TEXTILE TECHNOLOGY

Novel Studies of Non-Aqueous Volatiles in Lint Cotton Moisture Tests by Complementary Thermal Methods

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ABSTRACT

A preliminary study of non-aqueous volatiles (NAVs) in lint cotton moisture tests by thermal methods suggested that oxidation occurs during standard oven-drying conditions (105º to 110ºC in ambient air). The thermal methods in that study included thermogravimetric analysis-quadrupole mass spectrometry (TGA-QMS). Surprisingly, no specific volatile organics were detected. The objective of the current study was to investigate further the nature of the NAVs with the following complementary thermal methods: distillation, direct injection of the carrier gas in a closed system, and colorimetry after oven drying. Fifty g samples of cotton were distilled at 105ºC with dry air, nitrogen or argon as carrier gas. Distillates were analyzed for total organic carbon (TOC) content and the residue from the interior walls of the glassware was collected. The distillates were essentially pure water, regardless of carrier gas, supporting the earlier TGA-QMS results. However, the trace amounts of TOC and residue found were greater for samples distilled in dry air, suggesting that the NAV material is of low volatility and/or exists as fine particulate matter, not sensed by a mass spectrometer. Direct injection of the carrier gas (dry air, nitrogen, argon or helium) into sealed vials containing cotton samples heated at 105ºC produced similar findings. Within an hour of drying, samples heated in air resulted in a higher dry weight than nitrogen, suggesting oxidation of the sample material, helium and argon absorbed on the dry cotton. Colorimetry data on oven-dried cotton in ambient air at 105°C also implied oxidation.

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Preliminary studies of non-aqueous volatiles in lint cotton moisture tests by thermal methods suggested that these materials are oxidation decomposition by-products (Montalvo et al., 2010). Results by standard oven drying (ASTM D 2495) and thermogravimetric analysis-quadrupole mass spectrometry (TGA-QMS) revealed complicated side reactions – other than water removal – occur during oven drying in air at 105 to 110ºC. For example, 'waviness' was repeatedly observed in the plots of oven-dried cottons by successive weighings over 8-hr periods. The trends were observed in both gravity and mechanical convection ovens placed side-by-side. The induction time for the process to occur was in the range 3 to 5 hrs. There was short-lived accelerated gain in cotton sample weight followed by rapid weight loss.

The wavy profiles (mass versus time plots) were independently confirmed by the TGA-QMS studies by our collaborator in Germany using synthetic air as the carrier gas (Montalvo et al., 2010). Additionally, smooth rather than wavy profiles were observed in all of the mass 18 (water) ion current profiles (ion current versus time). The TGA-QMS running with nitrogen as the carrier gas did not reveal any wavy mass versus time plots. Unexpectedly, no specific organic volatiles were detected by the mass spectrophotometer in any of the studies. Either the material was of very low vapor pressure or existed as particulate matter. Other TGA runs on conditioned samples of cotton, with air and nitrogen as carrier gas, showed a significant reduction in weight loss in nitrogen compared to air. The preliminary studies (Montalvo et al., 2010) confirmed for the first time by NIR (Figure 1) that residual water remains in the cotton after oven drying in ambient air at 105ºC. The absorption peak at 1920-1940 nm corresponds to water in cotton.

A review of the literature indicates that the amount of non-aqueous volatiles (NAVs) produced in standard oven drying is in the range of 0.2 to 0.7% (Davidson and Shorter, 1930; Taylor, 1988; Morton and Hearle, 1993) of reported moisture content (wet basis). In 80 years of oven drying practices worldwide, there has been no definitive explanation of the nature of these materials (Montalvo and Von Hoven, 2008).
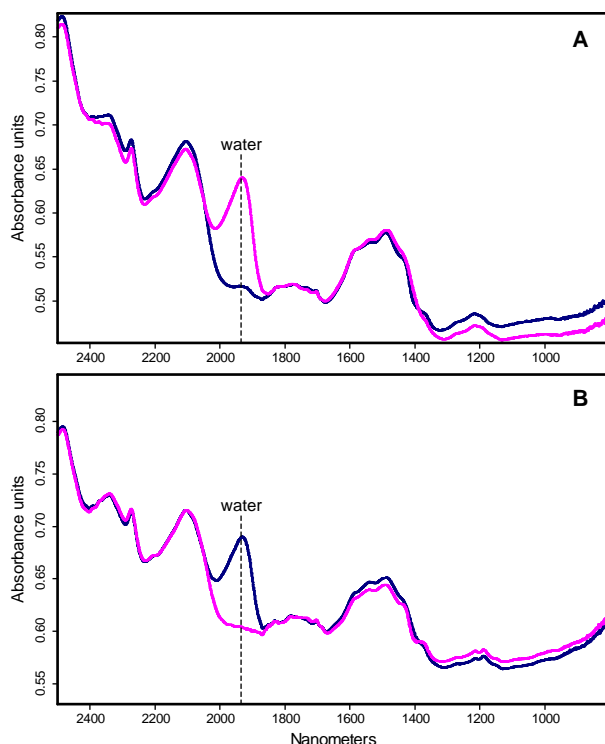
Figure 1. NIR absorption spectra of two cottons as a function of drying method: (a) control sample, conditioned (strong water peak at 1930 nm) and after drying for 24 h in a mechanical convection oven at 105ºC, and (b) AMS raw sample, conditioned and after 5 min drying in the Karl Fischer oven at 150ºC (Montalvo et al., 2010).

The objective of this paper was to produce NAVs by complementary thermal methods, explain why they occur, and provide a way to avoid the problem. Several kinds of thermal methods are included in the study: cotton distillation, direct injection of the carrier gas in a closed system (direct injection/ closed system, DI/CS), and cotton colorimetry. The research findings and laboratory conditions reported herein support the mechanisms by which NAVs in standard oven drying are created and can be avoided. Additionally, we demonstrate laboratory conditions that lead to accurate total water content determinations and explain how hysteresis in cotton is linked to the carrier gas in oven drying.

