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TEXTILE TECHNOLOGY

Probing Bias Reduction to Improve Comparability of Lint Cotton Water and Moisture Contents at Moisture Equilibrium

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ABSTRACT

The Karl Fischer Titration (KFT) standard test method is specific for water in lint cotton and designed for samples conditioned to moisture equilibrium. There is no standard method for equilibrium moisture content by oven drying (OD). The KFT technique is specific for water; in the OD procedure the weight of the loss volatiles at 105 to 110°C is the measure of moisture content, all of which is incorrectly attributed to water. The results from OD we call "moisture content" and from KFT "water content". Different OD procedures, with dissimilar sample conditioning systems, drying ovens, size, and number of weighing bottles in the oven, currently are used to make measurements. Yet, no comprehensive study of the multiple causes of the difference between equilibrium water and moisture content has been reported. To assist with explaining the observed disparity, the present effort develops a list of six potential OD biases. The origin of these biases is incomplete drying and weight change due to side reactions in opposite directions. Using a control cotton, the biases were measured at moisture equilibrium in four different OD procedures. The corrections were applied to the moisture content data from a dozen Mississippi cotton samples analyzed by the same OD methods. Method grand mean results were 7.73% water compared to moisture content before/after bias correction, respectively: 7.19/7.80, 7.50/7.80, 7.42/7.69, and 7.79/7.92. By changing OD features it was possible to suppress one bias over the other. Samples were conditioned to more stringent specifications to provide precise data to test the hypotheses in this research.

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New technologies have put additional stress on cotton and to better understand the relationships between spinning performance and fiber quality, the role of moisture in fiber utilization is of increased interest. The moisture content of cotton fibers affects both the properties of the bale and spinning performance (Backe, 2002), whereas fiber strength is proportional to lint moisture (Byler et al., 1993). Despite the oven-drying (OD) method to measure moisture content being widely used, there is industry concern about the reliability of the data.

Because the OD method will continue to be utilized worldwide due to its ease and economy of use, it is wise to explore the possible causes for differences in results between this method and any other established reference method. One key issue in oven drying is the assumption that all weight loss is water. Probing for bias in the OD method is an important project because this knowledge can be used to improve reliability of OD results and develop an ASTM standard OD method at moisture equilibrium.

A literature review of OD methods to measure moisture content (Montalvo and Von Hoven, 2008a) included critical analysis of the errors. One key paper identified the most prevalent errors as residual moisture remaining in the cotton after drying and substances other than water released during heating (Davidson and Shorter, 1930). Two other important papers were by Terrell (1967a, b). The first highlighted a seven-year, seven-part industry–ASTM study. The second documented a one-year interlaboratory project that included cotton among other materials. The most relevant conclusion of this major work was that the OD method has many unidentified errors that should be reduced, if not eliminated (Terrell, 1967a, b).

In response to the need for an equilibrium moisture standard, ASTM D7785 has been developed for water in lint cotton conditioned to moisture equilibrium (ASTM, 2012). Recovery of water available for titration was quantitative, > 99.99%, and the documented selectivity for water over the other

materials in cotton is high (Montalvo et al., 2011). To verify the robust nature of the KFT method, two applications measured water content in Mississippi cottons. The first study involved lint cotton from five cultivars, all grown in the same area, same crop year, and ginned with a fixed number of lint cleaners, but defoliated at different times to produce a range of micronaires and gin dried at two possible temperatures (Von Hoven et al., 2012). The mean water content across all 12 cottons analyzed was (%): raw, 7.83; mechanically cleaned, 7.69; and scoured and bleached, 8.10. Within cultivar water content range (%) of the averaged values did not differ significantly with removal of impurities: raw, 0.01 to 0.19; cleaned, 0.03 to 0.13; and scoured and bleached, 0.03 to 0.08. Between cultivar range (%) was essentially independent of fiber cleaning: raw, 0.20; mechanically cleaned, 0.20; and scoured and bleached, 0.25. These results were unexpected and can be attributed to the specificity of the KFT test method. The aim of the second study was to establish that the small difference in averaged water content between raw and mechanically cleaned cotton (< 0.2%) was real and not due to random error. Mathematical models were developed to predict the difference in water content before and after mechanical cleaning (Montalvo and Von Hoven, 2012). Although the water content in the trash particles was approximately twice that of the water content of the cleaned fibers, the mass fraction of impurities is the controlling factor in establishing the difference in water content before and after cleaning. The predicted difference agreed well with the experimental value.

The errors in the KFT-equilibrium water-content method have been minimized (see Montalvo et al., 2011 for detailed documentation) and all of the difference between water and moisture contents originates from the OD method. We call this difference the bias. In the terminology section of D7785 the measure of moisture content is the weight of the lost volatiles by oven drying at 105 to 110°C, whereas water content is the specific measure of the total amount of water in a test specimen by KFT.

ASTM D2495 (ASTM, 2007) standard test method for moisture in cotton by oven drying is used widely in ginning and was designed explicitly for cotton material at a specified time or under prevailing conditions. This standard stated "… do not precondition or condition the specimens after they are taken." In lieu of a standard ASTM test method for moisture content at moisture equilibrium, various modifications of D2495 currently are used to measure equilibrium moisture content (Cheuk et al., 2011; Montalvo et al., 2010). For example, the minimum recommended sample size for a specimen of lint cotton analyzed according to D2495 is 5 g; however, one change involves the use of a smaller sample size (1.0-1.5 g) and glass weighing bottles with ground-glass stoppers. This modification allows for placing 100 or more of the bottles on trays in a large oven. Another change involves the air entering the oven, which might come from a normal conditioned room (see Appendix for definition of terms and symbols) rather than the standard atmosphere in a textile testing room as specified in D2495. The biases related to the changes in D2495 have not been determined, but could be significant.

Extensive research has been done in this laboratory to confirm the reported biases in oven dying and discover new ones. In 2007, USDA scientists in New Orleans picked up where scientists left off more than half century ago. The studies confirmed the known biases, discovered new biases, and elucidated the underlying bias mechanisms (Cheuk et al., 2011; Fortier et al., 2014; Montalvo et al., 2010, 2014). Some water remains in the cotton. Particulate matter (trash, dust, broken and immature fibers) is removed from the cotton. Oxidation and decomposition reactions of cellulose and impurities produce nonaqueous volatile material of low vapor pressure not detected by a mass spectrometer (Montalvo et al., 2010). A decomposing odor is detected. Also, sample conditioning at standard textile testing conditions of 21 ± 1 °C and 65 ± 2% relative humidity resulted in a significant conditioning error in water content and can be reduced by placing a glove box in the controlled temperature environment containing a salt solution to control humidity to ± 0.5% (Montalvo et al., 2014).

This paper builds upon the bias discoveries in oven drying. The following 10 sources of variance can be considered in understanding the bias. Cotton sample source of variation include crop year, area grown, variety, defoliation date, number of lint cleaners in ginning, and gin-drying temperature. Oven-drying sources of variation include the four different OD procedures utilized in this laboratory. However, so many sources of variation and their interaction make the interpretation of statistical results more complicated. To simplify

the process, the main factors that influence the bias were limited to the OD methods themselves, as explained below.

For the set of Mississippi cottons discussed above, cotton characteristics (e.g., strength and micronaire) and water content were measured extensively in the raw cottons. Water content also was measured in the cleaned cottons. We know the "true water values". With crop year, area grown, and the number of lint cleaners held constant, the insignificant range of water values discussed above was independent of cultivar, defoliation timing, and gin-drying temperature. Thus, there are no other factors to consider that affect water level and emphasis can be placed on moisture concentration by oven drying.

The weight loss amount by oven drying is based on the difference between the wet and oven-dry weight. How well can weight loss level by oven drying match the corresponding water quantity by KFT? Consider one OD bias in more detail. At 65% relative humidity, incomplete oven drying of samples at moisture equilibrium can result in the OD weight overestimated by 0.5%, resulting in underestimating the actual water level by 0.5%.

