THE EFFECTS OF TEMPERATURE AND GAS ON MOISTURE LOSS AND REGAIN OF THE 2001 CY COTTON

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Abstract

The level of cotton moisture directly affects the mechanical, electrical, and dimensional properties of the fiber. However, the cotton industry lacks an accurate standard method for the measurement of cotton moisture. The weight difference between the standard oven drying (SOD) in air and the volumetric Karl Fischer titration (KFT) method can be attributed to factors other than moisture. Another problem with SOD is the lack of regain of the original moisture, thus the lack of retention of the original mechanical properties of the fiber. In this study, four gases, argon (Ar), nitrogen (N_2), helium (He), and dry air, were used at various temperatures on a ginned raw cotton (2001 crop year). KFT was used to verify the results. After the water was completely removed, as verified by *in vitro* NIR, the cotton weight loss was recorded, and the cotton container was left open in a standard conditioning lab (72°C and 65% RH) for over 48 hours and its weight was recorded thereafter. The average weight loss under N_2 at 75°C within 1 hour was within 0.1% of the KFT values and the cotton did not exhibit any hysteresis effects. Using less than 100°C, this method is referred to as the Low Temperature Distillation (LTD) method. Helium also was able to remove the moisture, but argon, even at 105°C after 3 hours, was not able to remove all of the water.

Introduction

Finding an accurate standard in the detection of the moisture content in cotton has eluded textile scientists for many years. Variables such as low molecular weight non-aqueous volatiles (NAVs) and fine particulates have been detected in certain sample configurations. The standard ASTM method used currently by the USDA calculates moisture content based on weight loss by oven drying cotton at 105°C, but involves oxygen at ~20% when using normal air. In comparison, the percentage weight loss is around 0.5% greater than more accurate methods, such as, the Karl Fischer titration, which uses nitrogen as a carrier gas.

Karl Fischer Titration (KFT) is the universal gold standard when it comes to measuring water content in *any* given substance. The KFT method is based on the Bunsen reaction, which has SO_2 oxidized to SO_3 in the presence of I_2 (reduced to I^-) and H_2O. One of the products of the Bunsen reaction, SO_3 is a desiccant in itself, reacting with another molecule of water to form sulfuric acid (H_2SO_4). The resulting H^+ ions are neutralized by a base, usually imidazole or an imidazole derivative (e.g., 2-methyl imidazole) and the solvent medium is an unreactive bulky alcohol. When determining the water content of a sample in the solid state, such as cotton, the sample is heated and the gases given off are carried by nitrogen into the titration cell, where water reacts in aforementioned reaction. The KFT reference method is not a green method compared to the Low Temperature Distillation (LTD) method as discussed in this paper. However, LTD can be used to help verify the latter method.

Oxidation is the most prevalent chemical process on Earth. Rust, aging, combustion, and metabolism are all oxidative processes. The presence of water can exacerbate or mitigate the oxidative process. In the case of cellulose, its nearly impossible to burn wet cotton, but, when all the moisture is removed, dry cotton suddenly becomes a fire hazard. Like all chemical reactions, oxidation is subjected to the Arrhenius equation, which states that a change in temperature will change the rate of reaction. Cotton is easily oxidized but the extent of the general sensitivity of cotton at any given temperature to oxygen is not known.

Research from several decades ago revealed that once moisture content in cotton is measured under standard oven drying (SOD) conditions, 105°C in air, the dried cotton *never* returns to its original weight when exposed to its original environment and the rheology of the fiber is permanently altered (i.e., hysteresis). The hysteresis of cotton has had several explanations, but has not been fully explored in the last decade and not linked to oxygen in the air. Preliminary drying experiments with nitrogen and air (or a synthetic 80%/20% N_2/O_2 mixture) have shown significantly different results with the larger weight loss when the drying is done in air.