MATERIALS AND METHODS

Dry Gases. Dry air (ultra zero grade), argon and helium (ultra high purity), and nitrogen (extra dry) in compressed gas cylinders was obtained from Airgas (New Orleans, LA). The certified moisture content for each gas was < 20 ppb (weight/volume).

Lint Cottons and Conditioning. Three cottons were used in the study, two commercial and the control cotton. The control cotton had been scoured and bleached and is readily available at commercial retailers nationwide as cotton balls. The commercial cottons were obtained from the Agricultural Marketing Service (AMS). One had been mechanically cleaned (AMS clean); the other was raw (AMS raw) from a different crop year compared to AMS clean. The cottons were conditioned for at least 24 h under standard textile testing conditions (70 ± 2°F, 65 ± 2 % RH). From each laboratory sample, random tufts were selected to prepare the specimens for testing.

Thermal Methods Overview. Several thermal methods were used to provide complementary information. The methods, in the order presented, include the following: distillation, direct injection/ closed system and colorimetry. First method: a large amount of cotton was distilled in a glass apparatus at 105°C with dry air, nitrogen or argon as the carrier gas. The transparent glass wall allowed for direct visual inspection of NAVs that may deposit on the inside of the wall. This material could then be removed and weighed to give quantitative information on NAV content. Second method: dry carrier gas was directly injected into a closed sample container (direct injection/closed system) at 105°C or 75°C using air, nitrogen, argon or helium. After a specific treatment, the container was weighed, the specimen reconditioned in the same or a different gas, and reweighed. The quantitative information (weight loss or gain) provided for comparison with initial specimen weight and KFT reference method results (total water content). Third method: colorimetry, after standard oven drying at 105ºC and oven drying at 150ºC in ambient air to provide oven-treated samples for moisture content and for visible spectral studies of heat-treated fibers. Drying at 150ºC provided for accelerated heat-treatment effects on the cotton (i.e., possible generation of additional NAVs).

Distillation. Two collection flasks in series were used to collect condensed vapors, one a 5 mL pear-shaped flask held at room temperature and the other a cold trap in a acetone/dry ice bath in a Dewar flask.

A modified standard glass distillation apparatus was set up to distill 50 g of cotton in 10 g batches, Figure 2(A). A 500 mL three neck round-bottom flask (angled) with 24/40 female ground joints with two thermometer adapters, one with a screw cap and another fitted with a ground joint, on the left and right necks, respectively. The flask was fitted with a heating jacket with a variable transformer. The ground joint fitting held a 250°C mercury thermometer which ex-

tended into the middle of the flask. The middle neck had a three way adapter with a West condenser on the angled attachment. The other end of the West condenser held a bent vacuum-distilling adapter with an enlarging adapter and a 5 mL pear-shaped collection flask at room temperature. A cold trap in an acetone/dry ice bath in a Dewar flask provided the second collection flask. Nickel-plated spring-steel joint clips were used to hold the joints in place.
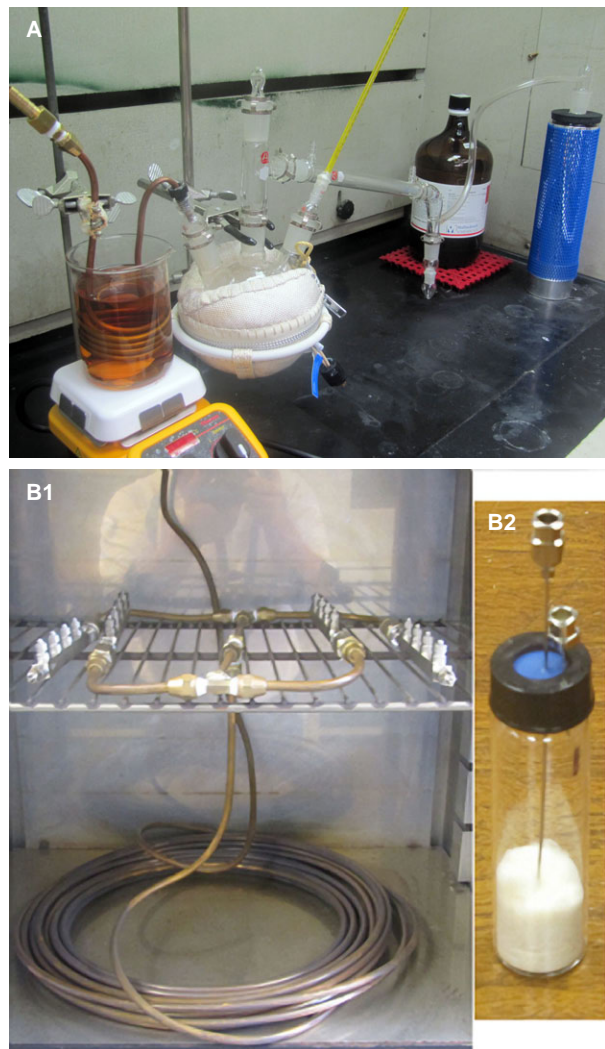

Figure 2. Experimental setups: (A) cotton distillation and (B) Direct Injection/Closed system (DI/CS). For safety purposes, all hoses have been disconnected in the distillation apparatus. The DI/CS shows the manifold assembly – image B1 – and sample vial with inserted needles – part B2.

Approximately 10' of 1/4" (O.D.) copper tubing was shaped into a coil with an inner diameter of 2.5" and a height of 2" so that the coil could fit inside a standard 600 mL beaker. Up to two-thirds of the beaker was filled with Silicone oil CR 100 (# 63148-58-3,

Sigma-Aldrich). The oil was stirred and heated to 180°C. The stirring speed was set to the point where a small vortex appeared at the surface of the oil. The stir/heating plate was raised using a laboratory stand to the point where the bent copper tubing could be inserted into the left neck of the flask holding the screw-cap thermometer adapter. The other end of the copper coil was prepped with a flare cap with a brass hose barb, so that reinforced tubing could connect to a regulator of a compressed gas cylinder.