The objectives of this paper are to: (a) select the four OD methods for the study that represent actual OD procedures utilized in the laboratory, (b) measure equilibrium moisture content in ginned lint from the Mississippi cultivars by the four OD procedures, (c) compare the small range of equilibrium water (from the prior work) and the unknown range of equilibrium moisture within each OD method, (d) select six potential biases in OD whose sum can represent a significant bias in moisture content values, (e) use a control cotton to measure directly the various biases by KFT or assign a value from the prior work, and (f) compare actual levels of equilibrium water and equilibrium moisture before and after bias correction.

FUNDAMENTALS

There are numerous sources of error in measurement of equilibrium moisture content in cotton by oven drying. To express the errors in appropriate formulae to compute the cumulative error or bias, each is first written in text format as a water recovery parameter and then in mathematical form (see Appendix for definition of terms and symbols). A water recovery parameter is given as a three letter acronym in capital letters. The corresponding math forms, e_{xxx} and $-e_{xxx}$, refer to a positive or negative bias (e) and the subscript is the acronym in lower case. As an example, consider the residual water that remains in cotton after oven drying: the acronym is RSW and the bias is $-e_{rsw}$. This bias is negative because it decreases the recovery of water (or weight loss) by oven drying.

In Eqs. [1] and [2], e_{aae} is the moisture pickup error after oven drying due to ambient air exposure between opening the oven door and closing the weighing bottles, e_{bwb} is the error (positive or negative) due to the change in weight of the blank weighing bottle before and after oven drying, e_{pic} the error resulting from the mechanical transport of particulates out of the sample matrix by the evolving water vapor, e_{oxd} the bias (positive or negative) due to oxidation of the sample during oven drying, and e_{con} the error (positive or negative) resulting from changes in the ambient air conditioning in textile testing.

By definition, a local bias is measured separately on each of the OD procedures in this report. In contrast, a global bias is measured by one procedure, not necessarily the OD procedures in this report, and applied equally to all OD methods in the current paper or fewer than all the methods if it does not apply to all.

$$e_{loc} = -e_{rsw} - e_{aae} \pm e_{bwb} \quad [1]$$

$$e_{glo} = e_{pic} \pm e_{oxd} \pm e_{con}. \quad [2]$$

Cumulative Error With and Without Direction. Now consider the quantitative recovery of water in the oven drying of cotton by incorporating all suspected biases to date. The six individual biases can operate in different directions and vary in magnitude. An online literature search "cumulative error without direction" produced more than 47 million results. This is a common measurement of error, and a handbook (Cleverley, 1989) provided simple ways to calculate this measure as well as the nomenclature used. When biases are combined, the result is referred to as the cumulative error with and without direction.

There are advantages and disadvantages in calculating the cumulative error with and without direction. If we allow direction, errors in opposite directions offset each other; the calculation has disguised the magnitude of individual errors. The cumulative error might be zero although no indi-

vidual error was a zero. If we ignore direction, the cumulative magnitude can be estimated without allowing error in different directions to offset each other. However, the cumulative direction is unknown (Cleverley, 1989).

In the example calculations in the handbook, the straightforward calculation of cumulative error with direction (e_{cwd}) is simply the algebraic sum of the individual biases. By contrast, the uncomplicated computation of cumulative error without direction (e_{cod}) is the absolute sum of the individual biases. Applying these two definitions to the cumulative error function in Eq. [3], the expanded error functions are given by Eqs. [4] and [5].

$$e_{cum} = \int(e_{loc}, e_{glo}) \quad [3]$$

$$e_{cwd}\,(\%) = -\,e_{rsw} - e_{aae} \pm e_{bwb} + e_{pic} \pm e_{oxd} \pm e_{con} \quad [4]$$

$$e_{cod}\,(\%) = \left|e_{rsw}\right| + \left|e_{aae}\right| + \left|e_{bwb}\right| + \left|e_{pic}\right| + \left|e_{oxd}\right| + \left|e_{con}\right|. \quad [5]$$

Note the right side of Eq. [5]. This expression calls for the sum of absolute values of each bias rather than the absolute value of the sum of biases. As a reminder, the sum of absolute values and the absolute value of the sum are not the same: $\left|-a\right| + \left|b\right| \neq \left|-a + b\right|$.

An example calculation will illustrate the practical difference between e_{cwd} and e_{cod} based on only two OD biases. If one bias is a negative 0.5% and the other a positive 0.4%, then $e_{cwd} = -0.5\% + 0.4\% = -0.1\%$ (with direction) and $e_{cod} = \left|-0.5\%\right| + \left|0.4\%\right| = 0.9\%$ (without direction). Note that as a result of confounding bias, the net amount of OD error (with direction) is only −0.1 % and the uncorrected result might not significantly differ from the observed water content value. However, the large absolute error (without direction) of almost 1% shows, in fact, that the OD result is strongly influenced by underlying side processes. The apparent agreement between the uncorrected oven drying and water values is coincidental.

MATERIALS AND METHODS

Cottons and Gin-Drying Treatments. Five cultivars (Table 1) were obtained from four seed companies. 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 micro gin at the Stoneville ARS research facility. For cultivars STV4554B2RF and STV4427B2RF, two bags of late defoliated and one bag of early defoliated were taken for each cultivar. Two bags of each of the remaining three cultivars were taken for a total of 12 bags.

Standard gin processing was used with dryer 1, cylinder cleaner, stick machine, dryer 2, second cylinder cleaner, extractor-feeder gin stand, one lint cleaner. The two possible dryer settings were 90°F (low) and 180°F (high) or 32.2°C and 82.2°C, respectively. Each bag was ginned separately. Emphasis in this study was on late defoliation and drying at low and high heat for all five cultivars (Table 1). In addition, two of the cultivars were defoliated early and dried at low heat.

Table 1. Ginned cottons sorted by cultivar.

Cultivar	Sample ID	Defoliation	Gin dryer heat
STV4554B2RF	A2	Early	Low
	A1	Late	Low
	A8	Late	High
STV4427B2RF	B4	Early	Low
	B3	Late	Low
	B9	Late	High
FM960BR	C5	Late	Low
	C10	Late	High
DP164B2RF	D6	Late	Low
	D11	Late	High
PHYTO485 WRF	E7	Late	Low
	E12	Late	High

The control cotton used in the bias estimates had been scoured and bleached and is available commercially as cotton balls.

Moisture Content at the Gin Lab. Three cans of lint from each bag were taken after the gin stand during ginning of the cottons for moisture content determination (Fig. 1). The containers were immediately closed with a tightly fitting lid and transported to the ginning laboratory for oven drying (Shepherd, 1972). Note that containers in the oven consisted of 75-mm x 160-mm wire baskets. There were three 20-g replicates per cotton. Sixteen baskets were placed in the mechanical convection oven (MCO) located in a normal conditioned room (NCR). Because 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 (%, wet basis) for all 12 cottons.

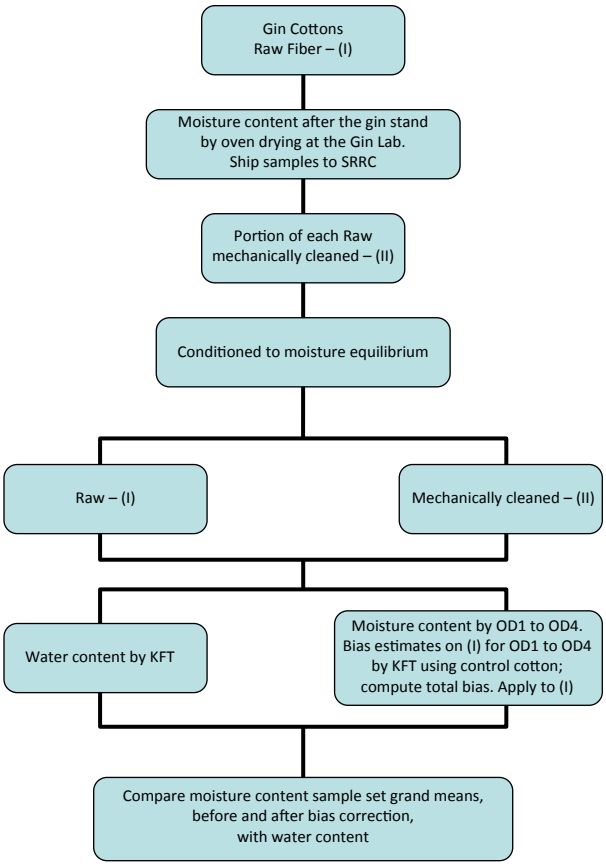

Figure 1. Flow chart illustrating creation of sample sets (I and II), water and moisture content determinations on all samples, bias estimates on raw cotton measured with a control cotton subjected to oven drying by the four OD procedures, and comparing moisture and water content.

