INFLUENCE OF DEFOLIATION DATE AND GIN-DRYING TEMPERATURE ON OVEN MOISTURE AND KFT WATER WITHIN COTTON CULTIVARS J. Montalvo T. Von Hoven Southern Regional Research Center New Orleans, LA R. Byler USDA-ARS Cotton Ginning Research Unit Stoneville, MS

<u>Abstract</u>

Water content by Karl Fischer Titration was compared to moisture content by standard oven-drying in the lint cotton from two cultivars. The cultivars had been defoliated at different times. Early defoliation cotton was ginned only at low gin-drying temperature. Late defoliation fiber was separated into two lots; one lot was ginned at a low gin-drying temperature and the other at high gin-drying temperature. Also, some of the ginned lint was further processed to produce mechanically cleaned, and scoured and bleached fibers. The samples were grouped by cultivar to examine the results at moisture equilibrium. *Within* cultivar moisture content range of the averaged values from the various treatments for the two cultivars was (%): raw gin lab, 1.70 and 1.77; raw SRRC, 0.49 and 0.62; and mechanically cleaned, 0.05 and 0.56. *Within* cultivar water content range of the averaged values from the various treatments for the cultivars was (%): raw SRRC, 0.10 and 0.13; mechanically cleaned, 0.07 and 0.13; and scoured and bleached, 0.07 and 0.08. The water content ranges are small compared to that by moisture content. For the scoured and bleached fiber, the averaged water contents from the various defoliation and gin-drying treatments were not significantly different (p < 0.05) *within* cultivars.

Introduction

Moisture measurements in cotton can be expressed as either moisture content or water content. Moisture content (ASTM D2495, 2007) refers to the weight loss by standard oven-drying (SOD) and is expressed as a percentage of the moist material; all weight loss is attributed to moisture. The method is nonspecific for water, some water remains in the cotton sample, and sample oxidation occurs (Montalvo et al., 2010; Rodgers et al., 2010; Cheuk et al., 2011). Water content, as measured by Karl Fischer Titration (KFT) is highly selective (specific) to the total amount of water, both free and bound, in lint cotton (Montalvo, Von Hoven, and Cheuk, 2011). In practice, the specimen tested is placed in a sealed glass container and heated in a small oven for five min at 150°C. Moisture released is transported by dry nitrogen carrier gas into the KFT cell where it is titrated with Karl Fischer reagent; iodine in the reagent reacts quantitatively with water. The end point is determined electrometrically with platinum electrodes.

Mayfield et al. (2011) stated that "Moisture is the most important single factor affecting fiber quality during ginning. The dependence of moisture content by standard oven-drying on gin-drying treatment has been reported (Hart et al., 1955; Hessler and Workman, 1959). The gin drying results showed that as gin-drying temperature increased, the moisture content of the lint cotton immediately following ginning decreased. However, when the ginned samples were brought to moisture equilibrium in a laboratory and then analyzed for moisture content, the data was found to be influenced by the drying history of the samples, the cultivar, and the extent of maturity.

No studies have been reported on the dependence of water content by KFT on defoliation time or gin-drying treatment. The influence of the impurities in lint cotton on moisture content has not been reported. Since the oven moisture content method is nonspecific for water in cotton, the impurities in the samples may confound interpretation of results.

This is a preliminary report of the influence of defoliation time and gin-drying temperature on oven moisture and KFT water content of two cultivars. Additionally, some of each of the lint cottons was further processed to produce mechanically cleaned, and scoured and bleached fiber.

Fundamentals

Consider a mass balance of the water content method by Karl Fischer Titration (W_{KFT}) and the moisture method by standard oven-drying (M_{SOD} ; e.g., ASTM D2495). Mass balance units are expressed in terms of percent relative to the moist cotton samples conditioned to moisture equilibrium at standard textile testing conditions (65% RH and 70°F).

A mass balance of the KFT analytical process in this context means that the mass of water, isolated from the cotton matrix by heating and sensed by the method's sensor, is equal to that present in the sample. All of the water in the sample in KFT is converted to water vapor (W_{vapor}) during heating and therefore, available for titration with the Karl Fischer reagent. To confirm that all of the water in the sample is removed by drying in the small oven attached to the Karl Fischer instrumentation, the following experiment was performed. Immediately after analysis of the sample by KFT the same sample vial was reanalyzed by KFT; no additional KFT reagent was consumed and no water peak was found by NIR at 1930 nm (Montalvo et al., 2010; Montalvo, Von Hoven, and Cheuk, 2011). Thus:

WATER MASS IN sample = WATER MASS OUT sample (1)

$$W_{\text{KFT}} = W_{\text{vapor}}$$
 (2)

The KFT oven is set at 150°C, dry nitrogen is the purge gas, and selectivity for water is high.