The 50 g cotton sample was divided into five 10 g ($\pm$ 0.01 g) aliquots and each aliquot was distilled in series at 105°C for 8 h. The exit gas flow rate was adjusted to 1 L/min. The accumulated distillate across the 50 g sample was analyzed using total organic carbon (TOC) analysis by AccuLabs (Marrero, LA) and the residue, which collected on the glassware, was removed and weighed. Because of the company's requirements and to preserve our cotton samples for further analyses, the distillates collected were diluted (one to 39 mL) prior to TOC analysis. Samples for TOC analysis were prepped using a sample vial acidified by phosphoric acid to remove any CO_2 that may be present in the water extract from distillation. The TOC content was determined after the complete oxidation of all organic carbon content to CO_2. The TOC analyzer (Hewlett-Packard 5890) has a detection limit of one part per million (ppm). Values given in Table 1 are adjusted accordingly.

Direct Injection / Closed System (DI/CS). Dry Gas Manifold Assembly. The system consisted of a cylinder of compressed gas and flowmeter. Placed inside an oven were copper coil to preheat the gas, gas splitters (T-joints), gas manifolds with Luer lock fittings, glass sample vials with septa caps, and a non-coring entry and exit needle with Luer lock fittings for each vial, Figure 2(B).

A ¼" O.D. x 50' copper coil was placed on the bottom of a gravity convection oven to preheat the carrier gas. . The exit end of the coil was split four ways via 1/4" brass T fittings to which nickel-plated male Luer locks (# R-31507-45, Cole-Parmer) were attached. Each male Luer lock was connected to a gas manifold (# 618, Cadence Science, Cranston, RI) with six Luer attachments (one male and one female lock arranged at either end with four male locks along the length of the manifold). The female Luer lock of the manifold was soldered to provide additional torsional strength after the joint failed during the initial experiments. Due to space constraints in the oven, the ends were plugged, leaving 16 male Luer attachments (one for each sample vial) perpendicular to the plane of the four manifolds.

Table 1. Distillation results of 50 g of the AMS Clean and AMS Raw cottons.[z]

Cotton	Carrier Gas	Distillates				Residue		Wt loss
		Volume (mL)	TOC (ppm)[y]	TOC (mg)[x]	TOC (%)[w]	(g)[v]	(%)[u]	(%)[t]
		I	II	III	IV	V	VI	VII
AMS Clean	Air	3.4	108	0.37	< 0.001	0.28	0.56	7.4
	N₂	3.4	< 40	< 0.14	< 0.0005	0.093	0.19	7.0
	Ar	3.2	< 40	< 0.13	< 0.0005	0.055	0.11	6.5
AMS Raw	Air	3.5	108	0.38	< 0.001	0.19	0.38	7.4
	N₂	3.4	< 40	< 0.14	< 0.0005	0.086	0.17	7.0
	Ar	3.2	< 40	< 0.13	< 0.0005	0.045	0.09	6.5

[z] Distillation of five 10 g samples at 105°C for 8 h each aliquot. Results shown are cumulative. Glassware reused on successive aliquots without rinsing.

[y] Parts-per-million (ppm) of Total Organic Carbon (TOC) in the distillate.

[x] Milligrams (mg) of TOC in the volume of distillate (III = I x II x 10⁻³).

[w] % TOC in 50 g cotton samples (IV = (III x1 g/1000 mg) x 100%/50).

[v] Amount of residue (g) collected from the interior wall of the glassware after the entire 50 g has been distilled.

[u] % of residue in regards to the total weight (50 g) of the cotton sample (VI = (V x 100%)/50).

[t] total % wt loss (VII = 100% x (I + V)/50).

Procedure. Cotton samples (1.00 g) were placed in 23 mL borosilicate glass vials with PTFE caps and silicone septa. For each vial, one non-coring entry and exit needle (20 gauge, 101.6 and 25.4 mm, female Luer attachment, # 7751-11, Hamilton, Co., Reno, NV) was placed through the center of the septum and sample. The gas flow (60 mL/min/vial) was controlled by adjusting the valve on the flowmeter. The oven was set at 105°C, unless stated otherwise and samples were attached to the manifold. After one hour of drying, the samples were removed and allowed to cool to room temperature in a jelly jar with a rubber septum (3 to 4 vials/jar). The jelly jars were opened in a standard conditioning lab (21 ± 1°C, 65 ± 2 %RH) and allowed to equilibrate for 10-15 minutes. Samples were weighed and weight loss was recorded.

In vitro near-infrared spectra for moisture analysis were taken through the bottom of the vial using a fiber optic NIR probe. A Bruker MPA (Bruker-Optics, Billerica, MA) was used with OPUS (version 5.5). Resolution was set to 8 cm⁻¹ and the average of three spectra was measured per sample (32 scans/spectrum).

Colorimetry. Samples of the three cottons were dried in a forced convection oven in ambient air at two temperatures: 105°C and 150°C. Samples of each cotton (6 x 1.00 g replicate for each variety and temperature for a total of 12 sets) were placed in 40 mL weighing bottles with ground joints, and then heated at 105°C (24 h) or 150°C (8, 24, 48 h). The average difference in weight was observed and compared to moisture levels determined by Karl Fischer Titration (Montalvo et al., 2010).