Using inert gases to remove moisture from a sample matrix is not a novel idea, but it has not been thoroughly studied in regards to cotton. Three readily available non-greenhouse gases were tested. Nitrogen and argon gas are two of the most abundant inert gases in the Earth's atmosphere, comprising of roughly 20% and 0.93%, respectively. Helium exists in the atmosphere at about 5ppm, but mostly isolated from natural gas wells. Nitrogen (N_2) is only known to react in specific reactions and the resultant product is usually unstable and reverts back to N_2 gas and the original reactant. Helium and argon, two of the most abundant noble gases, are commonly used to displace oxygen in places where the material easily undergoes oxidative reactions or oxygen is undesireable.

The objectives for this paper are: (1) identify and obtain gases of economical and scientific interest, (2) select a cotton with a known water content determined by KFT, (3) identify biases and hysteresis associated with the gases' effect on cotton and compensate accordingly, (4) compare the results of the dry cotton weight to that of KFT, and (5) recommend a gas and drying temperature <105°C that will serve as the basis of a new ASTM standard method.

Materials and Methods

A 2001 crop year (CY) cotton, provided by the Agricultural Marketing Service (AMS) of the USDA and identified as Bm8, was tested in a Curtin Matheson Scientific Equatherm oven and the temperature was monitored using a Cole-Parmer thermocouple (Model # 86460-05). Cottons were placed in a 40mL weighing bottle with a ground glass joint and weighed on a Mettler Toledo analytical balance (Model #XS205, 0.1/0.01mg). Copper tubing (1/4", 50ft) was purchased from Sigma-Aldrich and ¼" brass fittings were purchased from the local Ace Hardware store. The comprised gases, dry air (ultra zero), argon (ultra high purity, UHP), nitrogen (extra dry) and helium (UHP), were purchased from Airgas and used without further purification. All documentation for each gas indicated a water concentration of less than 20ppb. NIR measurements were made on a Bruker MPA with OPUS (version 5.5) output software.

The copper coil was placed on the upper wire rack in the oven with one end attached to a flowmeter, which was connected to a cylinder of compressed gas. The other end of the coil was split 4 ways and the 4 outlets were arranged beneath the copper coil and 6" parallel to the bottom wire rack. The gas flow was controlled by adjusting the valve on the flowmeter according to a chart provided from the manufacturer.

Kerr jelly jars (8oz.) were modified by drilling a hole, just big enough for a ¼" pipe, in the center of the lid. The copper pipe was affixed using a high temperature epoxy resin on both sides of the lid so that the bottom of the pipe was approximately 1" from the bottom of the jar. The copper pipes attached to the jelly jars were then further modified with brass fittings and curved at a 90° arc so that it could ease the attachment to the fittings extending from the copper coil. The resin was cured in the oven at 105°C overnight prior to use.

The cottons were allowed to condition in a designated standard textile conditioning lab (70°C and 65% RH) for at least 24 hours prior to use. The oven was adjusted to the desired temperature and equilibrated 1-2 hours before use. The cotton samples (1.0g) were weighed out to the 4th decimal (0.1mg) in the weighing bottles. The weighing bottles, with the cotton inside and the lid removed, were placed in the modified jelly jars. The copper pipe attached to the jelly jar lid was inserted about two-thirds down the height of the sample container and screwed in tight. A set of unmodified jar lids were set aside.

The gas flow, monitored by a CSI (Cambridge Scientific Instruments) 6000 Solid State Flowmeter, for each experiment was set to 325 mL/min/sample container for each gas. Each data point was recorded every 30 minutes and 1 hour after the first two hours. For each measurement, the jars were quickly detached from the manifold, the modified lids were removed, sample containers were capped within the jar, and the unmodified lids were used to cap the jar. After cooling to room temperature, the glass sample containers were removed from the jars, weighed, and one sample was selected for scanning by NIR *in vitro* through the closed glass container to study the extent of moisture removal. Disposable gloves were used when handling the samples. Mean sample weight values were computed from the four replicates in each experiment. The mean results were used to construct the figures and tables in this paper.

