50% weight loss. The research further indicated that cotton will continue to degrade over time.*(35), (36)*



NOTE 1—(1) Barium hydroxide solution or potassium hydroxide solution, (2) soil, (3) water, and (4) perforated plate.

Figure 20 Soil-Contact Incubation Apparatus*(36)*

2.5. Quantitative analysis

Quantitative analysis refers to the numerical determination of the mass, concentration, or relative abundance of components in a substance on the basis of content analysis or structural analysis. Quantitative analysis is crucial to the formulation and testing of food and drugs in all aspects of human life. For example, the quantitative analysis performed by mass spectrometry on biological samples can determine the abundance of specific proteins or metabolites and their relationship with cancer.*(37)*

2.5.1. Calibration Curve

Any quantitative analysis method needs to establish the relationship between the experimental measurement signal and the quantity of the analyte being analyzed. A calibration curve, also known as a standard curve shows the response of an analytical method to known quantities of the analyte. Fortunately, such relationships are usually established in mass spectrometry as well, so mass spectrometric signals can be used quantitatively and calibration curves can be set up.*(38)*

There are two commonly used quantitative methods, the external standard method, and the internal standard method. The external standard method uses a standard chemical *A* with a series of known quantities. This enables the unknown quantity of the test sample *A* response to be compared to that of the known quantities. The experiments need the following information: the amounts of the series of standard samples (known concentrations), the relative abundance of the standard samples, and the relative abundance of the unknown sample to be tested. This assumed that the response of sample *A* = constant * concentration, the quantity of the unknown sample to be tested can be calculated from this linear relationship. In order to determine samples with unknown quantities more precisely, the relative abundance of the standard sample needs to be as chemically similar as possible to the sample to be quantified in order to reduce the influence of the nonlinear response. Therefore, the commonly used external standard method measures a series of known standard samples, draws a calibration curve, and then uses a least square method to determine the unknown sample quantity. This external standard method has the following two limitations: 1) the standard sample and the sample to be quantified are independent experiments, and any accidental errors or changes in test conditions between the experiments cannot be

eliminated; 2) the matrices of the standard solutions and the unknown sample are different, which may also bring different effects that will generate errors.

To fix these limitations of the external standard method, the internal standard method adds a standard chemical *B* (known as the internal standard). Adding a known amount of standard chemical *B*, whose structure is similar to the components of the target sample, will help correct any matrix effects and minimize errors.*(39)* Because the concentration of the internal standard is the same in all the unknown sample concentrations, ideally, the intensity of the internal standard ions will be the same. However, the intensity is not always monotonous due to the ions' suppression and instrument error. However, the internal standard will correct any problem with ion suppression for quantification. The higher the intensity of the internal standard, the higher the intensity of the unknown concentration analyte because they have the same chemistry. Therefore, the ratio of these two ions' intensity can be considered the concentration of target analyte compared to the internal standard. In addition, collision-induced dissociation (CID) on the internal standard and the analyte provides improved accuracy for data and reduces any matrix effect.

Chapter 3

3. Experimental

3.1.Materials

3.1.1. Solvents

ACS grade solvents such as methanol, acetonitrile, ethyl acetate were purchased from Sigma-Aldrich and used without further purification. Deionized water was obtained from a Pure Lab Ultra water purification system from ELGA Lab Water. HPLC-MS Grade methanol and acetonitrile were purchased from VWR Analytical.

3.1.2. Auxiliaries

Dimethyloldihydroxyethyleneurea (DMDHEU) also called Permafresh 600 and dimethyldihydroxyethyleneurea (DMUG) named Arkofix NZF were obtained from Cotton Incorporated Company. DMDHEU with 83% purity was provided by Omnova Solution Inc. The structures of these components are shown in Figure 15 and Figure 16.

3.1.3. Fabrics

White knit 28 cut jersey fabrics (control samples, 100% cotton) and degraded and undegraded permanent press finished cotton fabrics were provided by Cotton Incorporated. For the DMDHEU treatment, the fabrics were dipped in Permafresh 600 with a concentration is 50g/L from Omnova Solutions Inc., which contained glycolated and non-glycolated DMDHEU. Drying was accomplished in a Mathis KTF-500 oven at 121°C for 90 seconds and curing was achieved in a Mathis KTF-500 oven at 171°C for 45 seconds. For the DMUG treatment, the fabrics were dipped into Arkofix NZF at a concentration of 80g/L from Archroma and then dried in a Mathis KTF-500 oven at 121°C for 90 seconds and cured in a Mathis KTF-500 oven for 177°C for 60 seconds.

3.1.4. Other chemicals

Sodium hydroxide with 97% purity, 2-imidazolidone with 96% purity, 0.1 M sulfuric acid solution, 1.0 M hydrochloric acid and cellobiose power were purchased from Sigma-Aldrich and used without further purification.

3.1.5. Other supplies

Aluminum TLC sheets, pH paper, 1 mL NORM-JECT® syringes, 13 mm polyvinylidene fluoride (PVDF) filters, and BD PrecisionGlide™ needles were purchased from Sigma-Aldrich. 15 x 45 mm glass vials were purchased from Fisher Scientific. 2 mL glass vials for HPLC were purchased from SUPELCO®. The cellulase, called CELLULYSIN® Cellulase, *Trichoderma viride*, was obtained from Calbiochem®.

3.2. Solvent extraction of cotton fabrics with wrinkle-free finishing

The purpose of this part of my experiment was to compare the differences between the chemical substances released from the degraded and undegraded fabrics. Both degraded and undegraded cotton fabrics with permanent finishing were used in this experiment. A 50 mg sample of each fabric was cut into smaller pieces and placed in a Fisher 5-ml vial before adding with 2.5 ml of ACS grade ethyl acetate. Then the vials were sonicated on a Branson 2210 sonicator for 10 minutes. Then ethyl acetate solvent was evaporated on a Buchi RE121 rotavapor coupled with Buchi 461 water bath and Brinkmann B-169 Vacuum Aspirator (Figure 21). The fabrics were removed from the vials, and 1 ml of HPLC graded menthol was added. The samples were then filtered by Phenex-PTFE 13mm syringe filter and transferred into a 2 ml HPLC vial.

Figure 21 Rotary evaporator system

3.3.Enzymatic digestion of cotton fabrics with wrinkle-free finishing

The digestion method used in this part of the experiment was the same with degraded and undegraded fabrics. The enzymatic treatment developed by a former group member was used in this study. A brief description of the method is as follows: a 3 mg of fabrics sample was placed in a 5 ml glass vial from Thermo Fisher Scientific. Then 100 µL of 3M (mol/L) NaOH was added to each vial containing the fabric sample. The vial was placed in a grip seal bag, and then the bag was placed into a container with ice (temperature maintained at 0℃) for pre-treatment. After 4 hours, the NaOH was removed from the vial and sample was first washed and neutralized with 500 µL of 0.5 M acetic acid for 1 min. After removing the acid, 1.5 mL of buffer solution (0.1 M sodium acetate, pH = 5) was added into the vial and incubated for 1 min. After removing the buffer solution, 1 mL of cellulase enzyme solution, which was prepared by dissolving 80 µg of cellulase powder in 50 mL of buffer solution, was added into the vials and then the vials were placed in a shaking water bath at 50 ℃ for 24 hours. After 24 hours, the vials were centrifuged at 3000 rpm

for 30 seconds, and the solution with fibers was filtered using a 0.2 mm PTFE syringe filter. The solution after filtration was transferred to a 2 ml HPLC vial purchased from VWR Analytical. The treatment was repeated at least three times to ensure reproducibility.

3.4. The determination of formaldehyde release with water extraction method

In order to test the amount of formaldehyde release, AATCC Test Method 206 was used to determine the amount of free formaldehyde that the fabrics contained. For this test, the Nash reagent was made by adding 2 mL acetylacetone, 3 mL acetic acid and 150g ammonium acetate in a 1000 mL volumetric flask which was made up with deionized water (Figure 22). First, 1g of degraded cotton fabric and 1g of undegraded cotton fabric were cut and added to each Erlenmeyer flask and 100 mL deionized water was added, making sure that the fabrics did not float on the surface of the water. Each flask was capped and placed in the water bath (Shaker) at 40 ± 1 °C (105 ± 2°F) for 60 ± 2 min. After sixty minutes, the flasks were removed from the water bath and the fabrics collected. Then the flasks were recapped and shaken to mix any condensation formed on the side of the flask. The solution was allowed to cool for 30 min. Then, 5 mL of the sample solution was added to a 20 mL glass tube and 5 mL of Nash reagent was added. A blank sample was prepared by adding 5 mL of the Nash reagent and 5 mL deionized water. Solutions were mixed and placed in a 40 ± 1 °C water bath for 30 ± 1 min. Finally, the tubes were removed from the shaker bath and their contents added to HPLC vials for MS detection. All steps were performed away from direct sunlight.*(40), (41)*

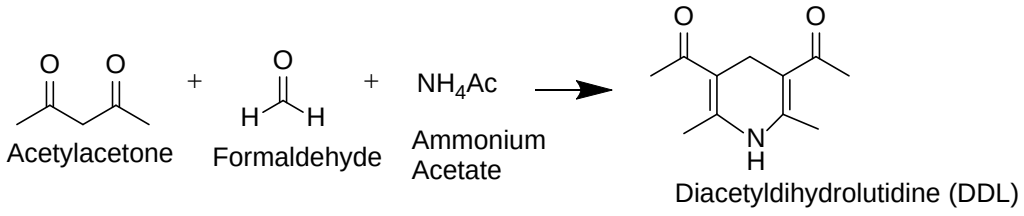


Figure 22 The reaction of Nash reagent with formaldehyde

3.5. Optimization of the cotton fabrics under wrinkle-free finishing with different acid and base conditions

In order to determine the degradation products of the cotton fabric, we decided to treat the undegraded cotton fabrics (control) and degraded fabrics with acid and base. Initially, a 50 mg sample of fabric with DMDHEU and DMUG finishing were cut into small pieces and added to a 5 mL Fisher® vial. To each vial, either sulfuric acid (0.001 M), hydrochloric acid (0.001 M) or sodium hydroxide (0.0125M) was added. The concentrations used in this study were based on previous research.*(42)* The vials were placed inside seal bags and put into a shaker bath (Figure 24) for different times and temperatures (see Table 1). Finally, these samples were neutralized with either 1.0M sulfuric acid or sodium hydroxide (Figure 23), using needles, syringes, and filters. Then the sample solutions were transferred into HPLC vials.