The colorimeter data was generated on the Gretag Macbeth Color-Eye 7000A unit with a Specular Component Included, D65 Illuminant, 10° observer and a 25 mm sampling port. The six individual oven dried samples (from the same cotton) were combined into one 6 g sample to run in five replicates on the colorimeter with a constant pressure of 30 psi in a Hunter Lab Compression Cell. The samples were run randomly to generate color data in CIE L*a*b* space in the wavelengths from 360 to 750 nm. The ΔE* parameters were calculated using Eq. 1. The untreated (unheated) cotton for each set was used as the reference point (i.e., ΔE* = 0) for normalizing the other treated samples.

Oven-Drying Methods Related to Moisture Determinations. Moisture content was determined by standard oven drying (ASTM D 2495). All of the weight loss is attributed to water; however, the method is not specific for water in cotton (Montalvo et al., 2010). Total water content was measured by Karl Fischer Titration (KFT) of the water in cotton. After heating the fibers at 150°C with dry nitrogen as carrier gas to transport the released moisture into the titration cell, the titration is carried out with Karl Fischer reagent. This is the established reference method for total water content of lint cotton (Montalvo et al., 2010). All water, free and bound, is included in the determination.

RESULTS AND DISCUSSION

Cotton Distillation. A large amount of cotton distilled in an all-glass apparatus using dry air, nitrogen, or argon as the carrier gas produced unexpected results. Argon was introduced as a drying gas due to its relative natural abundance (2% atmospheric concentration) and a report in the literature regarding its larger concentration (~4%) in green bolls (Jacks et al., 1993).

The volume of distillates collected in the cold trap from the distilled vapors shows that dry nitrogen and dry air are effective drying agents, whereas dry argon is not (Table 1, column I). No measurable amount of material was collected (i.e., condensed) in the 5 mL pear-shaped flask in any of the runs.

The 3.4-3.5 mL of distillates collected by air and nitrogen attribute to 6.8-7.0% (based on a 1 mL = 1 g approximation) of the initial cotton weight (50 g). Furthermore, the lesser amount of distillates collected by using argon as the carrier gas (3.2 mL using same time and temperature) indicated incomplete removal of moisture from the cotton sample. NIR analysis of dried cotton from subsequent experiments verified this claim.

Total organic carbon analysis of the distillate from the two AMS cottons produced nearly identical results (Table 1, columns II, III and IV). Only the dry air produced enough TOC to be detected by the analyzer (after dilution) and is significantly more than either N_2 or Ar. Therefore, the collected distillates (column I) was considered pure water in regards to weight loss analysis. In addition, the dry air produced the most thermal residue collected from the interior walls of the glassware (column V). Given nitrogen and argon's relative inertness, it is proposed that the 20% oxygen in air is causing the cotton to decompose more readily and, thus, to release more NAVs.

The data in Table 1 support the fact that NAVs were not detected by TGA-QMS in the prior study using air or nitrogen as the carrier gas (Montalvo et al., 2010). Previous literature has isolated and characterized compounds resulting from the oxidative thermal degradation of cellulosic materials (Rosenau et al., 2010; Wakelyn et al., 2007) at conditions other than standard oven drying. Rosenau et al. (2010) found these compounds to be in concentrations of ppb to ppm.

Total weight loss by distillation (Table 1, column VII) was calculated by adding the amount distilled (~1 mL = 1 g, column I) to the amount of residue collected from the sides of the glassware used during the distillation (column V). This particular residue, or NAVs, appears to be the result of thermal oxidative decomposition of cotton. The material is low in volatility and/or exists as fine particulate matter, not sensed by a mass spectrometer. The total weight loss for the two cotton varieties dried in air is 7.4%, while nitrogen and argon are 7.0% and 6.5%, respectively.

Direct Injection/Closed System (DI/CS). This method of drying closely resembles the KFT and thermogravimetric analysis (TGA) procedures, where the sample is heated in a closed system and a carrier gas is used to remove any volatile components from the fiber matrix. In this paper, the DI/CS approach is used to insert the preheated carrier gas directly into the center or the bottom of the cotton sample and allow the principle of diffusion to remove moisture from the fibers. The placement of the inlet carrier gas needle ensures even heating of the sample as opposed to SOD, where the sample is heated from the outside (Table 2).

Table 2. Comparison of experimental procedures for Standard Oven Drying (SOD, moisture content) and Karl Fischer Titration (KFT, total water content).

Standard Oven Drying[z]	Karl Fischer Titration
Open system	Closed system
Ambient air (N_2+O_2) convection	Direct N_2 injection
105°C for 24 hours	150°C for 5 minutes
Carrier gas is ambient air[y]	Carrier gas < 20 ppb water
1 g sample	0.1 to 0.2 g sample

[z] According to ASTM 2495.

[y] Moisture content of ambient (room) air entering the oven is the amount associated with 65 %RH and 21°C (~10 g H_2O per kilogram of air).

This modified setup in the oven allows for the study of the effect of gases (type, flow rate, and temperature), where the oven acts solely as a heating source and not the drying agent, as in SOD. Using a set of valves and tubing, we connected four different compressed gas cylinders (air, nitrogen, argon, and helium) to allow for switching of gases without disconnecting the tubing.

There has been some discussion about small fibers or fragments being lost in contribution to the bias in the SOD method (Montalvo et al., 2010). The closed system used has only a small exit < 0.5 mm, making the escape of 5 mg or any significant amount of cotton difficult over the time period measured.

