UNDERSTANDING THE BIAS BETWEEN MOISTURE CONTENT BY OVEN DRYING AND WATER CONTENT BY KFT AT MOISTURE EQUILIBRIUM

J. Montalvo
T. Von Hoven
Southern Regional Research Center
New Orleans, LA
R. Byler
U.S. Cotton Ginning Laboratory
Stoneville, MS

Abstract

Previous research in this laboratory has highlighted the differences between water content as determined by Karl Fischer Titration and moisture content by oven drying at moisture equilibrium. An extensive literature review revealed biases present in moisture content measurements; new biases were discovered in our laboratory. These biases were carefully estimated by varying sample conditioning, albeit within standard testing conditions, as well as oven drying techniques. The current list of biases (residual water remaining in cotton, ambient air exposure, blank weighing bottle, particulate matter, oxidation, and conditioning) is by no means exhaustive, nor was the study intended to suggest a preference for either method, but rather a means to explain differences between the two methods and decide if bias correction may be used to improve methods agreement. The current paper is an overview of the more detailed investigation.

Introduction

Water content by Karl Fischer Titration (KFT, ASTM D7785, 2012) was measured at moisture equilibrium in the lint cotton from five MS cultivars, all grown in the same area and crop year, but defoliated at different times and gin-dried at two possible temperatures (Von Hoven et al., 2012). Overall, the mean water content across all samples analyzed was (%): raw, 7.83; cleaned, 7.69; and scoured and bleached, 8.10. *Within* cultivar water content range of the averaged values was (%): raw 0.01 to 0.19, mechanically cleaned, 0.03 to 0.13, and scoured and bleached, 0.03 to 0.08. *Between* cultivar range was (%): raw, 0.20; mechanically cleaned, 0.20; and scoured and bleached, 0.25. These small ranges are presented to show how small these limits actually are, and that data can be seriously skewed by any biases that occur.

An exhaustive literature review of oven drying methods to measure moisture content (Montalvo and Von Hoven, 2008) included critical analysis of the errors. Key papers included Davidson and Shorter (1930), who indicated that residual moisture remained in the cotton after drying and substances other than water released during heating were the most prevalent errors. 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 inter-laboratory project that included cotton among other materials. The most relevant conclusion of this major work was that the oven drying method has many unidentified errors that should be reduced, if not eliminated (Terrell, 1967a, b).

The KFT and oven drying methods are inherently different and thus agreement must be demonstrated, particularly with small ranges at moisture equilibrium. While Karl Fischer Titration (KFT) specifically measures the total amount of water, both free and bound, in lint cotton (ASTM D7785, 2012; Montalvo, Von Hoven, and Cheuk, 2011), standard oven-drying (SOD) measures moisture content (ASTM D2495, 2007) as the total weight loss. Both results are expressed as a percentage of the moist material.

In a comprehensive study to probe bias reduction in oven-drying, and therefore, improve comparability of lint cotton water and moisture contents at moisture equilibrium, six biases were identified (Montalvo et al., in press). One bias was identified as particulates in cotton; another two were oxidation and the residual water remaining in the sample after drying (Montalvo et al., 2010; Rodgers et al., 2010; Cheuk et al., 2011, Fortier et al., 2013). Also, a blank weighing bottle, containing no sample, was placed in the oven to measure any moisture that may be present on the glass itself after treatment, dubbed as blank weighing bottle bias and represented the fourth bias. Next, the fifth bias was termed ambient air exposure and was concerned with the length of time the oven dried samples were exposed to conditioned air prior to being capped. The sixth and final bias dealt with sample conditioning. Even within the confines of a textile conditioned laboratory, variations do occur due to the cyclical nature of controlling the

environment to within 2°F and 2 % RH of the target values of 70°F and 65 % RH (ASTM D1776, 2008). A glove box containing saturated salts in a lab conditioned to textile conditions provided even tighter humidity control within the recommended tolerances. This bias is denoted as conditioning. A recent study concluded that conditioning in the glove box led to more consistent water results compared to conditioning in the room (Montalvo et al., 2013).

Another part of the comprehensive study (Montalvo et al., in press) used KFT where possible to estimate the identified oven-dried biases at moisture equilibrium. Due to their homogeneity, cotton fibers that have been scoured and bleached were used for bias estimations. Four different oven treatments were used representing different oven drying techniques. Table 1 summarizes the terminology in this paper. In the final segment of the study (Montalvo et al., in press), the estimated oven-drying biases estimated with scoured and bleached cotton were summed and added to the mean moisture contents of the MS cultivars to determine if the data would agree with KFT water content values. The purpose of the current paper is to give an overview of the more detailed investigation (Montalvo et al., in press).