Results and Discussion

To compensate for any fluctuations in relative humidity and/or temperature, which could affect the initial weight, in the conditioning labs, the graphs displayed plotted multiple data points of the average weight loss against time. If there was any significant change in the dry weight due to the use of the different gases, it could be monitored. Ideally, when using dry inert gases, all weight loss curves may have different initial approaches, but should approach the same 'dry' weight (Figure 1), if the mass lost is due solely to complete removal of water.

There may be some effect on the molecular scale leading to faster or slower rate of initial weight loss, but the end result should be the complete removal of water, which exists anywhere from 4-15 % weight of cotton, and the absence of confounding side reactions.

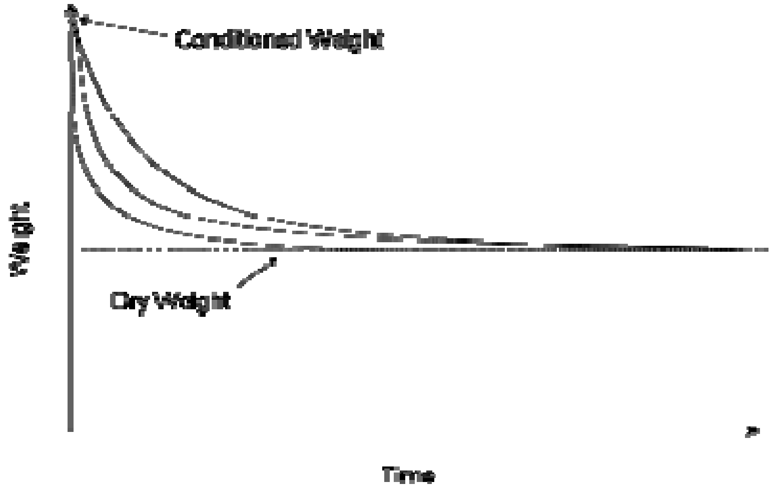

Figure 1. Ideal weight loss of a cotton sample in three inert atmospheres.

Cotton primarily consists of cellulose (90%), a polysaccharide made of $\beta(1\rightarrow4)$ linked D-glucose. Despite all of the hydroxyl groups of the linked sugar moieties, cellulose is insoluble in water, but its ability to retain water is well known. The amount of water can be correlated to the peak area in NIR at 1930nm (Figure 2). In Figures 4-7, the peak at 1940nm is either noticeably smaller or nonexistent.

In Figure 3, drying at 105°C under N_2, Ar, He, and dry air were evaluated. Drying under N_2 at 75°C, using previously dried cotton which has been reconditioned, showed that drying at lower temperature is just as effective at higher temperatures and N_2 produced no hysteresis effects.

Drying cotton in N_2

The drying profile under an N_2 atmosphere (Figure 3) shows a steady dry weight with about 7.1% weight loss. The cotton samples were reused and the weights were retaken, after conditioning 48 hours, prior to immediate use in a subsequent run. If the cotton was not used immediately, the cotton was reweighed prior to use. The same dry weight was obtained for the reused cotton sample. The standard deviation (σ) is shown for the four replicates. After 30 minutes in N_2 at 75°C the water is completely removed as indicated by *in vitro* NIR.