Ideally, if the same sample weights of the same cotton are dried using different methods (temperature, flow rate, gas, etc.), they would eventually have the same dry weight (Figure 3). If the samples exhibit any hysteresis, the dry weight and/or reconditioned weight might be altered. Using a dry carrier gas (%RH = 0), the free moisture dissipates (fast), leaving the bound moisture to diffuse through the cotton fiber (slow). The rate at which the free moisture dissipates is dependent on the surface area and chemistry of the cotton, the carrier gas' moisture saturation level and its diffusion rate throughout the cotton sample. The rate at which the bound water diffuses within and out of the fiber would depend on the characteristics of the fiber itself. Besides air, none of the other gases tested (nitrogen, argon and helium) are chemically active with cellulose. Any difference in the dry weights could be explained by the inert gases' physical interactions with the cotton fiber (adsorption, absorption, etc).
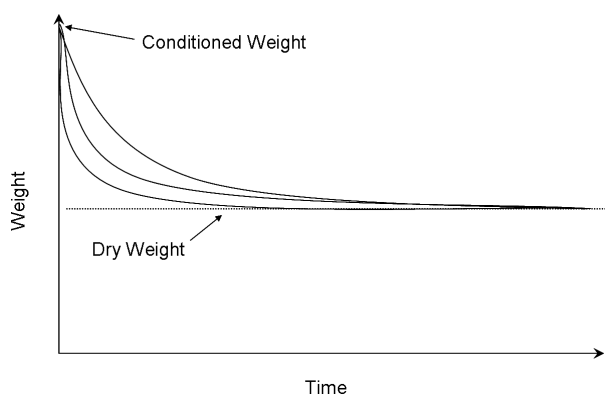

Figure 3. Ideal plot of moisture loss from the same cotton sample. Drying in different gases and temperatures resulting in different rate constants, but yield the same dry weight in the absence of side reactions (e.g. oxidation, absorption of the gas on the cotton fiber.)

Drying the AMS clean cotton under a flow of argon or helium resulted in statistically different results (two-tail t-test, $p < 0.05$, Figure 4). In addition, *in vitro* NIR indicated that after three hours, argon did not dry out the cotton; 0.5 to 1.0% moisture (based on the reduction of the peak height at 1930 nm) was retained even at 105°C. Moisture was removed by the helium, but took significantly longer (> 1.5 h) than air (which showed no absorption peak at 1930 nm, compared to Figure (1a)) and nitrogen, both of which took less than an hour at 105°C. The mass of the dry cotton after drying by helium and argon is not definitive due to the adsorption of the gases by the cotton fiber, which affected the buoyancy of the fiber. The same samples of AMS clean cotton that were dried under nitrogen at 105°C and reconditioned at standard textile testing conditions were also dried to the same weight within an hour in nitrogen at 75°C. Both dry weights corresponded to the moisture content indicated by KFT of the AMS Clean cotton (Figure 5).
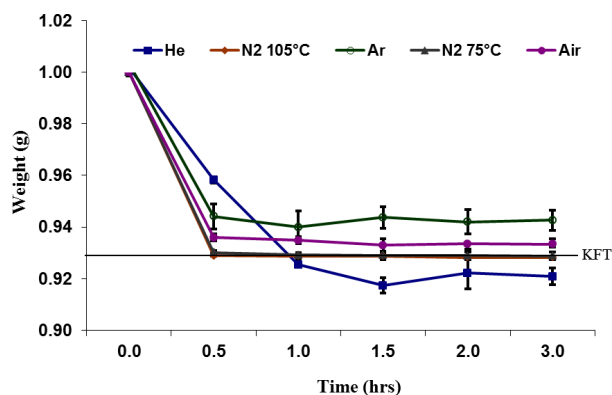

Figure 4. Experimental plot of weight loss of the AMS clean cotton. Temperature (105°C) and flow rate are kept constant (8 replicates/sample). Dry weight of 1.00 g AMS clean as determined by KFT.
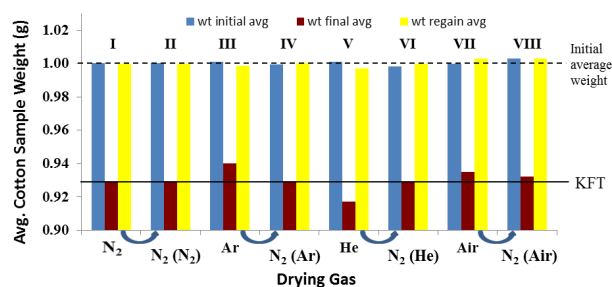

Figure 5. Initial/conditioned (70°C, 65 % RH) (blue), dried (red), and reconditioned (green) average weights of AMS clean cotton samples using the four gases N_2, Ar, He, and air (columns I, II, IV, VI, respectively). Reconditioned samples dried under Ar, He, and air were redried under N_2 (columns III, V, VII, respectively) using same conditions (105°C at 60 mL/min). Dry weight of 1.00 g AMS clean as determined by KFT.

The samples dried under nitrogen returned to their original reconditioned weight after 24 h (Figure 5, column I and II). The resulting same average dry and reconditioned weight indicates the physical and chemical characteristics are mostly, if not all, of the original sample, showing no hysteresis. Also, by lowering the temperature from 105°C to 75°C, not only was the amount of energy used to dry the cotton reduced by more than 35%, the amount of NAVs produced by thermal degradation is greatly reduced compared to SOD methods.

After establishing the lack of hysteresis of the cotton samples dried under nitrogen, samples of cotton dried by the other gases (argon, helium and air) were reconditioned (21 ± 1°C, 65 ± 2 %RH, 24 to 48 h), dried under N_2 at 105°C, and reconditioned again for 24 h (Figure 5). Argon is known for its inertness and is frequently used in the preservation and storage of chemically reactive materials. Differences of the dry and reconditioned weights (argon, column III) of the AMS Clean samples compared to those dried under other gases were due to the adsorption of argon to the cotton fiber, making the fiber appear to be 'heavy.' The lower dry weight of the reconditioned samples maybe due to the slow resorption of water caused by Ar present within the fiber. Redrying the Ar dried cotton samples (Figure 5, column IV) using nitrogen, displaced the residual argon and resulted in an identical dry and reconditioned weight compared to cotton samples initially dried under nitrogen.

The AMS Clean samples dried in helium appeared to have lost more weight than the rest of the samples analyzed under the other gases, even after reconditioning (Figure 5, column V). Like the cotton samples dried under argon, AMS Clean also has an affinity to helium (lower reconditioned weight), but is displaced with nitrogen (column VI) as the samples return to an identical dry and reconditioned weight compared to cotton samples initially dried under nitrogen.