Mechanical Cleaning of Lint Samples. Cotton fibers were mechanically cleaned using the Shirley Analyzer. In preparation for cleaning, half-gram tufts from the 100-g mass of each cotton sample were picked and then the tufts were mixed by hand. Samples were divided into two 50-g samples and fed into the Shirley. Each 50-g subsample was carefully opened and placed as a web on the feeding tray. Once cleaning of the subsample was complete, the cotton was then fed back into the Shirley, perpendicular to the original orientation of the fibers of the first pass. Operators wore gloves to handle the cottons at all times, repeating the process for all cottons in the study.

Equilibrium Moisture and Water Content. ***Conditioning Systems.*** Two conditioning systems were used. One was the textile testing room (TTR) set to 21 ± 1°C and 65 ± 2% relative humidity. The other was a glove box in the textile testing room (GBTTR) to control humidity within 65 ± 0.5% by the use of a saturated aqueous sodium nitrite solution (Wink and Sears, 1950). Heat transfer through the walls of the chamber provided for temperature control of 21 ± 1 °C. Cotton samples were conditioned in either the textile testing room (TTR) or GBTTR to moisture equilibrium for at least 24 h before measuring moisture or water content. Also, all laboratory (bulk) samples and glassware (weighing bottles and KFT vials) were conditioned for at least 24 h in the TTR and handled with gloved hands.

The GBTTR provided for more stringent sample conditioning of 21 ± 1°C and 65 ± 0.5%. The ASTM D7785 method as written specifies a tolerance of ± 2.0% relative humidity. With the tighter tolerance in the glove box, the samples are still in compliance with the humidity of 65 ± 2%. In a typical large TTR, the response from multiple humidity sensors is averaged to drive the hardware to achieve the desired conditions. Under the best conditions in the large TTR with very sensitive sensors, the range of individual sensors at the various work stations can be ≤ ± 2%, still within tolerance. In other words, a specified tolerance of ± 2.0% relative humidity is the allowed outer limit.

According to ASTM (see Acknowledgment), the tighter humidity tolerance ± 0.5% on D7785 can be documented as a note to the precision and bias section of the method, which is expected to provide for better precision. Everything else in D7785 remained the same. Justification for the smaller tolerance is the range of water in the Mississippi samples, 0.3%, and that the weight of a control cotton in a wire cylinder conditioned in the TTR varied by as much as 0.3% among: work stations in the room, morning and afternoon, and days (Montalvo and Von Hoven, 2008b).

Equilibrium Moisture Content by Oven Drying. Four OD methods were employed for this study (Fig. 1 and Table 2) involving two ovens in different environmental conditions, dissimilar conditioning prior to testing, as well as different post-testing conditioning. (These OD versions have been and are being used in our laboratory. There is no standard ASTM OD test method at moisture equilibrium. Thus, there is no reason to expect that within or between labs, the exact same procedure is being used.) All weights were made in the textile testing room. The weight of each empty container was recorded to four decimal places, filled with the specified sample size and reweighed to four decimal places. One of the laboratory ovens used was a VWR Model 1310 gravity convection oven (GCO) (VWR Scientific Products, Houston, TX) with an approximate capacity of 28.3L (1 cu ft) and a flow rate of approximately 0.04 L/sec that was placed in the TTR. The other was a Yamato DKN 600 MCO (Yamato Scientific Products, Santa Clara, CA) with a 150 L capacity, a mean flow rate of approximately 1.3 L/sec and was placed in a NCR.

Table 2. KFT[z] and oven-drying (OD[y]) methods summary[x].

Method	Sample wt.[w] (g)	Replicates per cotton[v]	Conditioning room		Drying oven		Weighing bottles in oven	
			TTR	GBTTR	Location	type	(I.D. x H, mm)	number
KFT	0.1[u]	6		✓	NCR	single sx	9 ml	1
OD1	1.0[t]	6		✓	TTR	GCO	25 x 50	12
OD2	1.0	3	✓		TTR	GCO	40 x 50	6
OD3	1.5	5	✓		NCR	MCO	40 x 50	no limit
OD4	1.0	3	✓		NCR	MCO	40 x 50	6
CGRU	20	3	no conditioning		NCR	MCO	75 x 160[s]	16

[z] Condition samples, weigh, seal vials with septum cap, then analyze by KFT equipment—includes oven dry in mini oven and titrate water vapor.

[y] Condition samples, weigh, oven dry in a laboratory oven, and reweigh.

[x] See Appendix for definition of terms and symbols, and additional details in Materials and Methods section.

[w] All samples and empty containers conditioned in textile testing room (TTR) prior to pre-weigh to target weight on balance in TTR; all additional weights as needed on same balance.

[v] For KFT and OD1 to OD4 there were the same number of raw and mechanically cleaned replicates per cotton; example, KFT 6 raw and 6 cleaned.

[u] Open KFT vials containing samples conditioned in glove box in textile testing room (GBTTR), sealed while in box, and final conditioned weight taken in TTR.

[t] Open weighing bottles containing samples conditioned in glove box in textile testing room (GBTTR), closed while in box, final conditioned weight taken in TTR, oven dried, and reweighed in TTR.

[s] Cylindrical wire basket.

After oven drying for 24 h, the samples were cooled in a desiccator for approximately 45 min while in the TTR. After removing the bottles from the desiccator, the bottles were allowed to equilibrate to TTR conditions for approximately 15 min. This allowed for the weighing bottle exterior to pick up roughly the same amount of moisture that it had prior to the initial weighing after conditioning. Mean oven moisture content (%, wet basis) and standard deviation were calculated from the weight-loss data. As a check for consistency of results (Von Hoven et al., 2012) the total number of weighing bottles in an oven at one time was half raw and half mechanically cleaned replicates from the same cotton. The expected positive difference between the raw minus the clean values is due to the water content in the trash is greater than that in the cleaned fibers.

All weighing bottles were cap type, so that it was possible to push down hard on the lid and close with minimum leakage. The bottles were then opened without breakage using the automatic bottle opener for cap-style weighing bottles (Montalvo et al., 2010).

Oven-Drying Technique #1 (OD1). To resemble more closely the geometry of the KFT vials, a weighing bottle 25-mm diameter and 50-mm height was used. Three 1.0-g replicates per cotton, raw and cleaned, were preweighed and placed in the GBTTR to condition. The bottles were capped, removed from the glove box, and a final weight was recorded in the TTR. Up to 12 weighing bottles (two cottons, each three replicates raw and three clean) were oven dried in the GCO located in the TTR.

Oven-Drying Technique #2 (OD2). For this portion of the study, 40-mm x 50-mm (Table 2) weighing bottles were used. Three 1.0-g replicates per cotton, raw and cleaned, were prepared and conditioned in the TTR. Six weighing bottles (one cotton, each three replicates raw and three clean) were oven dried at one time in the in the GCO in the TTR.

Oven-Drying Technique #3 (OD3). The 40-mm x 50-mm weighing bottles were used. Five 1.5-g replicates per cotton, raw and cleaned, were prepared and conditioned in the TTR. Dozens of bottles were placed on trays in the MCO located in the NCR to dry at one time; some applications of OD3 in this lab have involved 500 to 1000 bottles; drying 100 or more at one time was necessary. Following the oven heating, the trays were removed from the oven, placed on the lab bench, capped, and placed in desiccators. The desiccators were then moved into the TTR to cool.

Oven-Drying Technique #4 (OD4). The 40-mm x 50-mm weighing bottles were used. Three 1.0-g replicates per cotton, raw and cleaned, were prepared and conditioned in the TTR. Six weighing bottles (one cotton, each three replicates raw and three clean) were placed in the MCO oven in the NCR.

After oven drying, the bottles were capped while in the oven, and placed in a desiccator. The desiccators were then moved into the TTR to cool.