Figure 23 Samples containing fabrics with acid (HCl, H_2SO_4) and base (NaOH)

Figure 24 Shaker bath

Table 1 The different chemical conditions applied to fabrics

Chemicals / Temperature/Time	Sulfuric acid (0.001M)	Hydrochloric acid (0.001M)	Sodium hydroxide (0.0125M)
60˚C	1 hour	1 hour	1 hour
	2 hours	2 hours	2 hours
	3 hours	3 hours	3 hours
70˚C	1 hour	1 hour	1 hour
	2 hours	2 hours	2 hours
	3 hours	3 hours	3 hours
80˚C	1 hour	1 hour	1 hour
	2 hours	2 hours	2 hours
	3 hours	3 hours	3 hours

This experiment used high concentrations of acid and base, which meant after neutralizing the solutions the generation of salts was high, which would have a negative effect on ESI ionization.

In addition, when the solution would be introduced into the mass analyzer via HPLC, the salt could precipitate inside the HPLC and damage the system. Considering these limiting factors, it was decided to increase the amount of fabric instead of changing the acid or base concentration so as to obtain a higher concentration of analytes. From the initial experimental results, 70˚C was considered an ideal temperature to enhance the amount of analyte recovered. All the steps in the initial experiment were followed, but in the optimized experiment, the mass of fabric was changed to 150mg.

3.6.Quantitative analysis of the concentration of wrinkle-free auxiliaries on the cotton fabrics

As described earlier, mass spectrometry detects the relative abundance and intensity of ions; it does not represent the concentration of components in the solvent. The reason is the ionization of a component is decided by its polarity. The higher polarity, the higher the relative abundance and higher intensity. However, quantification can be done by tandem mass spectrometry (MS/MS). Thus, to quantify the amount of degraded products from the cotton fabric with different treatments, we developed an MS/MS method. A calibration curve was established for these MS/MS DMDHEU experiments.

The following procedure was followed: the internal standard (IS) solution was prepared by dissolving 0.01056g of the 2-imidazolidone with 96% purity into a 10 mL volumetric flask. Then a solution of MeOH: H_2O (50:50) was added to obtain a concentration of 1000 mg/L. This solution was then diluted from 1000 mg/L to 100 mg/L or 100 ppm. The stock solution (or target analyte solution) with a known concentration was prepared by adding 0.03012 g Permafresh 600 to a 25 mL volumetric flask and MeOH:H_2O (50:50) solution was added to obtain a concentration of 1000 ppm. By this method, each sample had a total volume of 1 mL. As shown in Table 2, a volume of

100 µm of internal standard solution was added to each solution of DMDHEU (50, 100, 200, 300, 400, 500, 600, 700, 800 and 900 ppm), to prepare the calibration solutions.

Quality control (QC) standards were prepared in the same way with concentrations of 250 ppm and 750 ppm. Unknown samples were prepared by adding 100 µL of internal standard solution to a vial containing 300 µL solution of the unknown sample and 600 µL of MeOH:H_2O (50:50) solution. The results showed that the unknown samples had concentrations ranging from 50 to 350 ppm. For this reason, a new calibration curve was made to have a range between 25 ppm to 350 ppm. Two new QC standard solutions with a concentration of 150 and 250 ppm were prepared (Figure 25). All experiments were repeated at least three times on three different days.

Table 2 Calibration solution preparation for DMDHEU

Type of the sample	Concentration of DMDHEU (ppm)	DMDHEU stock solution (1000ppm)	Internal standard solution (100ppm)	Blank solution (MeOH: H_2O) (50: 50)
Test sample	**50**	50µL	850µL	100µL
	100	100µL	800µL	100µL
	200	200µL	700µL	100µL
	300	300µL	600µL	100µL
	400	400µL	500µL	100µL
	500	500µL	400µL	100µL
	600	600µL	300µL	100µL
	700	700µL	200µL	100µL
	800	800µL	100µL	100µL
	900	900µL	0µL	100µL
Quality Control sample	**250**	250µL	650µL	100µL
	750	750µL	150µL	100µL

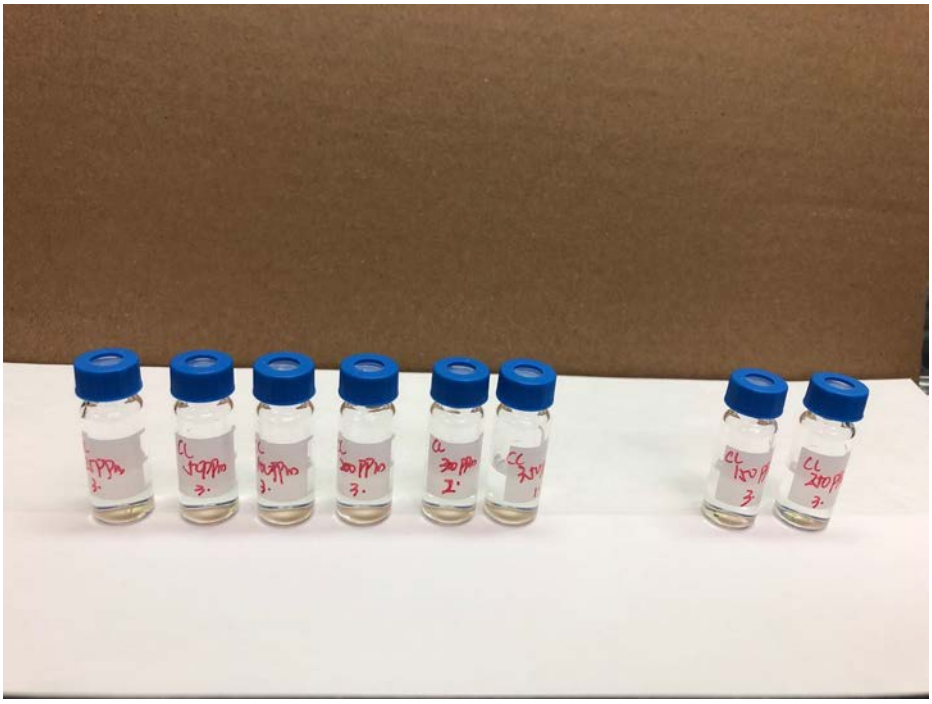


Figure 25 Solutions prepared for calibration

3.7. Instrument analysis

3.7.1. HPLC-Q-TOF-MS

To determine the concentration of permanent press finishing from the acid, base and enzymatic treatments mass spectrometry was used. All HPLC-Q-TOF-MS analyses were conducted by an Agilent Technologies 1260 High-Performance Liquid Chromatography (HPLC) system coupled with an Agilent 6500 Q-TOF mass spectrometer (Figure 26) using the same parameters used on the raw liquid analysis to ensure an equivalent comparison. To enhance separation, the mobile phase was made up of acetonitrile and water in isocratic elution at a ratio of 1: 1. For the stationary phase, an Agilent ZORBAX SB-Aq C18 (3.5 μm, 3.0 x 150mm) column was used. Ionization was performed via electrospray ionization (ESI) with the following parameters: gas temperature 350 ºC, drying gas 5 L/min, nebulizer 50 psi, Vcap voltage 3500 V and fragmentor voltage at 175 V. To improve the spectral accuracy, a reference mix acquired from Agilent was used via a dual ESI source.

Figure 26 HPLC-Q-TOF mass spectrometer

3.7.2. HPLC-LIT -MS

Tandem MS analysis was performed on both the double glycolated DMDHEU samples as well as the single glycolated DMDHEU samples to determine their dissociation pathways under collision-induced dissociation (CID). The experiments were performed on a Velos Pro Dual-Pressure Linear Ion Trap mass spectrometry (Figure 27) from Thermo Scientific^{TM}. Double glycolated DMDHEU ions with a m/z of 377 and single glycolated DMDHEU ions with a m/z of 289 were selected as precursor ions for CID experiments. Both precursor ions under CID conditions generate a fragment ion with a m/z of 129. Because single glycolated DMDHEU and double glycolated DMDHEU have a similar structure, the only difference between them is that double glycolated DMDHEU contains one more diethylene glycol unit. The internal standard ions with a m/z of 87 were subjected to CID and fragment ions with a m/z of 44 were obtained.