The cotton samples that were initially dried in air (column VII), showed a higher dry weight. This observation is in contrast to samples dried by other oven drying methods, which have a *lower* dry weight than indicated by KFT (Montalvo et al., 2010). The combination of the lower flow rate and the matrix effect of the cotton sample could lead to the entrapment of NAVs and fibrils created by oxidation that may be lost by the open system of the oven drying methods. After reconditioning and re-drying under nitrogen (column VIII), the average weights were still higher than the respective average weights of those initially dried under nitrogen, argon, and helium and re-dried under nitrogen. The higher weight of the air-dried cotton samples indicates a chemical and/or physical change of the cotton samples.

Relating NAVs to Cotton Color. The most obvious change in the oxidation of cellulose (and most organic material) is the browning or charring of the material. The discoloration of the material during heating is due to the decomposition products (Rosenau et al., 2010). However, a modicum of color change may not be noticeable to the human eye. Cotton is usually white or some variation thereof, making the observation of any small discoloration with a spectrometer in the visible wavelengths easily within reach. The goal of cotton colorimetry studies in this paper was to determine if a relationship exists between NAVs content in oven drying and changes in color.

The difference in color was quantified using the CIE color space system (Keuhni, 1983). The CIE 1976 L* a* b* (or CIELAB) was developed to quantify color using the L* (lightness of a color), a* (red: +, green: -), and b* (yellow: +, blue: -) coordinates. The difference between two colors ($\Delta E_{xy}*$) can be quantified [Eq. 1]. In perspective, $\Delta E*$ values of 1.0 or higher are distinguishable to the human eye upon side-by-side comparison to a reference sample.

$$\Delta E_{xy}* = [(L_x*-L_y*)^2 + (a_x*-a_y*)^2 + (b_x*-b_y*)^2]^{1/2} \quad [1]$$

Using the KFT water content (Table 3) expressed as wt %, the net weight loss differences between oven drying and the KFT values is NAV content (Figure 6). Further evidence of oxidative degradation of cotton and presence of NAVs were observed in the colorimetry data gathered (Figures 7-9). When the temperature in the convection oven was raised to 150°C, the range of the NAV wt% increased. Eight hours of drying at 150°C was more than enough to produce more than three times the amount of NAVs compared to the SOD method.

Table 3. Average weight loss (wt%) of laboratory oven-drying methods and Karl Fischer titration methods.

Conditions	Control	AMS Clean	AMS Raw
105°C, 24 h[z]	7.36	7.05	7.43
150°C, 8 h[z]	8.38	8.08	8.39
150°C, 24 h[z]	8.02	8.11	8.31
150°C, 48 h[z]	8.16	8.63	9.06
KFT[y]	6.90	6.59	7.05

[z] **Drying in mechanical convection oven, carrier gas is the ambient air, 1.00 g sample size in 40 mL weighing bottles.**

[y] **KFT: 150°C oven temperature, 5 min, drying carrier gas N_2, 0.1 g sample size, titrated water expressed as wt %.**
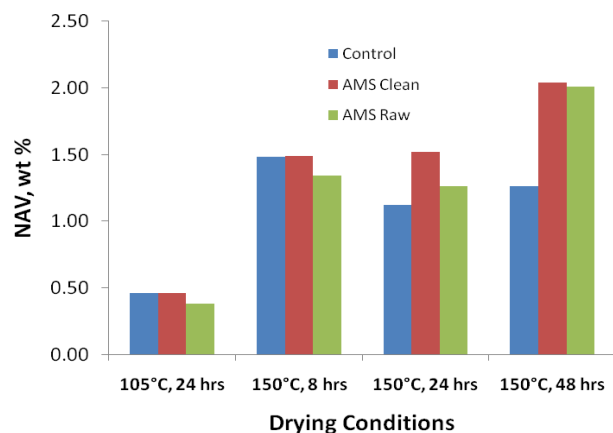
Figure 6. Net amount of non-aqueous volatiles (NAVs, wt %) for the three cottons after correction for moisture content. % NAV = (wt % loss by oven drying – KFT moisture content). See Table 3 for source data.
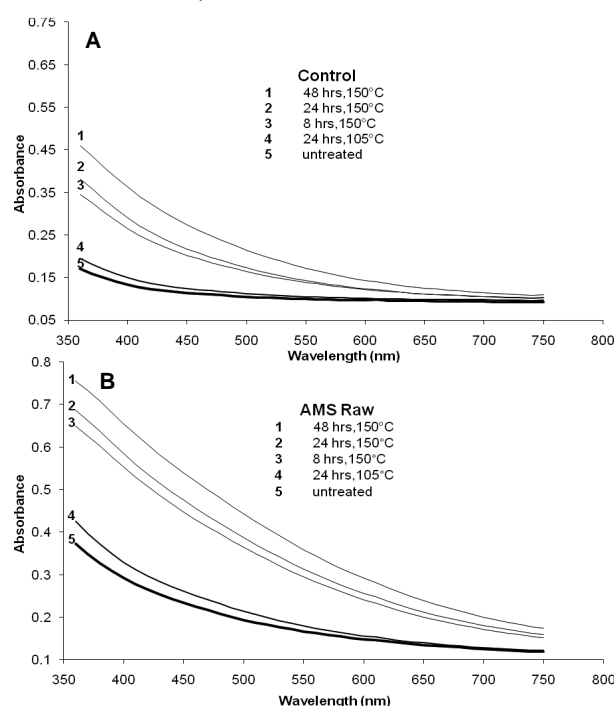

Figure 7. Absorbance in the visible spectrum: (a) control samples and (b) AMS Raw sample.