Equilibrium Water Content by KFT. The 9-ml glass vial recommended by the manufacturer was used. Six 0.1-g replicates per cotton, raw and cleaned, were prepared and conditioned in the GBTTR. Water content was determined by KFT, a procedure specific for water in cotton (ASTM, 2012; Cheuk et al., 2011; Montalvo et al., 2011). The Karl Fischer apparatus (Metrohm USA, Tampa, FL) consists of a fully automated Metrohm 774 sample processor oven held at 150°C and dry nitrogen to transport released water vapor into the titration cell. Other features include 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 KFT samples were conditioned, weighed, placed in vials, and capped while in the GBTTR. Using gloved hands, 0.1000 ± 0.0003-g samples were prepared, 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 carousel located in the NCR. Hydranal® composite 5K was used as the titration reagent and Hydranal® medium K was the solvent in the titration cell. Mean water content (%, wet basis) and standard deviation were calculated from the amount of reagent consumed.

Data Analysis. Excel 2003 was used to calculate sample averages, standard deviations, to setup regression equations and calculate slopes, intercepts, and coefficients of determination (R^2); SAS version 9.3 (SAS Institute Inc., Cary, NC) was used to calculate *p* values in tests for statistical significance by ANOVA.

RESULTS AND DISCUSSION

Design of the Comparability Study. Figure 1 and Table 2 details the design of the water (by KFT) and moisture content (by four OD procedures) comparability study at moisture equilibrium. The OD1 procedure should result in the best agreement with KFT because the sample conditioning was exactly the same, the GBTTR. Also note that the drying oven was a small GCO placed in the TTR. Emphasis in OD2, OD3, and OD4 was to gather data at standard conditioning (i.e., the TTR). The location and type of drying oven in OD3 and OD4 reflects the general practice at Southern Regional Research Center: the oven is placed in a NCR and a large MCO is utilized. As a final note, the smaller diameter weighing bottles used in OD1 allowed for placing more bottles in the small oven. The number of weighing bottles in a sample run was limited for OD1, OD2, and OD4, but not for OD3, which provided the opportunity to collect OD data using trays full of weighing bottles, 100 or more at a time in the oven.

The bias estimates on raw cotton were measured with control cotton subjected to the four OD procedures or an assigned value from the prior bias discovery work was calculated (Cheuk et al., 2011; Montalvo et al., 2010, 2011). Water and moisture content were compared before and after bias correction. Note that the individual sample OD biases were not measured. This would have required an excessive amount of time devoted to determining 288 bias values (six biases/cotton–OD method x four OD methods x 12 cottons = 288). Rather, the six biases were estimated using one control cotton (six biases/OD method x four OD methods x one cotton = 24 values max) to the extent possible. As a result, the standard error of each particular kind of bias is constant for all 12 cottons within an OD method.

Descriptive Statistics. Tables 3, 4, and 5 introduce the water and moisture content descriptive statistics. No moisture data in the table have been excluded as outlier and rerun because consideration of all the original data provides for a better understanding of the underlying processes in oven drying of cotton. The water content data in Table 3 are the original data published in the first series of studies with the Mississippi cultivars (Von Hoven et al., 2012).

Our strategy to check for consistency of results was to document the grand mean difference between raw and clean values within a particular analytical method (Table 3, last row). The range of differences, raw minus clean, is 0.12 to 0.18%. The raw values are all larger than the corresponding clean results because the water content is larger in the trash than the cleaned fiber. These differences fall within the range predicted by the models in the second series of studies (Montalvo and Von Hoven, 2012).

The bar graph of the grand means difference between moisture and water content (Table 5 and Fig. 2), all at moisture equilibrium, shows a negative value for each OD method. With common oven type, the extent of the trend actually decreased with a smaller number of bottles—and mass of water—in the oven at one time.

Table 3. Water content by Karl Fischer Titration (KFT) and moisture content by oven drying (OD) without correction[z].

Sx ID	Mean (%, wet basis)										
	Equilibrium water content - KFT		No cond.	Equilibrium moisture content – OD1 to OD4							
				OD1		OD2		OD3		OD4	
	Raw	Mech Cl	CGRU[y]	Raw	Mech Cl	Raw	Mech Cl	Raw	Mech Cl	Raw	Mech Cl
A2	7.79	7.65	5.53	7.17	6.94	7.53	7.30	7.29	7.54	7.90	7.61
A1	7.89	7.76	5.67	7.22	7.11	7.57	7.41	7.78	7.52	7.71	7.64
A8	7.92	7.78	3.9	7.23	7.16	7.46	7.40	7.50	7.49	7.97	7.84
A Mean	*7.87*	*7.73*	*5.03*	*7.21*	*7.07*	*7.52*	*7.37*	*7.52*	*7.52*	*7.86*	*7.70*
B4	7.84	7.73	5.28	7.28	7.13	7.64	7.20	8.02	7.60	7.89	7.46
B3	7.94	7.79	5.57	7.33	7.05	7.52	7.31	7.49	7.04	7.90	7.66
B9	7.86	7.72	3.87	7.19	6.94	7.52	7.30	7.40	7.40	7.87	7.83
B Mean	*7.88*	*7.75*	*4.91*	*7.27*	*7.04*	*7.56*	*7.27*	*7.64*	*7.35*	*7.89*	*7.65*
C5	7.80	7.67	4.72	7.23	7.07	7.39	7.27	7.31	7.36	7.65	7.56
C10	7.64	7.60	3.4	6.98	6.92	7.28	7.11	7.04	6.99	7.50	7.51
C Mean	*7.72*	*7.64*	*4.06*	*7.11*	*7.00*	*7.34*	*7.19*	*7.18*	*7.18*	*7.58*	*7.54*
D6	7.75	7.61	5.2	7.13	7.07	7.76	7.77	7.00	6.95	7.76	7.77
D11	7.74	7.49	3.6	7.06	6.95	7.18	7.13	7.10	6.97	7.53	7.55
D Mean	*7.75*	*7.55*	*4.40*	*7.10*	*7.01*	*7.47*	*7,45*	*7.05*	*6.96*	*7.65*	*7.66*
E7	8.01	7.76	5.3	7.33	7.17	7.55	7.26	7.59	7.39	7.92	7.76
E12	7.82	7.73	3.4	7.18	7.12	7.63	7.45	7.48	7.34	7.97	7.87
E Mean	*7.92*	*7.75*	*4.35*	*7.26*	*7.15*	*7.59*	*7.36*	*7.54*	*7.37*	*7.95*	*7.82*
Mean[x]	7.83 ± 0.07	7.69 ± 0.06	4.62 ± 0.07	7.19 ± 0. 10	7.05 ± 0.09	7.50 ± 0.12	7.32 ± 0.11	7.42 ± 0.12	7.30 ± 0.09	7.79 ± 0.10	7.67 ± 0.11
Check consistency of results by documenting mean grand difference (%) between raw and clean values											
Mean diff	0.14		n/a	0.14		0.18		0.12		0.12	

[z] See Appendix for definitions of terms and symbols, Table 2, and additional details in Materials and Methods.

[y] CGRU is USDA Cotton Ginning Research Unit

[x] Grand mean ± std. deviation of the 12 cottons; does not include the cultivar averages.

Table 4. Range (%) of avg. values within and between cultivars for raw cottons[z].

Cultivar	CGRU[y]	Water and moisture content at moisture equilibrium				
		Water content	OD1	OD2	OD3	OD4
***Within*:**						
A(3)[x]	1.77	0.13	0.06	0.11	0.49	0.26
B(3)	1.70	0.10	0.14	0.12	0.62	0.03
C(2)	1.32	0.16	0.25	0.11	0.27	0.15
D(2)	1.60	0.01	0.07	0.58	0.10	0.23
E(2)	1.90	0.19	0.15	0.08	0.11	0.05
***Between*:**	0.58	0.18	0.19	0.50	0.52	0.23

[z] See Appendix for definitions of terms and symbols, Table 2, and additional details in Materials and Methods.

[y] USDA Cotton Ginning Research Unit, OD1 to OD4 are oven drying methods to measure moisture content.

[x] Number of cottons within a cultivar.