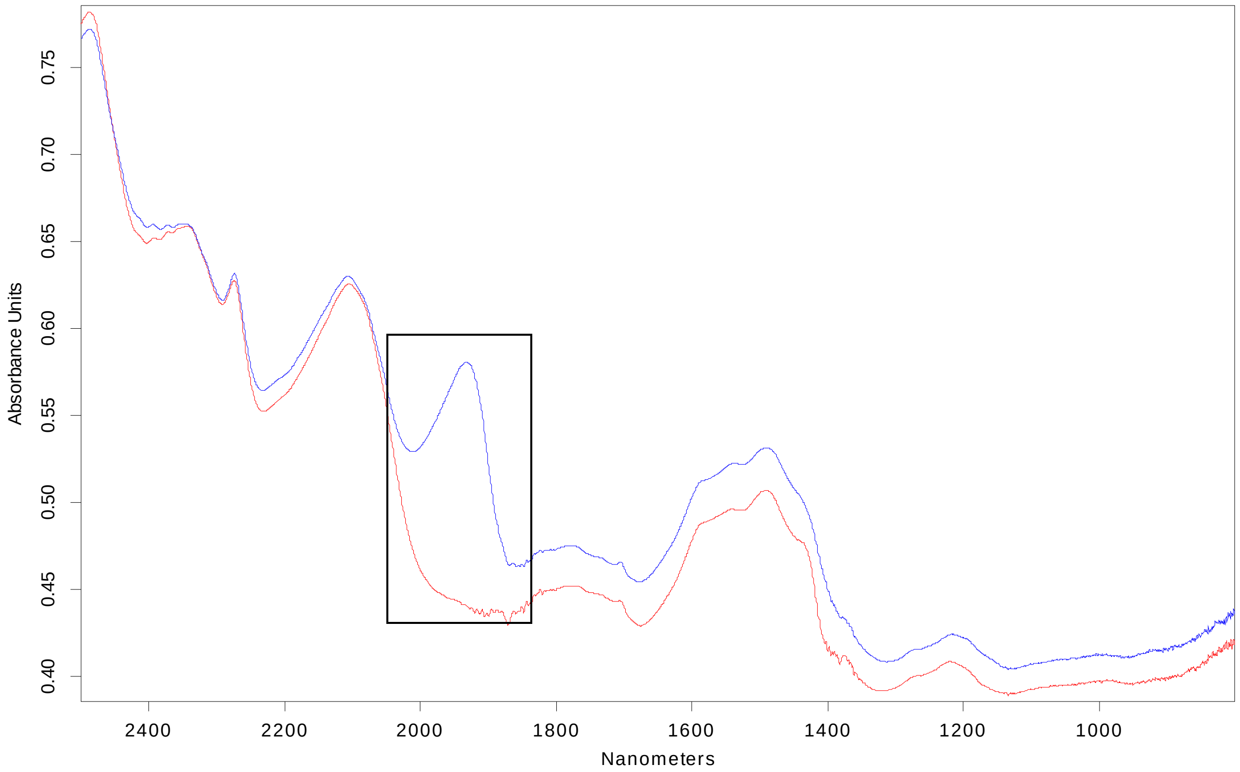

Figure 2. Typical cotton NIR spectra before drying (blue) and dried cotton (red).