Figure 27 Velos Pro Dual-Pressure Linear Ion Trap mass spectrometer

Chapter 4

4. Result and Analysis

4.1. Analysis of the cotton fabrics with wrinkle-free finishing auxiliaries by TOF MS

4.1.1. Solvent extraction on DMDHEU cotton fabrics

As described in Chapter 2, the fabrics provided by Cotton Incorporated used Permafresh 600 to offer anti-wrinkle ability. Permafresh 600 contains single and double glycolated DMDHEU. Results from solvent extraction on degraded cotton fabrics with DMDHEU finishing are summarized in Table 3.

It was noticed that two ions: Singly glycolated product (m/z 289.1006), as well as doubly glycolated product (m/z 377.1537), were in the undegraded cotton fabrics. So, these ions could be used as "tags" to track the changes in the finishes on the fabrics after degradation. In order to illustrate the shift of these ions before and after the degradation, their relative abundance was compared to a reference ion (see Table 3). All the ion structures from this section are shown in Figure 28. It was worthwhile to mention that although ESI is not a single-stage mass spectrometry due to ionization bias, the relative abundance of these ions could still be used to study the change in the finishes for two reasons. First, the samples from the degraded and undegraded fabrics were run on the same date with the same electronic conditions (instrument settings). Second, the solution of the reference ion, purine, was prepared according to the instrument manual and introduced into the system via a built-in Calibrant Delivery System (CDS). The relative abundance of the reference ion was stable across all the runs performed with all samples, which provided a basis for comparison. Based on this assumption, the change of relative abundance in comparison to the reference ion could be interpreted as the change of concentration for a specific ion across different samples.

The results in Table 3 show that the glycolated DMDHEU crosslinkers decreased on the fabrics during degradation, so these ions were not detected. A possible reason is that the crosslinkers degraded or they leached into the soil.

Table 3 Relative abundance of representative ions on cotton fabrics with DMDHEU before and after degradation

Ion of interest	DMDHEU monomer: m/z 201.0482	DMDHEU singly glycolated monomer m/z 289.1006	DMDHEU doubly glycolated monomer: m/z 377.1531	Reference ion: m/z 121.0509
DMDHEU-Fabrics	ND	0.91%	1.22%	100%
DMDHEU **Degraded** - Fabrics	ND	ND	ND	100%

Note: ND = Not detected

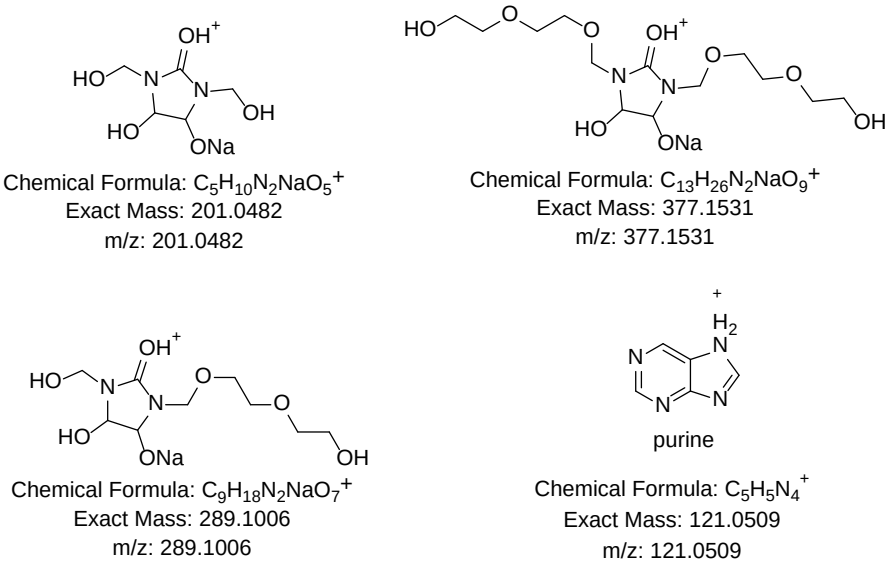


Figure 28 Structures of representative ions used in the study of DMDHEU degradation

4.1.2. Solvent extraction on DMUG cotton fabrics

The results in Table 4 show that the DMUG monomer and dimer were also decreased during degradation. The original concentrations of DMUG monomer and dimer were the same, but after degradation, some of the monomers still remained on the fabrics, but the DMUG dimer was not

detected. These results indicate that the dimers may be degraded to a monomer or leached into the soil. All the ions' structures described in this section are shown in Figure 29.

Table 4 Relative abundance of representative ions on cotton fabrics with DMUG before and after degradation

Ion of interest	DMUG monomer: m/z 147.0764	DMUG Dimer: m/z 199.1190	Ref peak: m/z 121.0509
DMUG-Fabrics	26.87%	26.67%	100%
DMUG-Fabrics-Degraded	1.33%	ND	100%

Note: ND = Not Detected

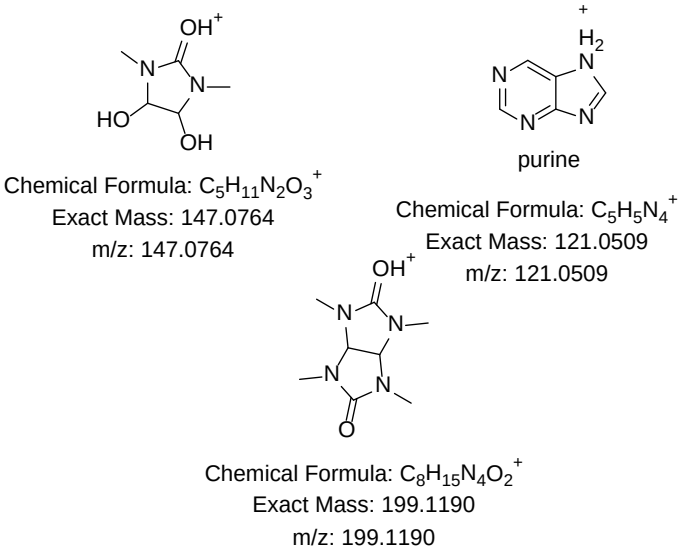


Figure 29 Structures of representative ions used in the study of DMUG degradation

4.1.3. Enzymatic treatment of undegraded cotton fabrics with wrinkle-free finishing

The results of mass spectrometry from the enzymatic treatment are shown in Table 5. In this part, the unit ppm is used to describe the relative mass accuracy which is the difference between the measured m/z value and the monoisotopic calculated m/z value. The ppm error is considered acceptable if is below ±5 ppm. According to the mass spectra following enzymatic treatment, there were two types of products observed: carbohydrates such as glucose and

cellobiose, and crosslinkers with a sugar moiety bonded to them. Table 5 clearly shows that the enzymatic treatment has been able to degrade cotton fabrics. Also, it was noticeable that all the digestion product ions were sodiated adducts, common with ESI. DMDHEU and DMUG crosslinkers were found to be bonded to a sugar moiety. The treatment of each kind of fabric was repeated at least three times to ensure reproducibility. The results were consistent across all replicates.

As mentioned in Chapter 2, the difference between DMDHEU and DMUG is that DMDHEU will release formaldehyde by a spontaneous hydrolysis reaction (Figure 30), whereas DMUG will not. It is, therefore, necessary to test for the presence of formaldehyde in the cotton fabrics after anti-wrinkle finishing as a precaution. In Table 5, it can be observed that both DMDHEU and DMUG crosslinkers were found bonded to a single cellobiose unit, which confirms the presence of the finish on the fabric and the efficiency of this method. The observed signals with a m/z of 701 and 493 for DMDHEU and DMUG respectively confirm the presence of these molecules on the degraded fabrics.

Table 5 Digestion products observed from the enzymatic treatment of cotton fabrics with durable press finishing

Sample	m/z observed	Formula generated	PPM error	Preliminary identification
Pure cotton	203.0533	$C_6H_{12}O_6$	-4.00	Sodiated glucose
	365.1064	$C_{12}H_{12}O_{11}$	-2.74	Sodiated cellobiose
	707.2229	$C_{24}H_{24}O_{22}$	-1.74	Sodiated cellobiose cluster
DMDHEU cotton fabrics	203.0523	$C_6H_{12}O_6$	1.20	Sodiated glucose
	365.1061	$C_{12}H_{12}O_{11}$	-1.85	Sodiated cellobiose
	701.2587	**$C_{25}H_{46}N_2O_{19}$**	**-2.14**	**Sodiated Doubly glycolated DMDHEU with cellobiose**
	707.2222	$C_{24}H_{24}O_{22}$	-0.98	Sodiated cellobiose cluster
DMUG cotton fabrics	203.0526	$C_6H_{12}O_6$	0.17	Sodiated glucose
	365.1054	$C_{12}H_{12}O_{11}$	0.00	Sodiated cellobiose
	707.2223	$C_{24}H_{24}O_{22}$	-0.86	Sodiated cellobiose cluster
	493.1628	**$C_{17}H_{30}N_2O_{13}$**	**2.05**	**DMUG with cellobiose**