Table 5. Raw cotton equilibrium water content subtracted from equilibrium moisture content, without correction[z].

Sx ID	Mean difference (%, wet basis)			
	OD1	OD2	OD3	OD4
A2	−0.62	−0.26	−0.50	+0.11
A1	−0.67	−0.32	−0.11	−0.18
A8	−0.69	−0.46	−0.42	+0.05
A Mean	*−0.66*	*0.35*	*−0.35*	*−0.01*
B4	−0.56	−0.20	+0.18	+0.05
B3	−0.61	−0.42	−0.45	−0.04
B9	−0.67	−0.34	−0.46	+0.01
B Mean	*−0.61*	*−0.32*	*−0.24*	*+0.01*
C5	−0.57	−0.41	−0.49	−0.15
C10	−0.66	−0.36	−0.60	−0.14
C Mean	*−0.61*	*−0.38*	*−0.54*	*−0.14*
D6	−0.62	+0.01	−0.75	+0.01
D11	−0.68	−0.56	−0.64	−0.21
D Mean	*−0.65*	*−0.28*	*−0.70*	*−0.10*
E7	−0.68	−0.46	−0.42	−0.09
E12	−0.64	−0.19	−0.34	+0.15
E Mean	*−0.66*	*−0.33*	*−0.38*	*+0.03*
Mean[y]	−0.64 ± 0. 04	−0.33 ± 0.15	−0.42 ± 0.25	−0.04 ± 0.12

[z] See Appendix for definitions of terms and symbols, Table 3, and additional details in Materials and Methods.

[y] Grand mean ± std. deviation of the 12 cottons; does not include the cultivar averages.

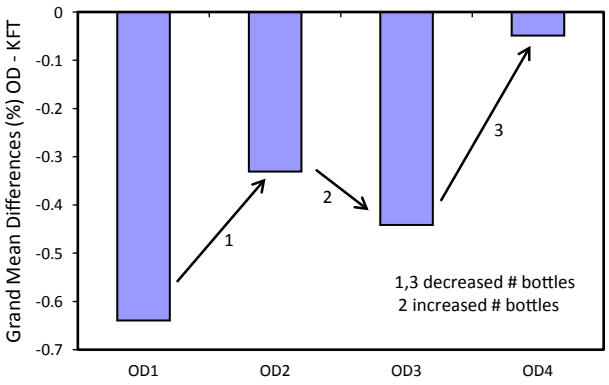

Figure 2. Grand mean difference for raw cotton between moisture content by oven drying (OD) and water content by Karl Fischer Titration (KFT), all at moisture equilibrium. Legends: OD1 and OD2 are oven-drying methods with common gravity convection oven; OD3 and OD4 are OD methods with common mechanical convection oven.

Cotton Ginning Research Unit Moisture Content. To probe for possible trends in the CGRU descriptive data, consider the grand means in Table 3 and the range of averaged values within and between cultivars (Table 4). The CGRU grand mean (4.62%) is significantly lower ($p < 0.05$) than that measured at moisture equilibrium. The five averaged moisture contents within cultivar (5.03%, 4.91%, 4.06%, 4.40% and 4.35%) are all significantly lower ($p < 0.05$) than that observed at moisture equilibrium.

Additionally, the range of averaged values within a cultivar for the CGRU results (1.32% to 1.90%) is significantly greater ($p < 0.05$) than that at moisture equilibrium. The range of averaged values between cultivars (0.97%) is significantly greater ($p < 0.05$) than similar data taken at moisture equilibrium.

Estimating the Local Biases. Moisture content is based solely on weight loss by oven drying; all weight loss is attributed to water. The sensor, an analytical balance, is unable to differentiate between molecules of water and particulate matter evolving from the sample, and cellulose oxidation in the moist, hot air in the oven. Consequently, the biases in oven drying are caused by changes in sample weight not due to water (positive and negative) and incomplete drying.

Six different biases in oven drying were identified and estimated (Table 6); three were classed as local and three as global biases (see Appendix). For each there is an associated moisture recovery parameter. Due to the KFT specificity for water, this sensor was used in the bias determinations whenever possible.

Table 6. Moisture recovery parameters and biases in oven drying (OD) methods: OD1 to OD4[z].

Parameter and bias	Parameter and bias (%[y]) – mean ± std dev				
	Sensor	OD1	OD2	OD3	OD4
Local Bias (e_{loc})					
Residual water (RSW, $-e_{rsw}$)	KFT	0.46 ± 0.03	0.51 ± 0.07	n/a	0.36 ± 0.03
Ambient air exposure (AAE, $-e_{aae}$)	KFT				
(sec)					
< 10		n/a	n/a	n/a	n/a
10				0.42 ± 0.07	
20				0.44 ± 0.03	
30				0.50 ± 0.04	
Blank weighing bottle (BWB, e_{bwb})	Balance				
(sec of AAE)					
< 10		0.00 ± 0.00	0.07 ± 0.06	n/a	0.09 ± 0.06
10				0.03 ± 0.02	
20				0.07 ± 0.01	
30				0.02 ± 0.05	
$e_{loc} = -(e_{rsw} + e_{aae}) + e_{bwb}$					
(sec)					
< 10		−0.46	−0.44	n/a	−0.27
10				−0.39	
20				−0.37	
30				−0.48	
Global Bias (e_{glo})					
Particulates in cotton (PIC, e_{pic})	Balance	0.14	0.14	0.14	0.14
Oxidation (OXD, ± e_{oxd})	KFT	−0.29		n/a	
Conditioning (CON, ± e_{con})	n/a	0.		n/a	
$e_{glo} = e_{pic} \pm e_{oxd} \pm e_{con}$		−0.15	0.14	0.14	0.14

[z] See Appendix for definitions of terms and symbols, Table 2, and additional details in Materials and Methods.

[y] Relative to target sample weight of 1.0 g except for OD3, 1.5 g.

The three local biases in Table 6 are presented in the following order: residual water (RSW, $-e_{rsw}$), ambient air exposure (AAE, $-e_{aae}$), and blank weighing bottle (BWB, e_{bwb}). The residual water in the cotton sample after oven drying was determined with a minimum of reabsorption of water when the oven door was opened, by immediately capping the KFT vial. This was done in < 10 sec between opening the oven and sealing the vials. For OD1 and OD2 this bias ($-e_{rsw}$) is about 0.50% compared to 0.36% for OD4. Placing the OD4 drying oven in a room with lower humidity (NCR) compared to the TTR and using a MCO could account for less water retention after drying. Noteworthy is that the residual water bias was not measured in OD3 due to no limit being imposed on the number of bottles in the oven at one time, and, therefore, might be influenced by the time of exposure to the ambient air (> 10 sec AAE).

Instead, the ambient air exposure bias associated with OD3 was measured at 10, 20, and 30 sec between opening the oven and sealing the KFT vials. This bias ranged from 0.42% to 0.50% water. The OD4 residual water bias (0.36%, assume 0 sec AAE) and the three OD3 ambient air exposure values were fitted to a linear line (Fig. 3, $R^2 = 0.968$). Ambient air exposure adds to the residual water. This work is in agreement with ASTM D2495 (ASTM, 2007). It is stated in D2495 that very dry

cotton can absorb as much as 0.7% moisture from the standard atmosphere during the first 30 sec after the container is opened. According to this ASTM test method, the diameter of each container should be greater than its height, which could account for the 0.7% finding in that study compared to 0.5% in the present investigation.

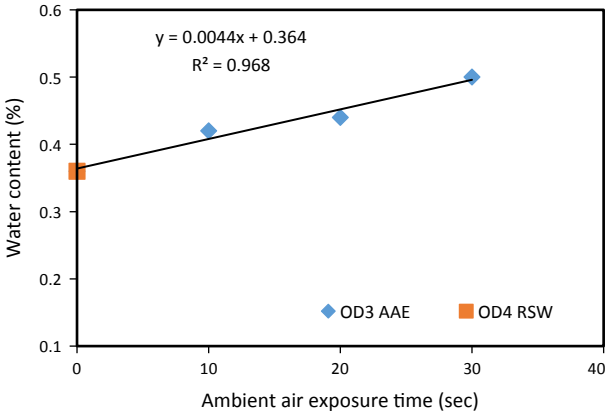

Figure 3. Influence of the ambient air exposure (AAE) time in OD3 on residual water (RSW) content of OD4.