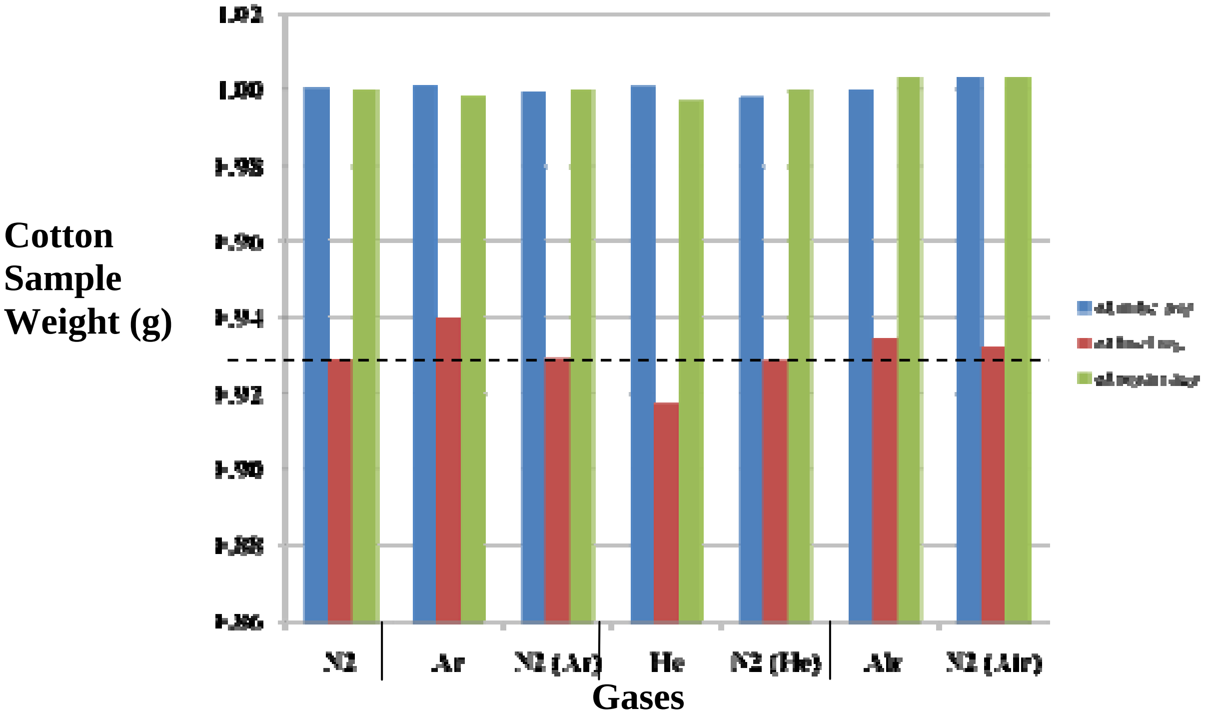

Figure 3. Drying profile of the Bm8 cottons under various gases at 105°C. Samples dried in Ar, He and Air were reconditioned and redried under N_2.