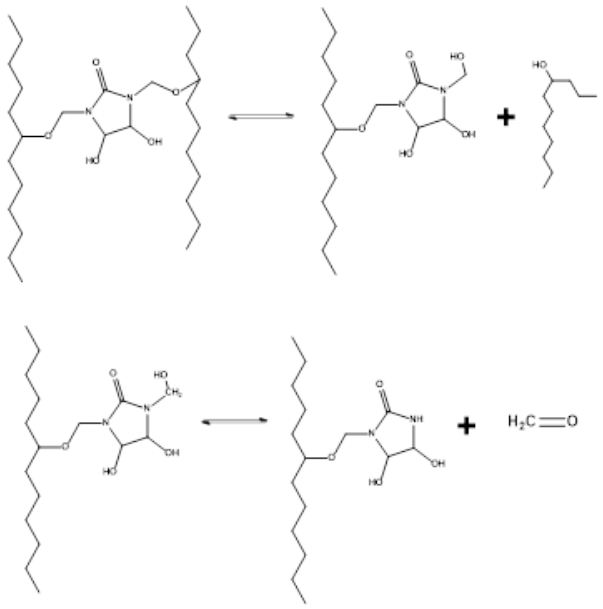


Figure 30 Hydrolysis of DMDHEU crosslink system with cellulose

4.1.4. Enzymatic treatment of degraded cotton fabrics with wrinkle-free finishing

Similar enzymatic treatments were performed on the degraded cotton fabrics, and the results are summarized in Table 6. The detection of these digestion products can help to reveal any changes in the finish after the degradation process. According to the results, sodiated glucose and cellobiose were detected, indicating that the cellulase was able to digest the cellulose polymer chain into single- or double-glucose sugar units. Besides observing the type of crosslinker with sugar moieties that was discussed before, Figures 31 and 32 show that digestion products have also been found with the DMDHEU crosslinker and the two glucose units. Figure 33 presents the MS spectrum of DMUG with cellobiose and its structure. From Table 6, all the crosslinkers were bonded to a cellobiose unit. In addition, a new product of DMDHEU crosslinker with cellobiose with a m/z of 613 was detected, which was not observed on the control. This product has one cellobiose unit attached to DMDHEU. We think that this compound could only be generated if the crosslinker was already detached from one side of the cellulose chains and lost a $C_4H_8O_2$ fragment prior to enzymatic digestion.

Table 6 Digestion products observed from the enzymatic treatment of degraded cotton fabrics with durable press finishing

Sample	m/z observed	Formula generated	ppm error	Identification
Pure cotton	203.0535	$C_6H_{12}O_6$	-4.23	Sodiated glucose
	365.1060	$C_{12}H_{22}O_{11}$	-0.67	Sodiated cellobiose
	707.2201	$C_{24}H_{44}O_{22}$	-2.32	Sodiated cellobiose cluster
DMDHEU cotton fabrics	203.0526	$C_6H_{12}O_6$	0.07	Sodiated glucose
	365.1057	$C_{12}H_{12}O_{11}$	-0.1	Sodiated cellobiose
	707.2186	$C_{24}H_{24}O_{22}$	4.53	Sodiated cellobiose cluster
	613.2042	**$C_{21}H_{38}N_2O_{17}$**	**3.42**	**Sodiated Singly glycolated DMDHEU with cellobiose**
	701.2558	**$C_{25}H_{46}N_2O_{19}$**	**4.13**	**Sodiated Doubly glycolated DMDHEU with cellobiose**
DMUG cotton fabrics	203.0526	$C_6H_{12}O_6$	0.18	Sodiated glucose
	365.1050	$C_{12}H_{12}O_{11}$	1.54	Sodiated cellobiose
	707.2201	$C_{24}H_{24}O_{22}$	2.03	Sodiated cellobiose cluster
	493.1630	**$C_{17}H_{30}N_2O_{13}$**	**2.45**	**DMUG with cellobiose**

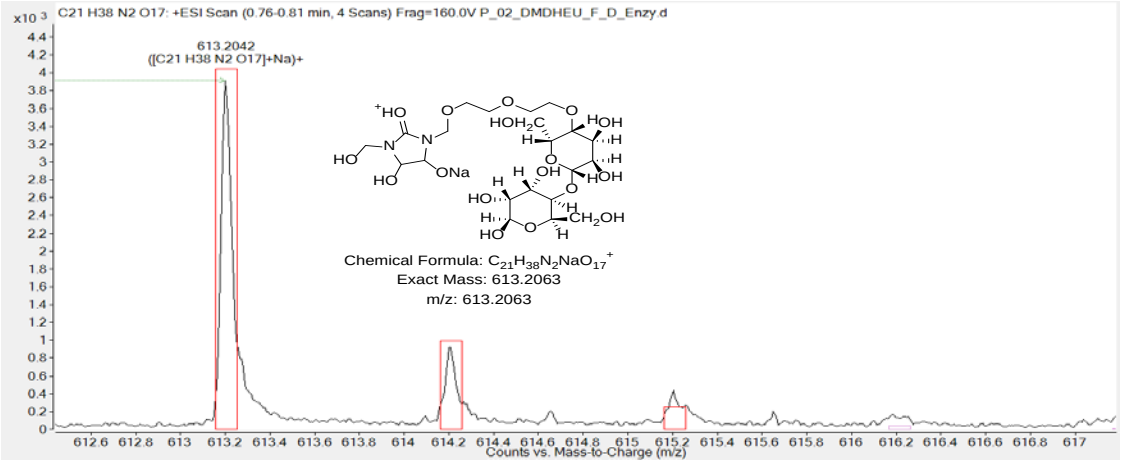


Figure 31 MS spectrum from enzymatic digestion of degraded DMDHEU fabrics featuring sodiated singly glycolated DMDHEU monomer with cellobiose

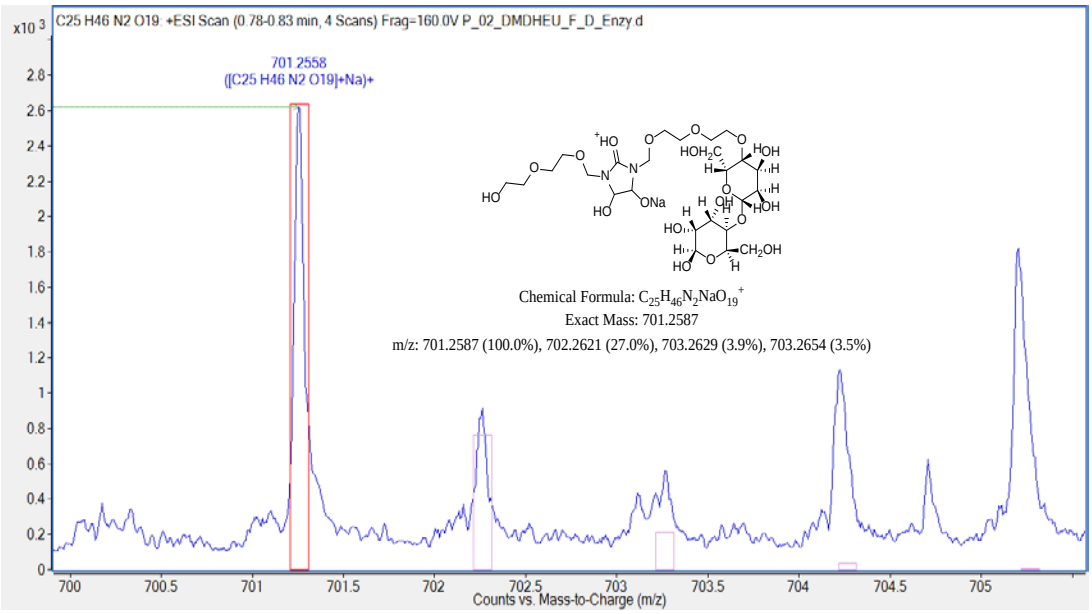


Figure 32 MS spectrum from enzymatic digestion of degraded DMDHEU fabrics featuring sodiated DMDHEU monomer with cellobiose

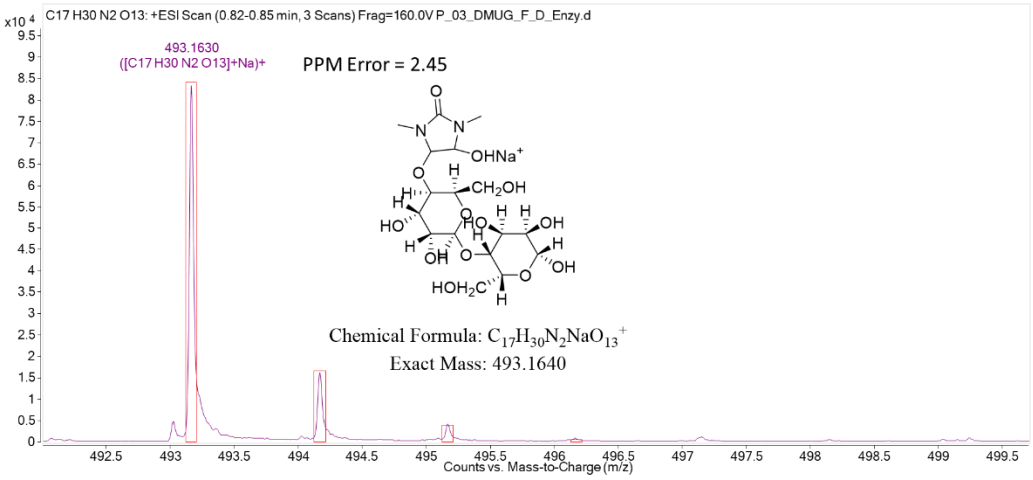


Figure 33 MS spectrum from enzymatic digestion of degraded DMUG fabrics featuring sodiated doubly glycolated DMUG monomer with cellobiose