In the standard oven-drying method, the actual amount of water in the sample that is sensed as loss in weight (W_{vapor} - $W_{residual}$), and the weight loss (M_{SOD}) is expressed as:

$$M_{\rm SOD} = (W_{\rm vapor} - W_{\rm residual}) + SRN \tag{3}$$

Note that W_{residual} is the small mass of water that remains in the sample during SOD and *SRN* is the mass of the net amount of side reactions due to oxidation and particulate removal from the fiber matrix. (The SOD oven is set at 105°C, conditioned air at 70°F and 65% relative humidity passes through the oven, and the sensor is nonspecific for water.)

The expected bias in the SOD approach is:

$$M_{\rm bias} = M_{\rm SOD} - W_{\rm KFT} \tag{4}$$

Inserting equations 2 and 3 into equation 4:

$$M_{\rm bias} = -W_{\rm residual} + SRN \tag{5}$$

The bias due to W_{residual} is always negative; weight loss is reduced. In regards to the bias contribution from *SRN*, some mass may be created or loss in chemical oxidation in heated air and mass is loss in particulate removal. Thus, the SRN bias may be negative or positive and therefore, $M_{\text{SOD}} < = > W_{\text{KFT}}$.

Materials and Methods

Cottons and Gin-Drying Treatments

Two cultivars (Table 1) were obtained for the study. The cottons were grown in Stoneville, MS and were from crop year 2009. After harvesting, bags of seed cottons were collected for ginning in the microgin at the Stoneville ARS research facility. Two bags of late defoliated and one bag of early defoliated cotton were taken for each cultivar for a total of six bags (Table 1).

Standard gin processing was used: dryer 1, cylinder cleaner (CC), stick machine, (SM), dryer 2, cylinder cleaner (CC), extractor-feeder/gin stand (EFGS), and one lint cleaner. The two possible dryer settings were 32.2°C (90°F, low) and 82.2°C (180°F, high). Each bag was ginned separately (Table 1).

Cultivar code	Gin ID	Defoliation	Dryer heat ^a				
STV4554B2RF	1	Late	Low				
	2	Early	Low				
	8	Late	High				
STV4427B2RF	3	Late	Low				
	4	Early	Low				
	9	Late	High				
^a Low dryer heat at 90°F and high dryer heat at 180°F.							

Table 1. Ginned samples for this study.

Moisture Content at the Gin Lab

During the ginning of the cottons, three cans of lint (from each bag ginned) were taken after the gin stand for moisture content determination. The containers were immediately closed with a tightly fitting lid and transported to the ginning laboratory for analysis by standard oven drying (ASTM D2495, 2007). Since the intent was to determine the moisture content of the raw material under prevailing conditions at the gin, the specimens were not conditioned before testing. Mean and standard deviations were computed for all bags or cottons.

Cleaning the Lint Samples

There were three levels of cleaning in this study: none (raw), mechanically cleaned, and scoured and bleached.

Mechanical Cleaning

One hundred gram samples of cotton fibers were mechanically cleaned using the Shirley Analyzer to provide for moisture content and water content analyses of this fiber matrix. Two passes were made through the analyzer.

Scoured and Bleached

Three grams of each of the six raw cottons were scoured and bleached to provide for analysis of this fiber matrix for water content. Moisture content determinations on this fiber matrix were not performed and would have required a much larger mass of cotton, with perhaps concomitant changes in the degree of cleaning, which would have adversely affected results.

The raw cottons were placed in separate cotton cloth bags and the bags closed by sewing with cotton thread. The bags were placed in a Werner Mathis Lab Jumbo Jet (JFO 15606) machine using the recommended solutions for scouring and bleaching. After the final rinse, the chamber was again filled with de-ionized water, the pH adjusted to 7.0 with acetic acid and drained. The small sacks of cotton were removed from the chamber and allowed to dry at room temperature. The scoured and bleached fibers were removed from the cloth bags, placed in paper bags, and stored in the conditioning room.

Oven Moisture and KFT Water Contents at Moisture Equilibrium

There were three levels of conditioning in this study: no conditioning (samples taken at the gin), conditioning in a room, and conditioning in a glove box in the room.