The local biases, estimated from the algebraic sum of the residual water, ambient air exposure, and blank weighing bottle biases ranged from −0.27% to −0.48%.

Estimating the Global Biases. The three global biases in Table 6 are presented in the following order: particulates in cotton (PIC, e_{pic}), oxidation (OXD, ± e_{oxd}), and conditioning (CON, ± e_{con}). In contrast to the local biases, measurement of the global biases is based on assigned values calculated from our published work. The calculations are presented in the Appendix. The global biases, estimated from the algebraic sum of the particulates in cotton, oxidation, and conditioning biases, ranged from −0.15% to 0.14%.

Cumulative Error. The estimated cumulative bias with direction (e_{cwd})—by algebraic sum of individual biases—for the four OD methods, ranged from −0.13% to −0.61% (Table 7). The grand means before bias correction ranged from 7.19% to 7.79%; after bias correction, the means ranged from 7.69% to 7.92%. The default KFT reference value was 7.73% water.

The estimated cumulative bias without direction (e_{cod})— sum of the absolute value of each individual bias— ranged from 0.59 to 0.89%. The bar graphs in Fig. 4 depict the grand mean moisture contents uncorrected and corrected. Overall, algebraic sum correction (with direction) of the biases provided the best agreement with the grand mean water content of 7.73% and lends support to the concept of multiple biases in opposing directions in moisture content determination by oven drying.

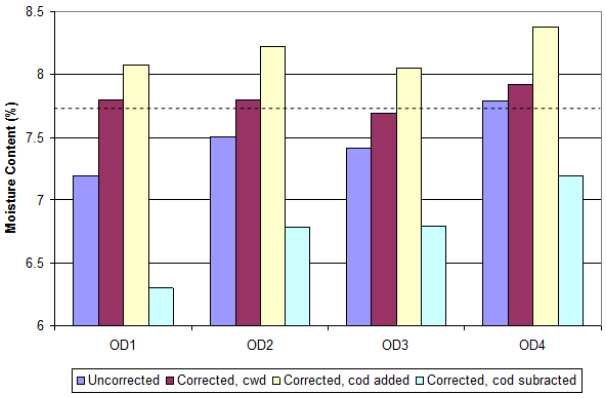

Figure 4. Grand means moisture content, uncorrected and corrected. Error symbols: cumulative with direction (*cwd*); cumulative without direction (*cod*).

Again, it is worthwhile emphasizing that the uncorrected moisture content by oven drying is derived from weight loss due to incomplete drying and weight changes due to underlying side reactions in conflicting directions.

Hypotheses and ANOVA Tables. In performing the analysis of variance, a two-part approach was used. The first part answered the question: Did the grand mean differ between any of the five treatments (OD1, OD2, OD3, OD4, and KFT)? Once differences were found, the second part became: Is there a difference between KFT and any specific OD method? Tables 8 and 9 summarize the SAS statistical findings.

Analysis of variance was performed on the data to test for whichever method differs (Table 8). In this analysis, OD treatment was a fixed effect. Cotton and cotton OD treatments were considered random effects. Least Squares estimates of treatment means were based on Fisher's Protected least significant difference (LSD). Note the null comparisons that were used. For example, consider the first comparison, F-test for noncorrected, H0: OD1 = OD2 = OD3 = OD4. Is the averaged moisture content different between any of these treatments? As another example, consider the more complex second comparison, F-test for correction with direction, H0: KFT = OD1 + .61 = OD2 + .3 = OD3 + .27 = OD4 +.13. In this case, is the averaged moisture content different between any of these treatments after adjusting for differences due to bias in oven drying?

Table 7. Raw cottons grand means (%) at moisture equilibrium, before and after bias correction[z].

	KFT	OD1	OD2	OD3	OD4
Error calculation summary: e_{cwd} **(cumulative with direction)** = $(-e_{rsw} - e_{aae} \pm e_{bwb}) + (e_{pic} \pm e_{oxd} \pm e_{con})$ e_{cod} **(cumulative without direction)** = $\lvert e_{rsw} \rvert + \lvert e_{aae} \rvert + \lvert e_{bwb} \rvert + \lvert e_{pic} \rvert + \lvert e_{oxd} \rvert + \lvert e_{con} \rvert$					
e_{loc} $(-e_{rsw} - e_{aae} \pm e_{bwb})$					
(sec AAE)					
< 10		−0.46	−0.44	n/a	−0.27
10				−0.39	
20				−0.37	
30				−0.48	
e_{glo} $(e_{pic} \pm e_{oxd} \pm e_{con})$		−0.15	0.14	0.14	0.14
e_{cwd} (cumulative with direction)					
(sec AAE)					
< 10		−0.61	−0.30	n/a	−0.13
10				−0.25	
20				−0.23	
30				−0.34	
Grand means (uncorrected and after correction via cumulative with direction):					
Uncorrected	7.83	7.19	7.50	7.42	7.79
	0.10[y]				
After corr.	7.73				
(sec AAE)					
< 10		7.80	7.80	n/a	7.92
10				7.67	
20				7.65	
30				7.76	
				7.69 avg	
Cumulative without direction error (to compare to cumulative with direction error):					
(sec AAE)					
< 10		0.89	0.72	n/a	0.59
10				0.59	
20				0.65	
30				0.66	
				0.63 avg.	

[z] See Appendix for definitions of terms and symbols, Table 2, and additional details in Materials and Methods.

[y] KFT blank value.

Table 8. Analysis of variance for grand mean difference between the five treatments (four OD and KFT)[z].

Fixed Effects	non corrected		*cwd*		*cod* added		*cod* subtracted	
	DF	F value	*p* > F	F value	*p* > F	F value	*p* > F	F value	*p* > F
OD	4	78.44	< 0.0001	6.77	0.0003	46.97	< 0.0001	379.7	< 0.0001
The following null comparisons were used:						Compare the five treatments:			
H0: KFT = OD1 = OD2 = OD3 = OD4						non corrected			
H0: KFT = OD1 + .61 = OD2 + .3 = OD3 + .27 = OD4 + .13						*cwd*			
H0: KFT = OD1 + .89 = OD2 + .72 = OD3 + .63 = OD4 + .59						*cod* added			
H0: KFT = OD1 - .89 = OD2 - .72 = OD3 - .63 = OD4 - .59						*cod* subtracted			

[z] See Appendix for definitions of terms and symbols.

Table 9. Analysis of variance for grand mean paired difference between equilibrium moisture and water content in the raw cotton[z].

	non corrected	*cwd*	*cod* added	*cod* subtracted
Standard Error of Least Squares Mean Differences				
OD1 - KFT	0.0401	0.0399	0.0396	0.0404
OD2 - KFT	0.0407	0.0406	0.0402	0.0409
OD3 - KFT	0.0431	0.0431	0.0429	0.0432
OD4 - KFT	0.0431	0.0431	0.0429	0.0432
***p* values of Least Squares Mean Differences (DF = 1), $p > \lvert t \rvert$**				
OD1 - KFT	< 0.0001	0.1590	<0.0001	< 0.0001
OD2 - KFT	<0.0001	0.3731	<0.0001	< 0.0001
OD3 - KFT	<0.0001	0.9775	<0.0001	< 0.0001
OD4 - KFT	0.0478	<0.0001	<0.0001	< 0.0001
Grand Means and Least Square Differences by Letter[y]				
KFT	7.70a	7.70a	7.70	7.70
OD1	7.19x	7.80ab	8.08ab	6.30
OD2	7.45b	7.80bc	8.11a	6.73a
OD3	7.43b	7.70c	8.06b	6.80a
OD4	7.79a	7.92	8.38	7.20

Example: the following OD1 null comparisons were used:	Compare paired treatment differences:
H0: OD1 – KFT	non corrected
H0: (OD1 + .61) – KFT	*cwd*
H0: (OD1 + .89) – KFT	*cod* added
H0: (OD1 - .89) – KFT	*cod* subtracted

[z] See Appendix for definitions of terms and symbols.