4.2. Analysis of concentration of acid and base during chemical treatments in the cotton fabrics with wrinkle-free finishing by LIT-MS

4.2.1. DMDHEU

In this phase of the study, we wanted to compare the chemical treatment with the enzymatic treatment from Sections 4.1.3 and 4.1.4. From the chemical treatment, the results of the fabrics with Permafresh 600 showed the detection of two ions, which correspond to the DMDHEU monomer with a m/z of 347 and 377. Figures 34 and 35 show the spectra of these two ions with their respective structures. The intensity of an ion in the spectrum does not have any meaning in relation to the concentration of the analyte in the solution. However, we can normalize the ion signals to help us determine if the intensity of the signal changes or not, which can be related to the analyte concentration. This can be done by adding the intensity of the two representative ions and then dividing each ion by the sum of the two ions. The two ions selected for normalization were the products of our experimental treatments. We used them to determine any significant differences in the degradation products from the degraded sample when compared to the undegraded sample. None of the spectra of DMDHEU cotton fabrics showed degradation products in which the crosslinker was attached to glucose units as observed on the enzymatic treatment. In addition, it can be concluded that the optimum temperature was 70˚C (Figure 36 (a), (b) and (c)) for all acid and base treatments. In respect to the time of each chemical treatment, it is depended on the specific acid and base conditions used.

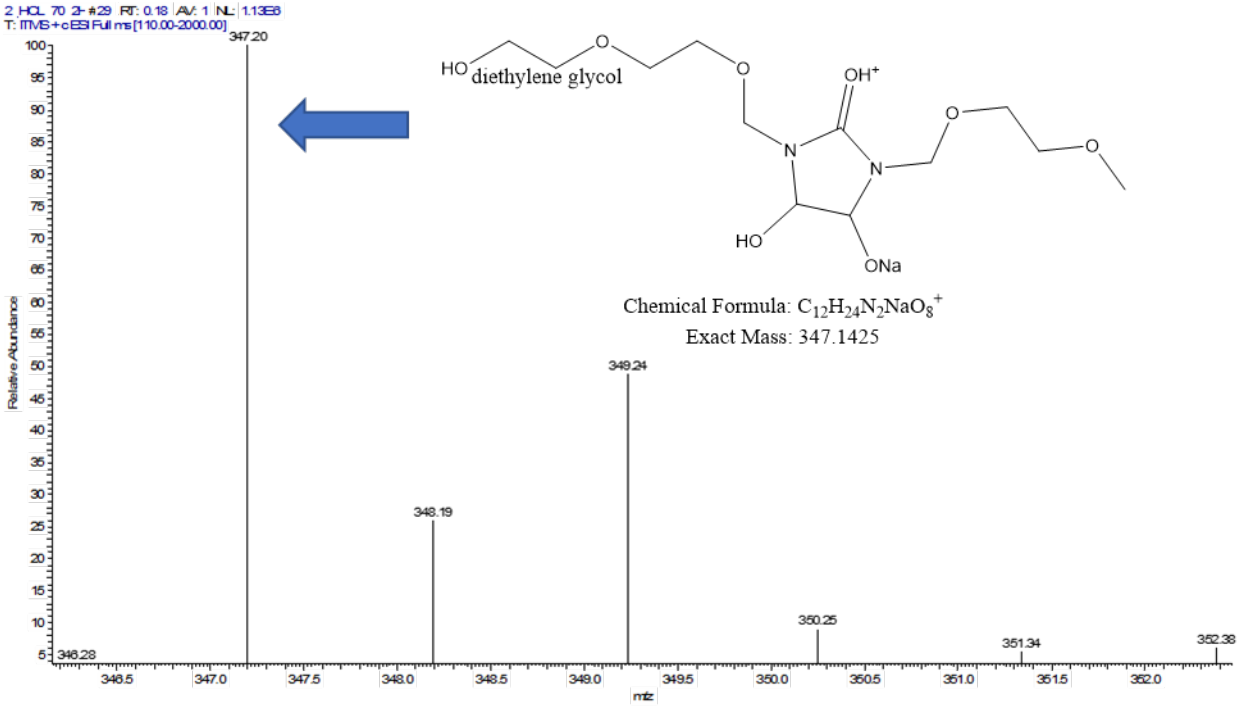


Figure 34 The spectrum of DMDHEU degradation product

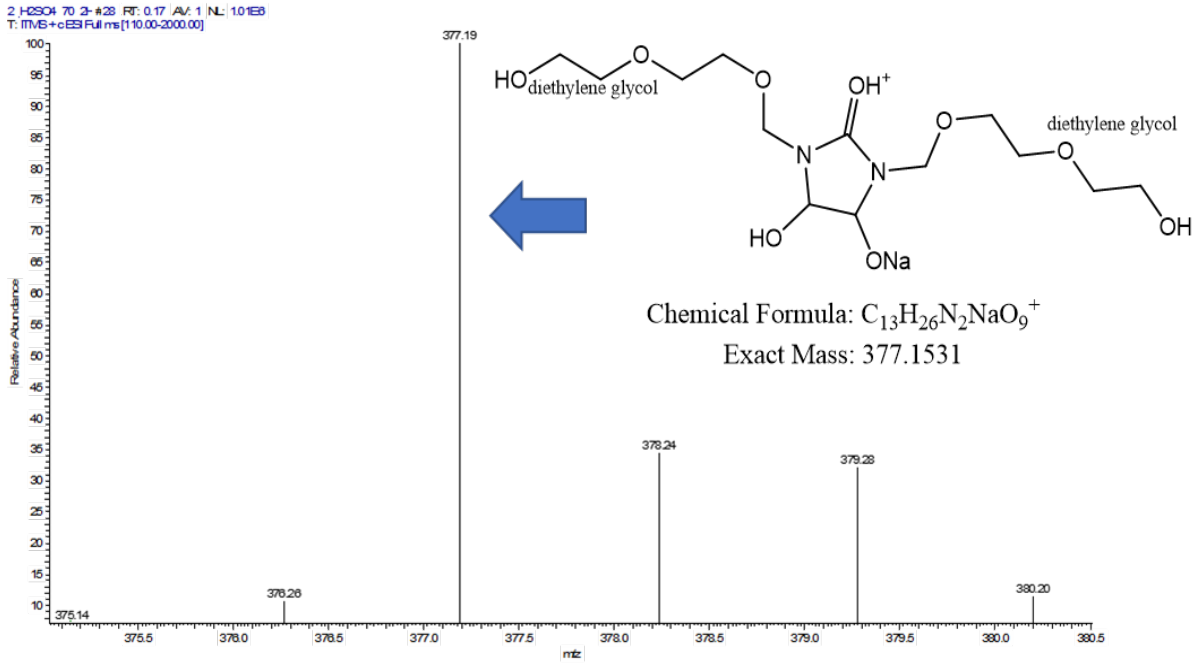
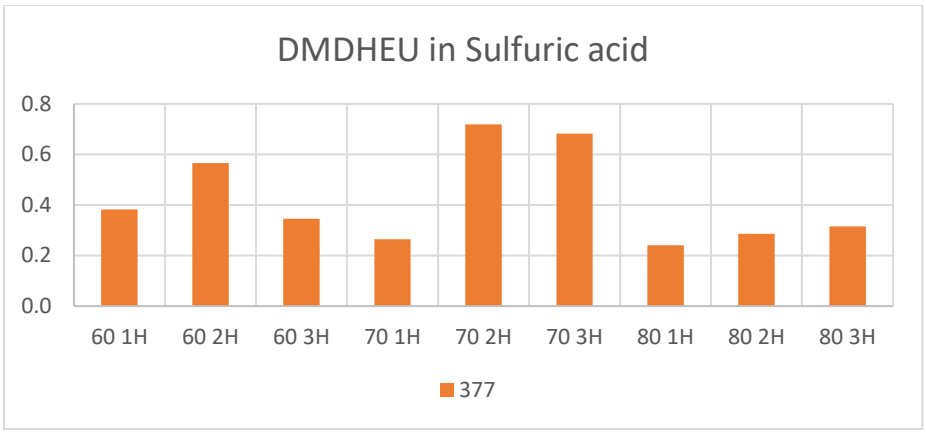
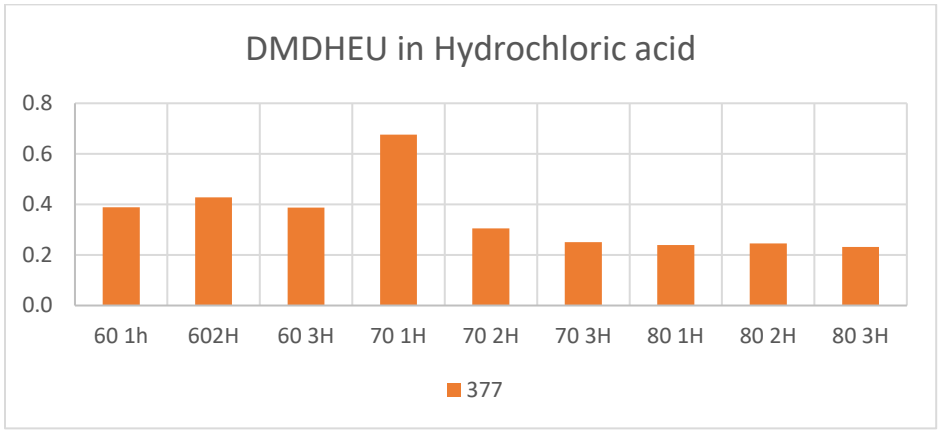