Figure 8. Relationship between ΔE* and NAVs for the: (a) control cotton, (b) AMS Clean, and (c) AMS Raw. The untreated (not heated) sample was used as the reference point. The y-axis values are the difference between weight loss by oven drying and the amount of moisture as determined by KFT.

Figure 9. Using the ΔE* raw data (not normalized) to observe changes in color of the AMS raw samples. The y-axis values are the difference between weight loss by oven drying and the amount of moisture as determined by KFT.

We propose here that heating cotton in air causes two competing events, other than loss of moisture: the loss of NAVs and the oxidation of cellulose. The former causes additional weight loss, while the latter causes weight gain. During oven drying, these three processes are present, just at different rates. Initially, not much of the cotton is being oxidized, while most of the heat is transferred to the removal of moisture and NAVs [Eq. 2a] leading to weight loss. As the drying process continues, little to no more water is present to transfer heat, oxidation of cellulose and cellulosic components of cotton begin to oxidize at an exponential rate, as seen in Figures 7 and 8, resulting in weight gain [Eq. 2b].
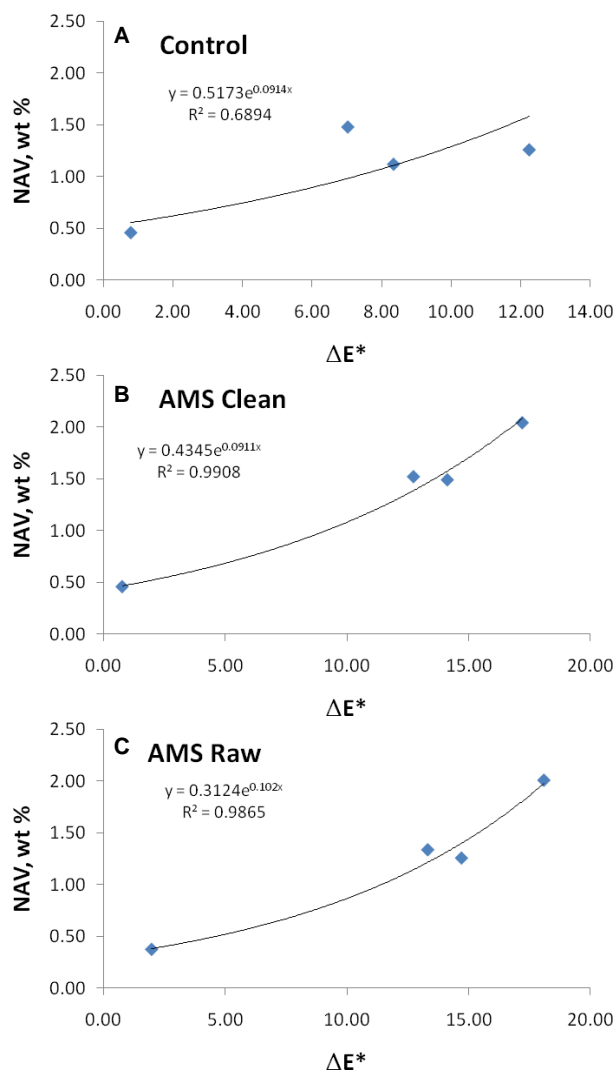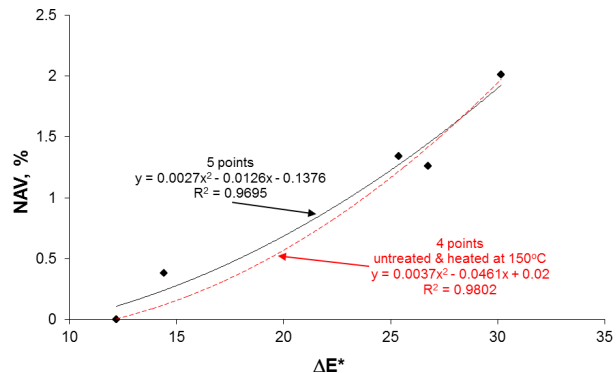
oxidation of cellulose < loss of NAVs +
moisture loss → weight loss   [2a]

oxidation of cellulose > loss of NAVs +
moisture loss → weight gain   [2b]

The weights after 24 h at 150°C changed significantly for the AMS cottons (ΔNAV wt% > 0.5%). The AMS clean and raw cottons were not chemically treated and may have continued to lose more cotton wax, which has a melting point at 72°C, contributing to the NAVs [Eq. 2a].

Changes in cotton color during oven drying of the control and AMS raw samples were observed through the absorption of the visible spectrum, 400-750 nm (Figure 7). The "yellowing" of the samples were observed below 550 nm. At SOD conditions, the increase in absorption at 400 nm (A_{400}, 14% for both samples) and color change are notable (Figure 8, ΔE* = 0.79 and 1.89, respectively). In stark contrast, oven drying in air for just 8 h at 150°C, where NAVs have greatly increased, A_{400} increased for both the control (over 103%) and the AMS raw samples (74%).

The L*, a*, and b* coordinates (Table 4) data gathered from the colorimeter of the untreated cottons were set as a reference point to normalize the data and provide a direct comparison (ΔE*) to the oven dried cottons in their respective sets using Eq. 1. For example, the color change, ΔE*, of the AMS raw cotton dried at 150°C for 24 h relative to the untreated cotton is 14.716. By comparing the ΔE* to the amount of NAVs produced (Table 3 oven data minus water content by KFT; Figure 8), there is a clear positive trend. The most notable exception is the control samples (Figure 8(a)), where there is a large decrease in NAVs while there is an increase in the ΔE* parameter. The large decrease in the NAV wt%, possibly due to the oxidation of the cellulosic portion of the cotton fibers, resulted in a poor correlation between the NAV wt% and ΔE*. The NAV wt% and ΔE* correlation of the AMS raw and clean cotton samples, Figure 8(b and c), respectively, have better R^2 values. The better correlation might be due the presence of NAVs (i.e., waxes, pectins, etc.) resulting in slower oxidation of the untreated cotton.