[y] Means not followed by a common letter are significant based on LSD comparisons at $p <= .05$

The extremely large F value (Table 8) for the uncorrected oven data provides statistically significant evidence that average moisture content is different between two or more of the five treatments. When three different corrections are applied, the F value drops nearly nine fold for the data corrected with direction. Without direction corrections saw an increase in the F values due to divergence of the means. This provides significant statistical evidence that the individual biases are not all unidirectional. Because of the dramatic drop in F value for with direction correction and the increase for without direction corrections, with direction sum is the best correction option, thus reducing the dramatic effect of OD treatment. Clearly, the effect of incomplete drying of cotton and the underlying side reactions, such as oxidation and release of particulate matter, produced a variance in weight loss with positive and negative components that could be corrected via algebraic correction.

Because a significant difference was found between at least two of the five treatments, pair-wise comparisons are used to identify a difference between KFT and any specific OD treatment (Table 9). Assuming common variances among the five treatments, then the best estimate of error is to combine variances across the five treatments into one estimate of error. The standard error of the mean is error/n; so if all treatments have the same number of observations in the mean then they will all have the same standard error of the mean. KFT and OD1 have same number of observations and OD3 and OD4 have same number of observations. The standard errors and *p* values are calculated by the Least Squares Differences. The mean comparisons that are of most interest are the KFT and four OD method comparisons.

There are 16 *p* values listed in Table 9 that represent the statistical results for differences between a particular OD method and KFT. At the 5% level of probability, all pair-wise differences are significant except for correction with direction: OD1– KFT, OD2 – KFT, and OD3 – KFT. From another perspective, the letters on the mean comparisons are the same as a Fisher's Protected LSD comparisons and in this case, a good enough adjustment for multiple comparisons.

CONCLUSIONS

A set of Mississippi cultivars, grown in the same location and crop year, were subjected to two possible defoliation times and gin-drying temperatures. Moisture content was measured during ginning by oven drying. Equilibrium moisture content was measured by four different OD methods (OD1, OD2, OD3, and OD4) along with equilibrium water content by the ASTM KFT reference method. The different equilibrium moisture content methods utilized different conditioning systems, different sample weights, drying oven type, location of oven in standard or normal atmosphere, and diameter and number of weighing bottles in the oven. As to the equilibrium water content method by KFT, all samples were subjected to more stringent conditioning requirements.

For all cottons the grand means equilibrium water content was about 7.73% compared to the moisture content taken during ginning, about 4.6%. The different versions of equilibrium moisture content methods did not produce the same results. The grand means equilibrium moisture content by the four OD methods for the raw cottons was (%): OD1, 7.19; OD2, 7.50; OD3, 7.42; and OD4, 7.79.

The hypothesis that the multiple biases in oven drying would not affect the difference in the equilibrium moisture and water content was developed in this study. This hypothesis was tested before and after bias correction with direction for the OD1, OD2, OD3, and OD4 grand means.

Six OD biases were measured using a control cotton and applied to the Mississippi raw cotton data. The hypothesis was accepted as true after bias correction for the grand means of all cottons analyzed by three of four OD methods (OD1 to OD3). This pilot study highlighted the need for a standard method to determine equilibrium moisture content by oven drying. The standard should include specifications for oven size, flow rate, and number of bottles dried at one time.

Additionally, when faced with a small range of moistures, having the option of tighter humidity control, such as with the saturated salts in a glove box, is essential in measuring both water and moisture contents to reduce the variability in the samples before they are tested. The form of the new standard might be a new OD method added to the existing test method for OD samples during ginning (ASTM, 2007). That concept is well established in ASTM.

DISCLAIMER

Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the USDA and does not imply approval of a product to the exclusion of others that may be suitable.

ACKNOWLEDGMENT

Appreciation is extended to Philip Godorov, Director, ASTM International Interlaboratory Study Program, for the appropriate referral to the standard water test method, ASTM D7785, with the more stringent sample conditioning of 21 ± 1 °C and 65 ± 0.5% relative humidity rather than 21 ± 1 °C and 65 ± 2.0% relative humidity in the method as written, which is expected to result in better precision of results.

ABBREVIATIONS

AAE (ambient air exposure); NCR (normal conditioned room); BWB (blank weighing bottle); CON (conditioning); GBTTR (glove box in TTR); GCO (gravity convection oven); KFT (Karl Fischer Titration); MCO (mechanical convection oven); OD1 (oven-drying method 1); OD2 (oven-drying method 2); OD3 (oven-drying method 3); OD4 (oven-drying method 4); OXD (oxidation); PIC (particulates in cotton); RSW (residual water); TTR (textile testing room); e_{aae} (bias associated with AAE); e_{bwb} (bias associated with BWB); e_{con} (bias associated with CON); e_{oxd} (bias associated with OXD); e_{pic} (bias associated with PIC); e_{rsw} (bias associated with RSW); e_{glo} (sum of e_{pic} and e_{oxd} and e_{con}); e_{loc} (sum of e_{rsw} and e_{aae} and e_{bwb}); e_{cum} (cumulative error, function of e_{loc} and e_{glo}); e_{cwd} (cumulative error with direction); e_{cod} (cumulative error without direction)

APPENDICES

GLOSSARY OF TERMS AND SYMBOLS

Conditioning Rooms and Laboratory Ovens

Textile Testing Room (TTR): room maintained at 21 ± 1°C and 65 ± 2% relative humidity

Glove Box in Textile Testing Room (GBTTR): humidity chamber (370 L) in the textile testing room containing an aqueous salt solution (sodium nitrite) to produce 65 ± 0.5% relative humidity

at 21 ± 1°C, temperature maintained by heat exchanged through the walls of the chamber

Normal Conditioned Room (N**CR):** room maintained at normal building conditions, heated in the winter and air conditioned in the summer

Gravity Convection Oven (**GCO):** 1 ft^3 internal volume natural convection oven

Mechanical Convection Oven (MCO): forced convection oven

Equilibrium Water and Moisture Contents

Equilibrium water content: specific measure of all water (free plus bound) by Karl Fischer Titration in the cotton test specimen after equilibration for at least 24 h in the GBTTR, expressed as a percentage of the mass of the specimen taken for analysis (wet basis in this paper)

Equilibrium moisture content: measure of all weight loss by OD methods in the cotton test specimen after equilibration for at least 24 h in either the GBTTR or TTR, expressed as a percentage of the mass of the specimen taken for analysis (wet basis in this paper)

Water: the chemical compound H_2O

Oven-Drying (OD) Methods

Standard Oven Drying (SOD): classic OD method (ASTM D2495) to determine moisture content (wet basis) at an oven temperature of 105°C to 110°C at a specified time or under prevailing conditions, samples are not conditioned

Oven-Drying Method #1 (OD1): specific OD method to determine equilibrium moisture content (%, wet basis) by conditioning in a GBTTR, drying in a GCO placed in the TTR at 105°C, and a specified size and number of weighing bottles in the oven

Oven-Drying Method #2 (OD2): specific OD method to determine equilibrium moisture content (%, wet basis) by conditioning in the TTR, drying in a GCO located in the TTR 105 °C, and a specified size and number of weighing bottles in the oven

Oven-Drying Method #3 (OD3): specific OD method to determine equilibrium moisture content (%, wet basis) by conditioning in the TTR, drying in a MCO placed in a NCR at 105 °C, and a specified size but no limit on the number of weighing bottles in the oven

Oven-Drying Method #4 (OD4): specific OD method to determine equilibrium moisture content (%, wet basis) by conditioning in the TTR, drying in a MCO placed in a NCR at 105°C, and a specified size and limit on the number of weighing bottles in the oven

Moisture Recovery Parameters and Related Biases in Oven Drying

Local bias (e_{loc})

Residual Water (RSW): residual water (%, wet basis) retained in oven drying, simulated by measuring water retained in 0.1 g cotton in a KFT vial, after oven drying the oven door opened and vial immediately capped

Ambient Air Exposure (AAE): moisture pickup (%, wet basis) retained in oven drying when handling a large number of weighing bottles in the oven, simulated by measuring water retained in 0.1 g cotton in a KFT vial, after drying the oven door opened and a delay of at least 10 sec before the vial is capped, moisture pickup is greater than residual water