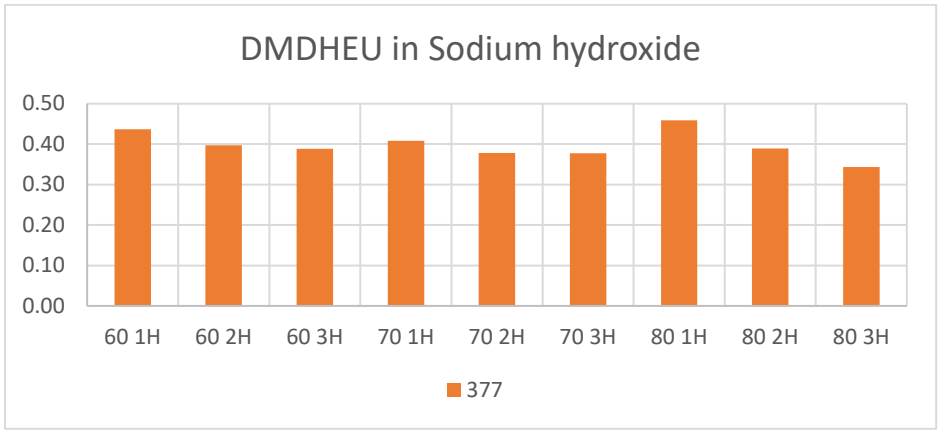
Figure 35 The spectrum of double glycolated DMDHEU



(a)



(b)



(c)

Figure 36 The relative intensity of double glycolated DMDHEU concentration following different chemical treatments.

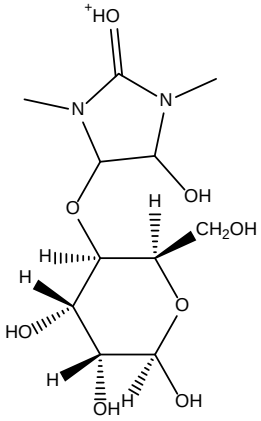
Table 7 summarizes all the concentrations found under this new method that was developed. It can also be observed that the highest concentrations of each analyte can be easily monitored and can be used to determine the best time for each chemical treatment.

Table 7 Concentration of target ions at 70˚C chemical treatment with Permafresh 600 cotton fabrics

Peak 289(Single glycolated DMDHEU)		Peak 377(Double glycolated DMDHEU)	
Chemical-Time	Concentration(ppm)	Chemicals-Time	Concentration(ppm)
DMDHEU-H2SO4-70◦C-1H	105	DMDHEU-H2SO4-70◦C-1H	143
DMDHEU-H2SO4-70◦C-2H	195	DMDHEU-H2SO4-70◦C-2H	109
DMDHEU-H2SO4-70◦C-3H	206	DMDHEU-H2SO4-70◦C-3H	308
DMDHEU-HCl-70◦C-1H	47	DMDHEU-HCl-70◦C-1H	126
DMDHEU-HCl-70◦C-2H	113	DMDHEU-HCl-70◦C-2H	145
DMDHEU-HCl-70◦C-3H	33	DMDHEU-HCl-70◦C-3H	278
DMDHEU-NaOH-70◦C-1H	34	DMDHEU-NaOH-70◦C-1H	206
DMDHEU-NaOH-70◦C-2H	48	DMDHEU-NaOH-70◦C-2H	226
DMDHEU-NaOH-70◦C-3H	66	DMDHEU-NaOH-70◦C-3H	213

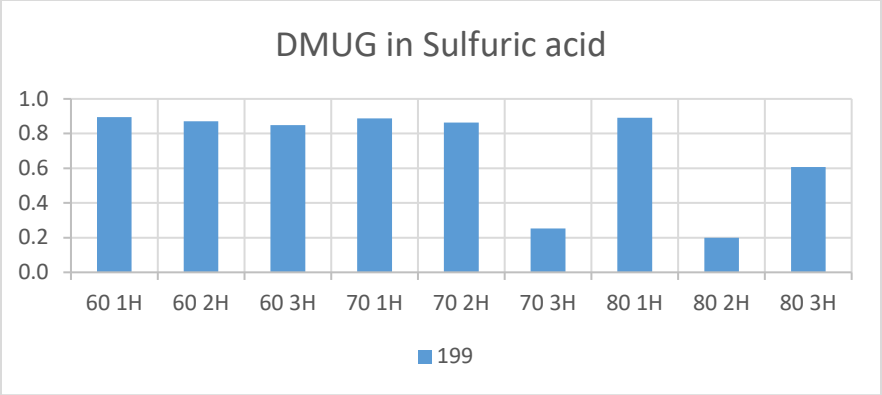
4.2.2. DMUG

In the experimental results of enzymatic treatment of fabrics with Arkofix NZF, two ions were observed including the DMUG dimer and DMUG monomer with a m/z of 199 (Figure 29) and 309 (Figure 37) respectively. Both crosslinkers were bonded to a glucose unit. The same data analysis method from Section 4.2.1 was applied for the Arkofix NZF experiment. In the case of the chemical treatment it was confirmed that the best temperature was 70˚C for NaOH and 60 ˚C and 70 ˚C for HCl and H_2SO_4 (Figure 38 (a), (b) and (c)).

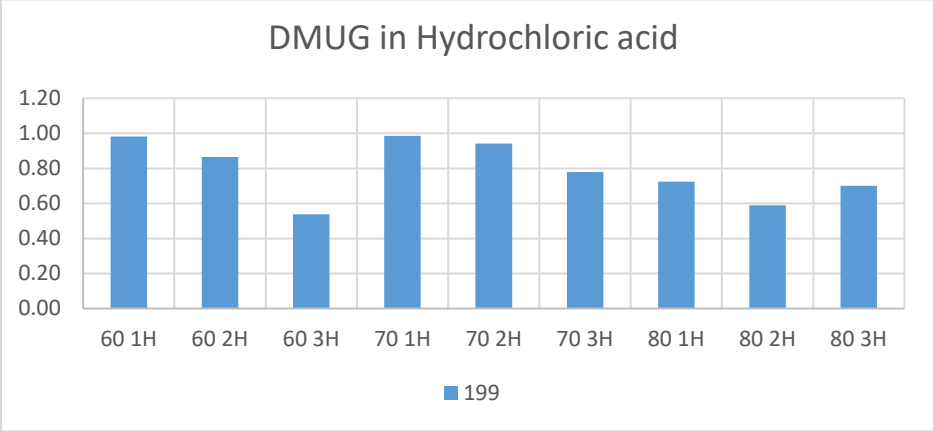


Chemical Formula: $C_{11}H_{21}N_2O_8^+$
Exact Mass: 309.1292

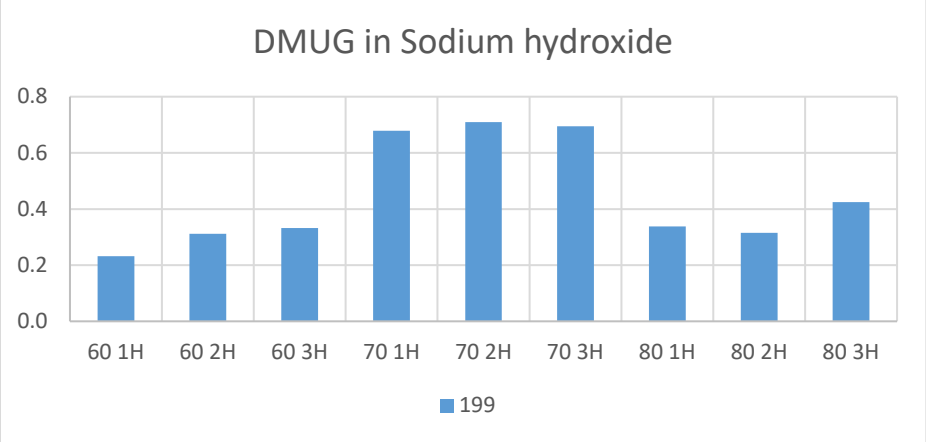
Figure 37 DMUG crosslink attached to one glucose



(a)



(b)

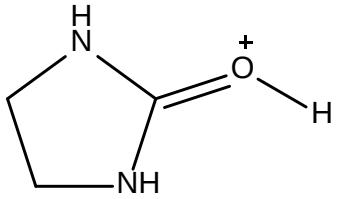


(c)

Figure 38 The relative intensity of DMUG dimer concentration following different chemical treatments.

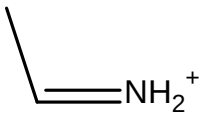
4.3.Determination of the concentration of DMDHEU in the cotton fabrics with wrinkle-free finishing

In this section, the measured concentration of DMDHEU in solution is presented and the differences between enzymatic digestion and chemical degradation are compared. The internal standard which was used in this experiment was 2-imidazolidone (Figure 39 (a)). Figure 39 (b) shows the structure of 2-imidazolidone after CID. Two calibration curves were set up to measure the quantity of DMDHEU on the fabrics. One curve was for double glycolated DMDHEU (m/z 377), and the second was for single glycolated DMDHEU (m/z 289) (Figure 28). Because of the similar structure of these two target analytes, the ions after CID were exactly the same as shown in Figure 39(c).