As further proof of oxidation, Figure 9, the values of ΔE* based on the 'white tile' standard between the dried and conditioned (unheated) sample can be observed. The five point fitted line represents the transition from no oxidation (untreated) to known oxidation (discoloration); R^2 is 0.9695. The four point line (only untreated and heated at 150°C) R^2 value is 0.9802. Inclusion of the SOD data point (NAV = 0.38%) retained the high R^2 of the relationship between NAV and ΔE*. This provides additional evidence that the NAVs produced under SOD conditions most probably originated from oxidation rather than being synthesized *in vivo* during the development of the cotton fiber.

Table 4. Averaged CIE L*a*b* data generated by Gretag Macbeth Color-Eye 7000A for the cotton samples used in Table 4.[z]

	Conditions	L*	a*	b*	ΔE*[y]
Control	**Untreated**	91.390	-0.092	1.914	0.000
	105°C/24 h	90.916	-0.088	2.542	0.787
	150°C/8 h	88.080	0.448	8.092	7.030
	150°C/24 h	87.698	0.546	9.372	8.346
	150°C/48 h	85.366	1.288	12.488	12.248
AMS Clean	**Untreated**	85.040	1.086	9.604	0.000
	105°C/24 h	84.500	1.212	10.156	0.782
	150°C/8 h	74.080	4.390	17.884	14.128
	150°C/24 h	75.992	4.216	18.006	12.738
	150°C/48 h	71.638	5.552	19.416	17.200
AMS Raw	**Untreated**	85.852	0.670	8.290	0.000
	105°C/24 h	84.848	1.090	9.948	1.983
	150°C/8 h	76.356	3.868	17.080	13.329
	150°C/24 h	75.136	4.170	17.750	14.716
	150°C/48 h	72.080	5.166	19.144	18.102

CIE: (*France*) international commission on illumination

[z] The six one gram replicates from laboratory oven drying (Table 4) were combined to form a six gram sample.

[y] The untreated samples were set as the reference point (i.e., ΔE* = 0) to which all other treated samples were respectively normalized.

CONCLUSIONS

The difference between KFT and SOD data can be explained by the NAVs collected in the distillation experiments. These results suggest that during the process of SOD, the major source of the bias of drying cotton in open air (especially forced air convection) is weight loss from oxidation by-products. These materials are of low volatility and may also exist as particulate matter created chemically and mechanically as a result of oxidation of dry cellulosic fibers. With the DI/CS drying method, a plausible explanation for the difference in results between open and closed systems is that the oxidation of cotton components in the closed system causes the slight weight gain. Furthermore, the oxidation of the dry cotton fibers in the dry air may lead to brittleness and breakage due to the convection within a typical SOD oven. The closed system may prevent this loss due to the small opening in the exit needle (~0.5 mm).

The oxidation of cotton is further evidenced by the change in color with respect to the untreated cotton samples. The changes in color for the samples dried by the SOD method were not noticeable to the eye, but were noted by the increase in ΔE^* and absorbance (e.g < 550 nm). Also, our studies demonstrate that at 75°C and under N_2, a 1 g sample of cotton can be completely dried (no residual water bias) without oxidation (no NAVs bias) within one hour and with good precision. Work is ongoing to test additional cottons by this method, called Low Temperature Dstillation (LTD). Low temperature distillation could provide a low cost, robust and facile transition to a more accurate reference method of the determination of total water content in cotton.

ACKNOWLEDGEMENT

DISCLAIMER

Any mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

REFERENCES

American Society for Testing and Materials. 2001. ASTM D 2495 Standard Test Method for Moisture in Cotton by Oven-Drying. ASTM, West Conshohocken, PA.

Davidson, G.F., and S.A. Shorter. 1930. The dry weight of cotton. J. Text. Inst. 21: T165-T178.

Jacks, T.J., T.P. Hensarling, M.G. Legendre, and S.M. Buco. 1993. Permanent gases inside healthy and microbially infected cotton fruit during development. Biochem. Biophys. Res. Comm. 191: 1284-1287.

Keuhni, R.G. 1983. Color: essence and logic. Van Nostrand Reinhold Company. New York, NY.

Montalvo, J.G., and T.M. Von Hoven. 2008. Review of standard test methods for moisture in lint cotton. J. Cotton Sci. 12: 33-47.

Montalvo, J.G. T.M. Von Hoven, and S.Y. Cheuk. 2010. Preliminary studies of non-aqueous volatiles in lint cotton moisture test by thermal methods. Tex. Res. J. 80: 1360-1376.

Morton, W., and J.W. Hearle. 1993. "Physical properties of textile fibers." 3 Ed. The Textile Institute, England.

Rosenau, T., K. Krainz, H.U. Suess, T. Dietz, K. Mereiter, A. French, and A. Potthast. 2010. Mechanistic studies on aging and chromophore formation in cellulosics. ACS National Meeting & Exposition. 21-25 Mar. 2010. San Francisco, CA. [Online]. Available at http://www.softconference.com/ACSchem/sessionDetail.asp?SID=210102.

Taylor, R.A. 1988. Predicting the moisture content of materials containing oven sensitive volatiles by NIRS, in "Analytical Applications of Spectroscopy." Creaser, C.S. and A.M.C. Davies (Eds.). The Royal Society of Chemistry, London. p. 158-163.

Wakelyn, P.J., J.V. Edwards, N.R. Bertoniere, B.A. Triplett, L. Hunter, A.D. French, M.-A. Rousselle, D.D. McAlister, D.P. Thibodeaux, W.R. Goynes, and G.R. Gamble. 2007. Chemical Properties of Cotton: Pyrolysis or Thermal Degradation, in "Cotton Fiber Chemistry and Technology." Lewin, M. (Ed.). CRC Press, Boca Raton, FL. p. 94-98.