Blank Weighing Bottle (BWB): change in weight (%, relative to cotton sample weight) of a conditioned blank weighing bottle, before and after heating in the drying oven

Residual Water Bias (e_{rsw}): RSW expressed as a bias (%, wet basis) with proper algebraic sign

Ambient Air Exposure Bias (e_{aae}): AAE expressed as a bias (%, wet basis) with proper algebraic sign

Blank Weighing Bottle Bias (e_{bwb}): BWB expressed as a bias (%, wet basis) with proper algebraic sign

Local Biases (e_{loc}): biases measured in each of the four oven drying methods, OD1 to OD4, algebraic sum of e_{rsw}, e_{aae}, and e_{bwb}

Global bias (e_{glo})

Particulates in Cotton (PIC): amount of particulates (%, wet basis) removed from cotton during oven drying in an inert atmosphere, not confounded by oxidation (measured at 105°C by method of Cheuk et al., 2011), applied equally to the four OD methods OD1 to OD4

Oxidation (OXD): measured as the amount of water (%, wet basis) consumed as a reactant at 105°C in

OD1, simulated with 0.1 g cotton in a capped KFT vial and applied to OD1 because air flow in the oven is low, does not apply to OD2 to OD4, global bias because the approach accounts for entire scope of study

Conditioning (CON): change in water content (%, wet basis) in cotton due to conditioning error (drift) relative to conditioning the samples for water content by KFT, assigned the value zero percent for OD1, because KFT and OD1 samples conditioned in the same way, glove box in textile testing room (GBTTR), does not apply to OD2 to OD4, global bias because the approach accounts for entire scope of study

Particulates in Cotton Bias (e_{pic}): PIC expressed as a bias (%, wet basis) with proper algebraic sign

Oxidation Bias (e_{oxd}): OXD expressed as a bias (%, wet basis) with proper algebraic sign

Conditioning Bias (e_{con}): CON expressed as a bias (%, wet basis) with proper algebraic sign

Global Biases (e_{glo}): biases measured in each of the four OD methods, OD1 to OD4, or measured by a technique applied only to OD1 and the result does not apply to the other three OD methods, algebraic sum of e_{pic}, e_{oxd}, and e_{con}

Cumulative and Confounding Error

Cumulative Error (e_{cum}): function of e_{loc} and e_{glo}

Cumulative Error with Direction (e_{cwd}): algebraic sum of the six individual biases

Cumulative Error without Direction (e_{cod}): sum of the absolute values of the six individual biases

Confounding Error: confounders are individual biases that affect the cumulative error with direction outcome due to opposing signs in summing

ESTIMATING THE GLOBAL BIASES

Particulates in cotton (PIC). Our first hint that particulate matter in cotton was released in oven drying was when we noted that the inside of the gravity convection oven used to dry samples was dirty in appearance (Fortier et al., 2014; Montalvo et al., 2010). After cleaning, it appeared dirty again when the oven was used to dry cotton. Some of the material was captured for qualitative image analysis by placing a sticky glass slide face down atop the weighing bottles. The images were quite revealing and showed broken fibers and particulate matter from the trash and dust.

To quantify the particulates being released, 50 g of cotton was distilled at 105°C in an all glass apparatus equipped with a water condenser followed by two collection traps in series, one held at room temperature and the other in a acetone/dry ice bath (Cheuk et al., 2011). Three dry carrier gases for transporting the recovered water vapor and PIC to the condenser or downstream traps, were available for distillation: air, nitrogen, and argon. Two commercial cottons were distilled in all three gases. Particulate matter was deposited on the inside wall of the water condenser; recovered water was found in the collection trap at room temperature. No measureable amount of organic material was found in either of the two traps.

The dry air produced the most thermal residue compared to the other two gases (%, wet basis, average of the two cottons): air, 0.47 ± 0.13; nitrogen, 0.18 ± 0.01; and argon, 0.10 ± 0.01. Given nitrogen and argon's chemical inertness, the oxygen in the dry air caused the cotton to decompose more readily and produce additional particulate matter associated solely with oxidation. However, other studies have shown that the weight loss in oxidation of cotton in oven drying is also accompanied by some weight gain (Cheuk et al., 2011; Montalvo et al., 2010).

Assigning the particulates in cotton bias (e_{pic}) the value 0.47% is obviously incorrect; that value is inflated by oxidation of cellulose and needs to be offset by the weight gain associated with cotton oxidation. Unfortunately, we do not know the correct value to assign to the weight gain. Thus, we make the simplifying assumption that the net weight loss bias in oven drying due to particulates in cotton (e_{pic}), and not confounded by oxidation, is that which is produced in an inert carrier gas. The results for the two cottons, in nitrogen and argon, were averaged: $(0.18 + 0.10)/2 = 0.14 \pm 0.05\%$. In Table 5, the e_{pic} bias is assigned the value 0.14% to all four OD methods.

Oxidation (OXD). As discussed in the above section, weight loss, weight gain, and generation of particulate matter have all been implicated in oxidative mechanisms in the oven drying of cotton. Another mechanism we considered here and perhaps the most promising approach to estimate the oxidation bias (e_{oxd}) in OD1 is the possible consumption of water during thermo-oxidative degradation of cotton in a sealed KFT vial. We asked the question "What is the role of water in thermo-oxidation of

cellulose?" Most of the published work in this area deals with paper. Its effect on oxidative degradation mechanisms is complex, but water is also a reactant (Strlic et al., 2005). The rate of cellulose degradation increases with relative humidity.

To summarize the OD1 method, drying was performed with the GGO in the TTR. One dozen tall, narrow diameter weighing bottles containing 1.0-g samples were placed in the small oven (air exchange rate = 10.3 min compared to 1.92 min in the MCO). The grand means moisture equilibrium content for OD1 (Table 3) was, in fact, smaller than that of the other OD methods. (This was confirmed with the control cotton that had been bleached and scoured.)

To account for this difference, we made the simplifying assumption that the water is held in the still, warm air in the towering weighing bottles for a longer period of time, and that a fraction of the water is consumed in oxidative degradation of the cellulose. The assumption was tested with the control cotton conditioned to moisture equilibrium in the TTR, 0.1-g samples in KFT vials sealed with septum cap, placed in the OD1 oven, the septum caps weighed down with a metal weight to ensure a leak-free seal, and thermo-oxidation allowed for 1 h (trial time selected from thermogravimetric analysis data) at 105°C. After cooling, the vials were assayed by KFT along with similar vials that had not been heated in the oven. The measured water content after thermo-oxidation was, in fact, 0.60% smaller than without the oxidative step.

This value was normalized to actual OD1 conditions before taken as the estimated oxidation bias. The corrections involved calculating the pressure in the sealed vial at 105°C and a more exact reaction time estimated from thermogravimetric analysis-quadrupole mass spectrometry (TGA-QMS) results. The calculated pressure in the sealed reaction vial at 105°C was 1.19 atm (sample contained 0.444 mmoles of water, vial volume of 9 mL). For the reaction time computation, we selected TGA because the crucible in the TGA oven is a small gravity convection oven with porous cover; carrier gas flow into the QMS picks up released water at a point outside of the crucible. The continuous mass 18 (water) ion current versus time plot for the control cotton using dry air as carrier gas at 105°C and 1 atm (Montalvo et al., 2010, Figure 8b) was examined. Linear extrapolation of the initial rate of drying and plateau of the curve produced two lines that intersected at the estimated drying time of 34 min. Therefore, by normalizing the 0.60% water consumption in thermo-oxidation to 34 min and 1 atm, the estimated oxidation bias in OD1 is

$$e_{oxd} = -0.60\% \text{ x } (34/60)(1/1.19) = -0.29\%.$$

In Table 5, the e_{oxd} bias was assigned this value for OD1 only. This approach to estimating e_{oxd} does not apply to the other three OD methods; there was a smaller number of bottles in the oven or a mechanical convection oven was used.

Conditioning (CON). As to the fiber conditioning bias (e_{con}), only OD1 and KFT samples were conditioned in the same environment with tighter humidity control, i.e., the GBTTR (Table 2), so that e_{con} = 0% water for OD1. This bias does not apply to the other OD methods.

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