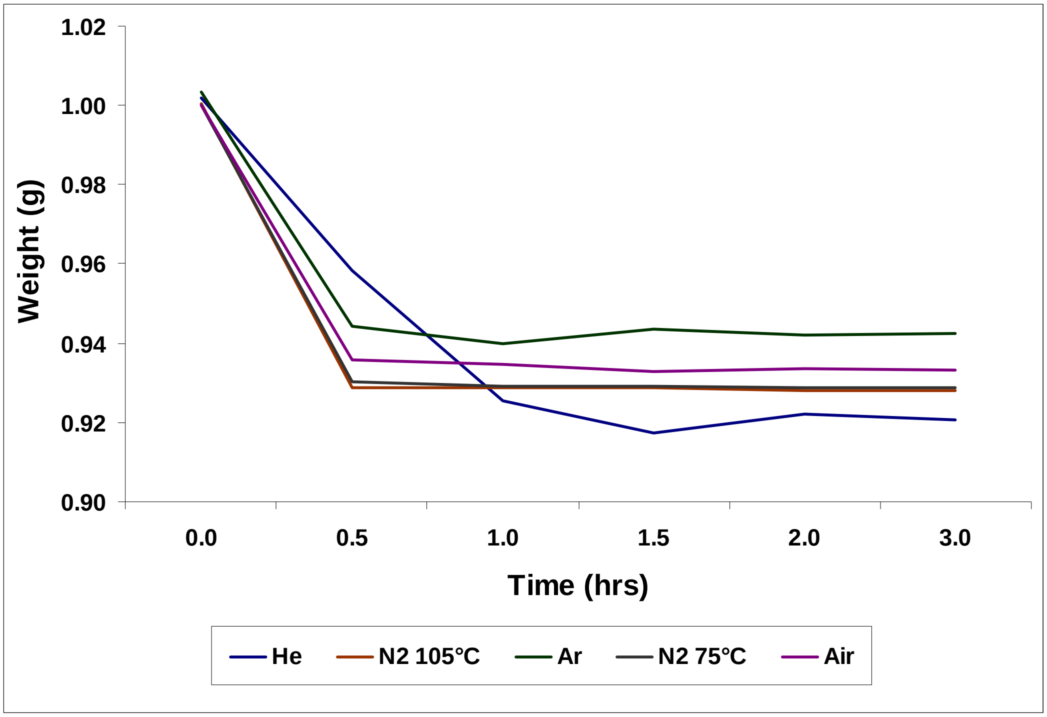

Figure 4. Weight loss of the 2001 CY cottons monitored over time at 105°C with helium (dark blue), nitrogen (brown), argon (green), and air (purple). The weight loss profile under the N_2 atmosphere at 75°C is also displayed (grey).

Drying cotton in argon

The cotton samples used in the nitrogen drying were used again in argon. After reconditioning the cotton samples, they were subjected to nitrogen and the same dry weights were found. The cottons tested were not able to be completely dried in argon over the time and temperatures tested (75°C, 105°C). Above the boiling point of water, the NIR spectrum after 1 hour shows that there is a significant amount of water (~2-3%) remaining in the cotton. During the next two hours the sample continues to lose moisture slowly. After 3 hours, the amount of retained water remains constant (~0.5%). In a 1.0g sample, that amount constitutes to 5mg or 5μL of water after 3 hours of argon flowing at 60mL/min at 105°C. At a 7% moisture level (cotton is 90% cellulose) there are roughly 2 molecules of water for every 3 glycosyl monomers of cellulose. Correspondingly at 0.5%, the ratio moves to 1:20. Under argon, a water molecule is left trapped between 20 glycosyl monomers of cellulose. Perhaps computer modeling will give us some idea of how argon is inhibiting the evaporation of water.

The affinity of cotton for argon and other compounds are documented and were later corroborated by dehydrating the cotton samples using N_2 (105°C) (Figure 3). Gases collected from unripened cotton fruit (Jacks, et al., 1993) revealed more than twice the normal atmospheric concentration of argon. Given that the cotton fruit is not a completely closed system, cotton fibrils must have an affinity for argon. The size of an argon atom is 142pm or 1.4Å. In Figure 4, the weight fluctuates around 6% with moisture no longer in the cotton sample, as if the system was approaching equilibrium.

Drying cotton in helium

Helium, unlike argon, was able to dry cotton in less than the 3 hours tested at 105°C. After 3 hours at 75°C, NIR indicated there was a little to no moisture left, far less than argon. Another note was the rate at which moisture was lost. In Figure 3, the initial weight loss measurement after 30 minutes was a lot less than that of both Ar and N_2. However, like Ar, the weight loss in He seemed to fluctuate around a value (8%). This method may not be suitable for the field but for further analyses (i.e. GC/MS) using helium may prove useful. The regain weight of helium (Figure 3) was notably less than that of the original sample, but this could be attributed to an affinity of cotton for helium (like argon). This assumption was verified by running the sample again, under N_2, as the original weights of the cotton samples were obtained.

Drying cotton in air

Prior to the measurements of the cotton samples dried in air, the odor of decomposing carbohydrates, also given off by SOD done in a gravity convection oven, was noted. Contrary to a 7.5% weight loss as observed by SOD, results from these experiments give 6.5% weight loss (Figure 3). In a separate study (Montalvo et al, 2010), cotton samples in a TGA run in air (closed system) over 24 hours revealed that cotton does steadily lose weight but at a specific point the cotton sample gains weight. However, in this study, this observation was not observed for the other samples dried in inert gases. After reconditioning, the samples had a higher observed weight than the original sample. The cotton samples were dried again in N_2 and the same dry weights (in air) were reacquired, indicating a permanent change to the cotton samples. Though not statistically significant, the small gain in weight (0.3%) suggests that cellulose has been oxidized. The percent weight loss of the cotton samples in N_2 after drying in dry air (7.06%) is similar to the percent weight loss of drying in just N_2 (7.05%).