Conditioning Systems

Following standard textile testing conditions, a conditioning room set to 70°F and 65% relative humidity was used. Cotton samples were conditioned to moisture equilibrium for 24 hrs before measuring moisture content (1.5 g specimens) and water content (0.1 g specimens). A glove box was used within the conditioned lab to improve humidity control in acclimatizing the 0.1 g samples for measuring water content by KFT. Humidity in the glove box was held constant at 65% RH by the use of a saturated aqueous sodium nitrite solution (Wink and Sears, 1950). Lack of space in the glove box prevented conditioning of the larger oven moisture samples. The glove box also contained a fan and a balance.

Moisture Content by Standard Oven Drying

Following the standard conditioning period to moisture equilibrium in the conditioned room, moisture content was determined by standard oven drying (ASTM D 2495, 2007 with specific changes in the procedure as noted below to allow for 1.5 g samples). Oven drying was carried out using the Yamato DKN 600 mechanical convection oven.

Approximately 1.50 ± 0.01 gram samples (five replicates/cotton) were weighed using gloved hands. Glass caps and weighing bottles were also conditioned and were weighed to four decimal places. The conditioned samples were placed in the bottles, reweighed prior to oven treatment, and placed in the 105°C oven for 24 hours. Following the oven heating, the bottles were capped while in the oven, placed in a desiccator and allowed to cool. The desiccators were then moved into the conditioned lab; the samples removed from the desiccators to re-acclimate for 30 minutes and were reweighed. Mean oven moisture content (%) and standard deviation were calculated from the weight loss data after correction for the blank.

Water Content by Karl Fischer Titration

Following the standard conditioning period to moisture equilibrium in the glove box as noted above, water content was determined by Karl Fischer Titration, a procedure specific for water in cotton (Montalvo, Von Hoven, and Cheuk, 2011; Cheuk et al., 2011). The Karl Fischer apparatus consists of a fully automated Metrohm 774 oven sample processor oven held at 150°C, with a 35 glass vial carousel, an 800 Dosino with an electronic burette, an 801 stirrer, an 803 Ti stand for the titration cell with platinum electrode, and the Tiamo 1.2 titration software.

Note that the Karl Fischer samples were conditioned, weighed, placed in vials, and capped while in the glove box. Using gloved hands, 0.1000 ± 0.0003 g samples (six replicates/sample) were weighed to four decimal places, placed in KFT glass vials and immediately crimped with septum caps. To maintain the conditioned environment, the sealed vials were placed in acclimated Mason jars where they remained until just prior to being placed on the KFT carousel. Hydranal® composite 5K was used as the titration reagent and Hydranal® medium K was the solvent in the titration cell. Mean water content (%) and standard deviation were calculated from the amount of reagent consumed after correction for the blank.

Results and Discussion

Hypothesis Tested

A hypothesis that the different genetic backgrounds of the two cultivars, the range of micronaire and maturity levels, and two gin-drying temperatures (Table 1), would not affect KFT water content of cleaned samples *within* cultivars was developed for statistical test at p < 0.05. (Statistical significance tests follow the section below on non-statistical comparative analysis.)

Non-statistical Comparative Analysis

Mean moisture and water contents within cultivars are listed in Table 2. The results depended on the method of analysis (SOD or KFT) and the extent of fiber cleaning: raw (none), mechanically cleaned, or scoured and bleached. The grand means for all 6 cottons is depicted in Figure 1. The grand means show the moisture content of the raw fibers taken after the gin stand was only 4.97% compared to 7.58% and 7.43%, respectively, for the raw SRRC and mechanically cleaned set. In contrast, the water content grand means was (%): raw SRRC, 7.87; mechanically cleaned, 7.74; and scoured and bleached, 8.08. Table 2 also shows the range of moisture and water content results of all cotton treatments *within* and *between* cultivars. The range of oven moisture averaged values *between* cultivars (Table 2) was (%): raw Gin Lab, 0.12; raw SRRC, 0.12; and mechanically cleaned, 0.02; and scoured and bleached, 0.07.