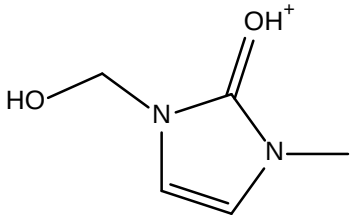
Chemical Formula: $C_3H_7N_2O^+$
Exact Mass: 87.0553

(a) 2-Imidazolidone ion



Chemical Formula: $C_2H_6N^+$
Exact Mass: 44.0495

(b) 2-Imidazolidone ion after CID



Chemical Formula: $C_5H_9N_2O_2^+$
Exact Mass: 129.0659
(c)

Figure 39 (a) Protonated 2-imidazlidone, (b) CID product of 2-imidazlidone and (c) structure of fragment ion of DMDHEU after CID

The range for calibration after multiple experiments was set between 25 ppm and 350 ppm. R^2 is a statistic which is the ratio between the sum of regression squares and the sum of total squared deviations. The larger the ratio, the greater the proportion of the sum of regression squares to the sum of the total deviations of squares, and the more accurate the model.*(43)* It was noticed that the R^2 of peak 377 is always lower than that of peak 289 (Figure 40(a) and (b)). This is because the intensity of the double glycolated DMDHEU ion is much lower than the single glycolated DMDHEU ion, which magnifies the error of bars.

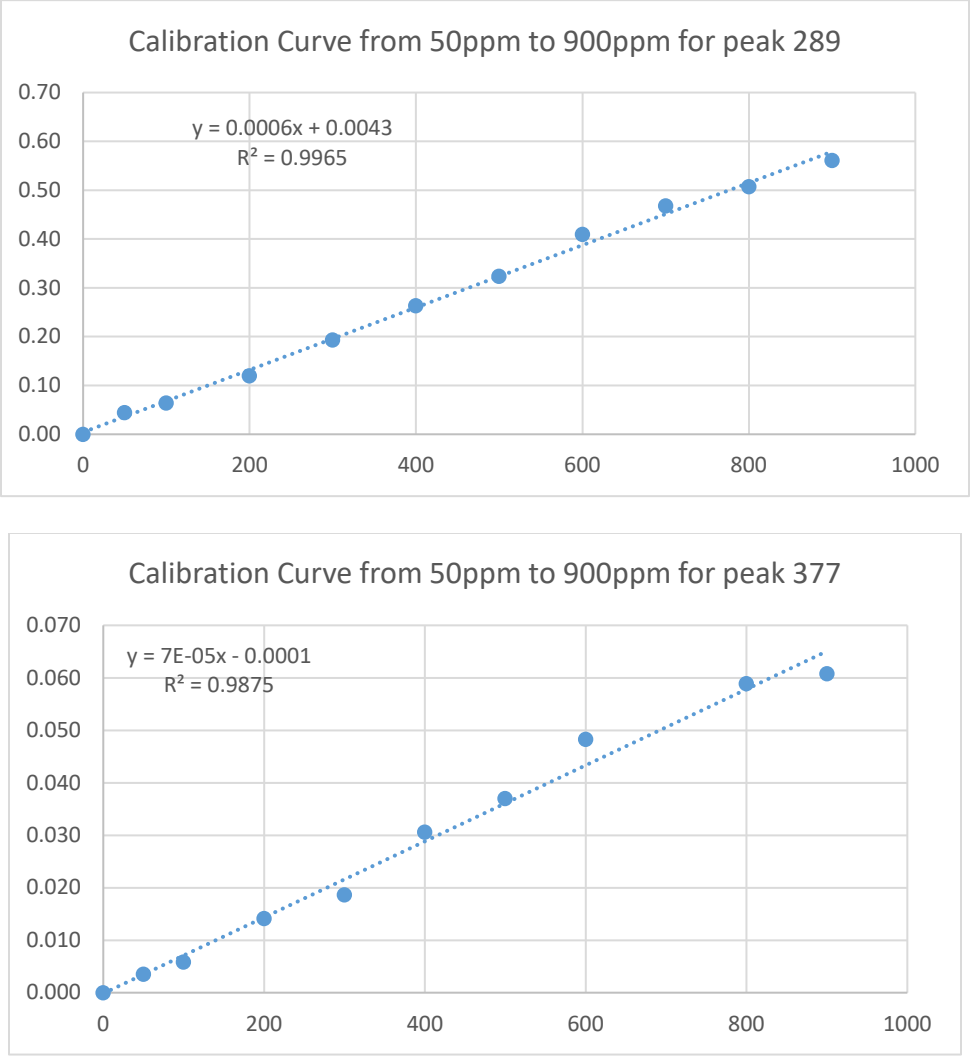


Figure 40 Calibration curves from 50ppm to 900ppm for single and double glycolated DMDHEU

Figures 41 and 42 are the final calibration curves for the single glycolated DMDHEU, the error bars showed the standard deviation of the ratios by repeating the experiment 3 times a day for three days.

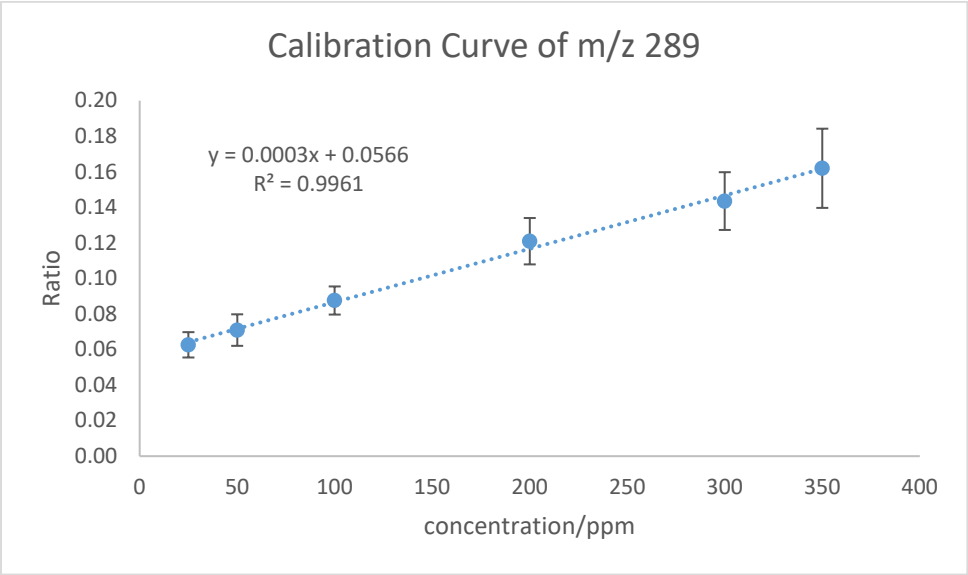


Figure 41 Calibration curve for single glycolated DMDHEU

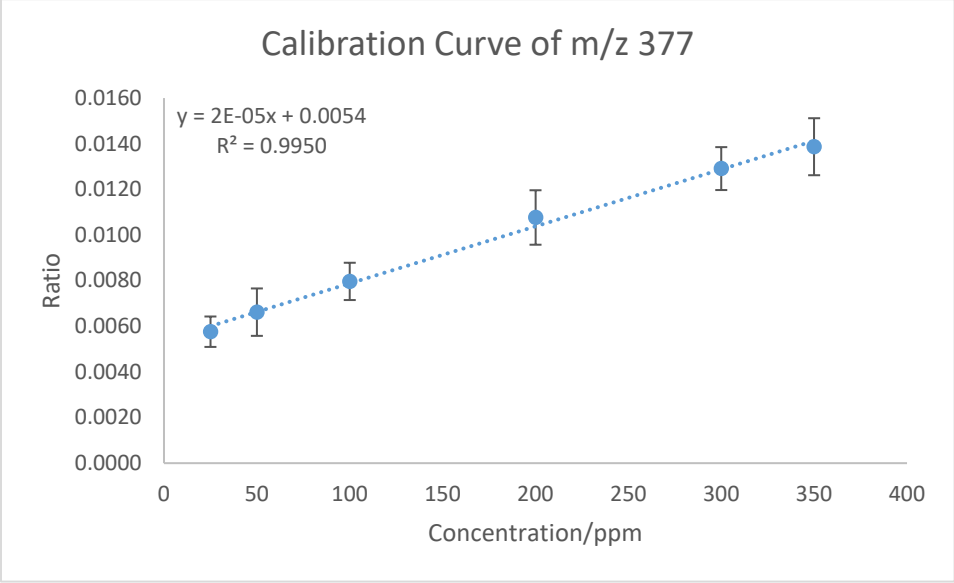


Figure 42 Calibration curve for double glycolated DMDHEU

The accuracy of the calibration curves can be evaluated in two ways: (1) comparing the data of each curve with the theoretical value on one day and across three days, and (2) offering the

quality control samples (150 mg/L and 250mg/L) to appraise the accuracy of the curve. Table 8 shows the %CV which means the percentage coefficient of variation. The intra-day and inter-day accuracy of the experimental aggregates were well within the acceptable ±15% limit.*(44)* Precision was also evaluated by comparing intra-day and inter-day data. They both lay well within the acceptable ±15% limit (see, Tables 8 and 9). By comparison with the literature the two quality control standards also provided an experimental accuracy within the acceptable range of ±15% (Table 6) *(45)*. According to Table 8, at 25 ppm (mg/L), the intra-day precision and accuracy present well with acceptable data for both 289 and 377 peaks.