If the cotton sample was partially oxidized, then the 6 position of glycosyl monomers would undergo oxidation giving the corresponding aldehyde. Further oxidation results in the formation of the glycosyluronic acid (Figure 4) and a gain in overall weight, but a 0.3% weight change is not easily observed by NIR. The carbonyl group is located at 2060-2150 nm in NIR, which also happens to appear in unoxidized carbohydrates, thus making monitoring this change in structure difficult. The carbon of the *C*-6 methylene group (-*C*H_2OH, 2110nm, Figure 2) also becomes difficult to detect because of the saturation in that area.

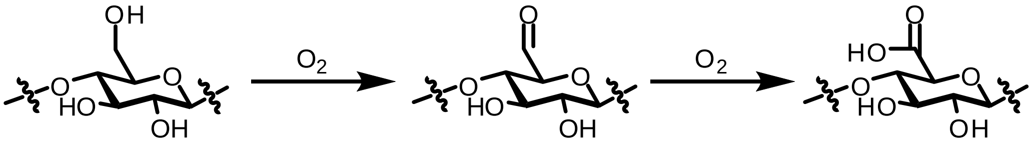

Figure 4. Possible oxidation of the glycosyl monomer of cellulose

Conclusions

Although the sample size was small, the data is repeatable and had good precision (small variance). A larger sample size was employed for a test run using nitrogen with an increased number of samples (9) was carried out and a similar mean and variance was found to that of smaller sample sizes. Future experiments will use a sample size of 12 for better statistical analysis.

Water is not the only substance that comes off of cotton when it is heated at SOD conditions. The presence of oxygen comes into consideration when the data between SOD and KFT have an average difference of 0.5 wt%. Drying in dry air gave results contrary to SOD but mimicked TGA results. Without the presence of oxygen, no oxidation of the fiber takes place. The near 100% regain for all samples and constant dry weight under N_2 (after drying in Ar and He) implies the mechanical properties are not changed. The percentage weight loss of the samples dried in dry air and then again in N_2 exhibited similar percentage weight loss incurred by just drying under N_2, but the dry weights were permanently increased. The study of repeatedly drying cotton samples in dry air will be done to mimic the effect of commercial drying of cotton fabric. If the effects are cumulative and the repeated drying results in a statistically significant change, this will mean that the chemical structure of cellulose has been altered. This change can be monitored by C^{13} NMR, whereby the acetal (95-105 ppm) and the carbonyl (of the carboxylate) peaks (150-175 ppm) of the oxidized glycosyl monomer become discernable or FT-IR where the carbonyl signal (1600-1800 cm^{-1}) is strong.

Even with the small sample sizes, the difference in drying in noble gases (argon and helium) and nitrogen are statistically different. When drying under an inert (e.g. no oxygen) atmosphere, the regain on all of the cottons was 100% and the drying weight did not change significantly. Although with the noble gases, some adsorption of the gas may have taken place. Helium was effective but the drying process took about 3 hours. Argon was not able to completely dry the cotton. N_2 was able to dry cotton effectively with results comparable to KFT. Drying cotton under N_2, even at lower temperatures than SOD (105°C), gas provides a readily available and ‘green’ alternative to KFT. This new procedure (drying cotton samples under N_2 at 75°C) is dubbed Low Temperature Distillation (LTD) to define this method exclusively from SOD. Directly injecting of the inert gas into the cotton sample, as done by the KFT instrumentation, as opposed to an open diffusion of gases, resulted in a faster time in which results could be gathered. Freeze drying cotton is another, more energy consuming, alternative, but could be used in conjunction with the LTD method. Further tests and more analyses are needed before directly injecting nitrogen gas into cotton samples for standard use, but the future prospect of such use would only need simple modifications to current oven drying systems.

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