		Moisture Content by Standard Oven		Water Content by Karl Fischer Titration					
			Drying						
		Raw	Raw		Raw				
Cultivar	Gin ID	Gin Lab	SRRC	Mech Cl	SRRC	Mech Cl	S & B		
Mean Values (%) ^a									
STV4554B2RF	2	5.53	7.29	7.54	7.79	7.65	8.09		
	1	5.67	7.78	7.52	7.89	7.76	8.16		
	8	3.90	7.50	7.49	7.92	7.78	8.09		
STV4427B2RF	4	5.28	8.02	7.60	7.84	7.73	8.00		
	3	5.57	7.49	7.04	7.94	7.79	8.08		
	9	3.87	7.40	7.40	7.86	7.72	8.03		
Grand mea	ans	4.97	7.58	7.43	7.87	7.74	8.08		
Range (%) of Averaged Values, <i>Within and Between</i> Cultivars									
Within cultivars:			-						
STV4554B2R	$(3)^{b}$	1.77	0.49	0.05	0.13	0.13	0.07		
E Low, L Low,	L High ^c								
STV4427B2F	RF (3)	1.70	0.62	0.56	0.10	0.07	0.08		
E Low, L Low,	L High								
Between cultivar	s:	0.12	0.12	0.17	0.01	0.02	0.07		
^a Pooled standard deviations (%): moisture content – raw gin lab, 0.16; raw SRRC, 0.12; and mechanically									
cleaned, 0.076; 0.074.	water con	tent - raw SR	RC, 0.071; n	nechanically c	leaned, 0.057;	and scoured an	nd bleached,		
^b Numbers in parenthesis refer to number of cottons of different treatments <i>within</i> a cultivar.									
^c E is early defoliation, L is late defoliation, Low is low gin-drying temperature (90 ^o F), and High is high gin-									
drying temperature (190°F).									

Table 2. Both cultivars - Mean values (%) and simple range (%) of avg. values, within and between cultivars.



Figure 1. Grand means (%) of moisture content (MC) with standard error bars by standard oven-drying and total water content (TWC) by Karl Fischer Titration of all cottons and fiber matrices.

Sensitivity of the standard oven drying method to maturity has been reported (Gamble, 2004; Rousselle and Thibodeaux, 2006). The source of the discrepancies between the oven drying and Karl Fischer results is due to the fact that the oven moisture test method is nonspecific for water and not all of the water is removed in oven drying. Perhaps there were changes in the amount of water remaining in the samples when oven drying in conditioned air, changes in the extent of sample oxidation with varying maturity, or unexplained variance in relative humidity in room conditioning. The three levels of conditioning may have contributed to the differences in results. For example, a recent study concluded that conditioning in the glove box led to more consistent water results compared to conditioning in the room (Montalvo, Von Hoven, Cheuk, and Byler, 2011).

These problem areas would lead to poorer standard deviations of moisture content compared to KFT water content. The pooled standard deviation for moisture content was, in fact, greater than that for water content.

Test for Statistical Significance

For oven moisture content results, the bias in the data confounds testing of the hypothesis and could lead to erroneous conclusions. The hypothesis is now tested for statistical significance to determine if the different genetic backgrounds of the two cultivars, with different maturity levels, and gin-drying temperatures, would not affect the average of the water content of cleaned samples *within* cultivars. For the scoured and bleached cottons, both cultivars (three cottons each) showed the sample averages *within* a cultivar were not significantly different (STV4554B2RF, p = 0.083 and STV4427B2RF, p = 0.372). Thus, the hypothesis is accepted as true but only for the scoured and bleached cottons. Scouring and bleaching the fiber removed the impurities. The gin-drying history of the cottons was negated by the contact with liquid water in the cleaning process; all samples were dried and conditioned at the same settings.

Conclusions

A hypothesis was developed that genetic backgrounds of different cultivars, maturity levels and gin-drying temperatures would not affect water content (measured by Karl Fischer Titration) within cultivars. The hypothesis was accepted as true, but only for the scoured and bleached samples. Scouring and bleaching made the gin-drying history constant for all the cottons and removed the impurities. Relative humidity conditioning of the scoured and bleached samples in the glove box – which was placed in the standard conditioned room – contributed to the consistency of water content results. The fact that there were three levels of conditioning in this study – none (samples taken at the gin), conditioning in the room, and less variable moisture conditioning in the glove box placed in the conditioned room – will cause differences in results. A study of the variability associated with the different levels of conditioning might be helpful.

The moisture content values, measured by standard oven-drying, were sensitive to maturity levels and the impurities in raw and mechanically cleaned cottons. Sensitivity of this weight loss method to different fiber maturities is consistent with findings in the literature but it appears to be due to, at least in part, to change in the weight loss bias. A weight loss balance of the moisture content method, derived from prior work, shows the expected bias.

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