Table 8 Accuracy and precision comparison between peak 289 and peak 377

Concen-tration (mg/L)	LIT							
	Peak 289(Single glycolated DMDHEU)				Peak 377(Double glycolated DMDHEU)			
	Intra-day		Inter-day		Intra-day		Inter-day	
	Precision (%CV)	Accuracy (%error)	Precision (%CV)	Accuracy (%error)	Precision (%CV)	Accuracy (%error)	Precision (%CV)	Accuracy (%error)
25	7.8	7.0(23.25mg/L)	11	23(19mg/L)	1.7	-0.8(25.2 mg/L)	11	43(14 mg/L)
50	6.7	8.5(45.75mg/L)	12	8(46mg/L)	15	0.7(49.6 mg/L)	15	7(47 mg/L)
100	8.5	8.3(91.63mg/L)	9	1(99 mg/L)	4	-6.3(106.3 mg/L)	10	3(97 mg/L)
200	4.0	-0.7(201.50mg/L)	10	-3 (207mg/L)	6	-7.8(215.7 mg/L)	11	-1(202 mg/L)
300	5.2	12.3(263.10mg/L)	11	7(279mg/L)	1	-0.7(302.1 mg/L)	7	6(282 mg/L)
350	4.1	5.0(332.40mg/L)	13	3(338mg/L)	5	4.2(335.0 mg/L)	9	9(318 mg/L)

Table 9 Validation parameter comparison between peak 289 and peak 377

	LIT	
	Single glycolated DMDHEU	Double glycolated DMDHEU
Linearity(R^2)	0.993±0.002	0.992±0.003
Accuracy (mean % error)		
Quantitation standard		
Intra-day	-4.4±5.6	-3.8±8.0
Inter-day	-6.5±2.0	11±3
Quality control standards		
150	6.7±5.0	5.3±6.0
250	9.6±8.0	1.6±10.0
Precision (mean CV%)		
Intra-day	5.00±0.03	7.00±0.08
Inter-day	11±2	10.5±3.2

Chapter 5

5. Conclusions and Future Work

This work showed the development of a new method to quantify the concentration of DMDHEU in cotton fabrics with wrinkle-free finishing. In addition, the method can be used to compare the degree of degradation of chemical treatments or biodegradation on cotton fabrics with permanent press finishing. Based on the results, for the first objective, most of the residual crosslinkers from anti-wrinkle finishing remained on the cotton fabrics. After composting, few of the chemical crosslinkers were detected by mass spectrometry on the cotton fabrics, which suggest that most of the residual crosslinkers were degraded by or leached into soil. For the second and third objectives, the different treatments (acid, base and enzymatic) generated different reaction products. Both the acid and base chemical treatments caused more degradation than the enzymatic treatment as described on Chapter 4. Fourth, the calibration curves of the two representative component ions from Permafresh 600 were successfully established and the concentrations measured.

Based on the conclusions of this study, one part of the future work will be to analyze the soil where the fabrics were degraded and to set up a calibration curve for the concentration of DMDHEU in the soil. In the next phase of the project with Cotton Inc. company, it is a time to start the analysis of cotton fabrics colored with reactive dyes and finished with permanent anti-wrinkle finishes. This will play an increasingly important role in selecting the preferred way to dispose of large amounts of cotton by composting fabrics.

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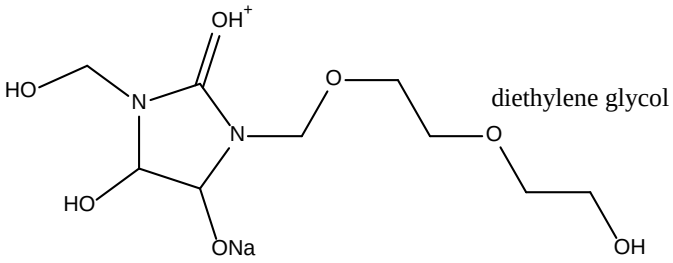
APPENDICES

Appendix A

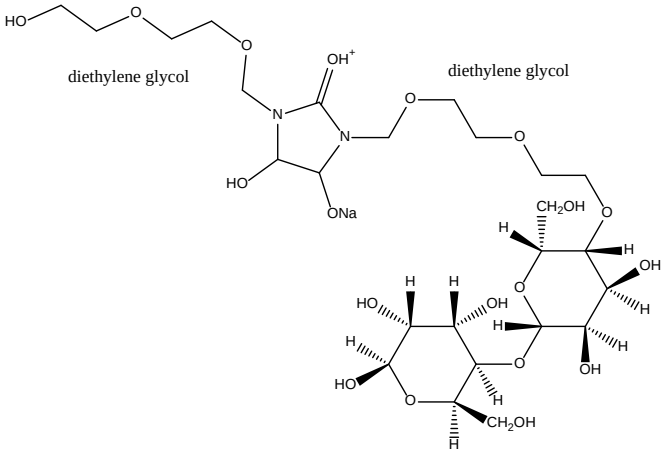
All structures of digestion of cotton fabrics with anti-wrinkle finishing

Single glycolated DMDHEU ion



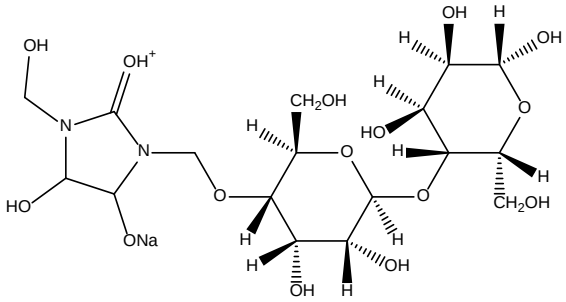
Chemical Formula: $C_9H_{18}N_2NaO_7^+$
Exact Mass: 289.1006

Double glycolated DMDHEU ion with cellobiose



Chemical Formula: $C_{25}H_{46}N_2NaO_{19}^+$
Exact Mass: 701.2587

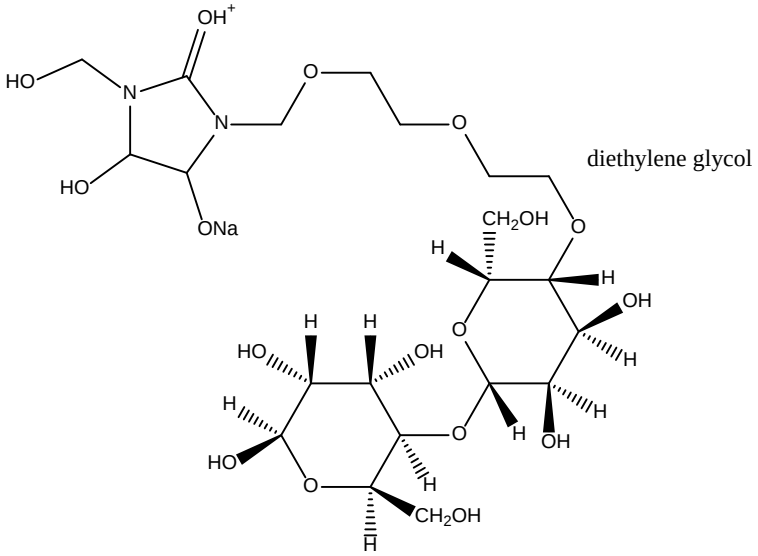
DMDHEU ion with cellobiose



Chemical Formula: $C_{17}H_{30}N_2NaO_{15}^+$
Exact Mass: 525.1538

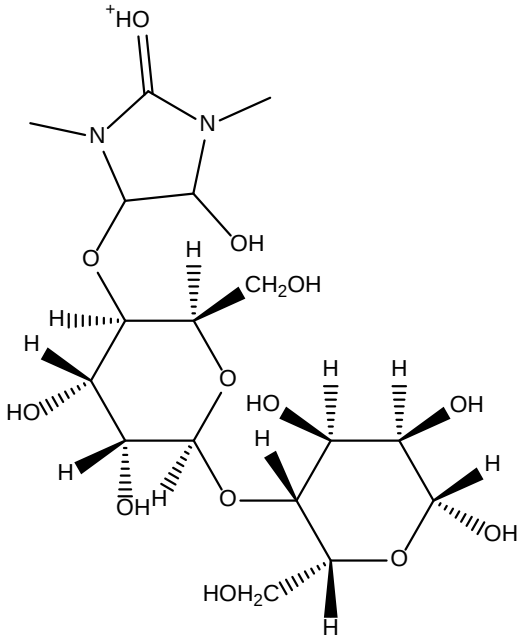
Appendix B

Single glycolated DMDHEU ion with cellobiose



Chemical Formula: $C_{21}H_{38}N_2NaO_{17}^+$
Exact Mass: 613.2063

DMUG ion with cellobiose



Chemical Formula: $C_{17}H_{31}N_2O_{13}^+$
Exact Mass: 471.1821