We should note that the failure to the industry-supported-ASTM study to understand the errors in oven drying of cotton samples (Terrell, 1967a,b) was probably due to (a) failure to limit the number of independent variables including crop year and area grown, which may be associated with additional biases and (b) not using the more specific Karl Fischer Titration method, which was already developed as a manual method at that time.

Table 1. Glossary

Term	Definition
Equilibrium water content	Water in test specimen by KFT after moisture equilibrium in a glove box in textile testing room (GBTTR), wet basis (%)
Equilibrium moisture content	Measure of weight loss in test specimen by oven drying methods after equilibrium in GBTTR ot TTR, wet basis (%)
Oven-drying (OD) methods	Specific oven-drying methods, OD1 to OD4, to measure equilibrium moisture content with particular oven attributes: location, type of oven, # weighing bottles in oven
Individual biases (six)	Residual water remaining in test specimen (1), ambient air exposure (2), blank weighing bottle (3), particulates in cotton (4), oxidation (5) and conditioning (6)
Total bias	Algebraic sum of individual biases

Materials and Methods

Conditioning Systems

Following standard textile testing conditions, a conditioning room set to 21 ±1°C and 65 ±2% relative humidity was used. Cotton samples were conditioned to moisture equilibrium for 24 hrs before measuring moisture and water content in a textile testing room (TTR). To improve humidity control, a glove box (GBTTR) was used within the conditioned lab with a saturated aqueous sodium nitrite solution to control to 65% ± 0.5% RH (Wink and Sears, 1950).

Cottons

Twelve cottons that have been studied previously (Von Hoven and Montalvo, 2013) were used in this overview of detailed work. Five cultivars grown in Stoneville, MS in 2009, were micro-ginned at the ARS facility there. Standard gin processing was used with dryer 1, cylinder cleaner, stick machine, dryer 2, second cylinder cleaner, extractor-feeder gin stand, 1 lint cleaner. The two possible dryer settings were 32.2°C (Low) and 82.2°C (High). In addition, two cultivars had an early defoliation date, thus 12 samples (Table 2). Each bag was ginned separately.

Moisture Content by Standard Oven Drying

Two laboratory ovens were used (Table 3 and Figure 1), one a gravity convection oven (GCO) VWR Model 1310 GCO 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 textile conditioned lab (TTR). The GCO was used in two of the four oven drying methods used in this study (Table 3). The other was a Yamato DKN 600 mechanical convection oven (MCO) with a 150 L capacity, a mean flow rate of approximately 1.3 L/sec and was placed in a non-conditioned laboratory (NCR), used in two of the oven drying methods (Table 3). For all OD procedures, samples were weighed with gloved hands. Glass caps and weighing bottles were also conditioned and were weighed to ± 0.0001g. The conditioned samples were placed in the bottles, reweighed prior to oven treatment, and placed in the 105^{o}C oven for 24 hours. Following the oven heating, the bottles were capped while in the oven, placed in a desiccator with desiccant and allowed to cool. The desiccators were then moved into the conditioned lab; the capped bottles were 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.

Table 2. 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

Table 3. Experimental: KFT and Oven Drying (OD) Methods Summary

	Conditioning Room		Drying Oven		Bottles in oven	Vial Size
Method	TTR	GBTTR	Location	Type	#	mm x mm
KFT		yes	NCR	single sx	1	9 (ml)
OD1		yes	TTR	GCO	12	25 x 50
OD2	yes		TTR	GCO	6	40 x 50
OD3	yes		NCR	MCO	100	40 x 50
OD4	yes		NCR	MCO	6	40 x 50

In OD1 and OD2 (Table 3), the gravity convection oven located in a textile testing conditioned lab is utilized. For OD1 glove box conditioning and slender vials are used because they better replicate the vials used in KFT. Twelve 0.1 g samples were in the oven at one time, 3 replicates cotton. For OD2, 1.0 g samples were condition to standard textile conditions and the standard weighing bottles were used in the GCO with 3 replicates per cotton.

For OD3, the testing room conditioned samples, approximately 1.50 ± 0.01 gram with five replicates per cotton, were weighed and the weighing bottles were used in the MCO. OD 4 utilized the standard weighing bottles in the

MCO, with 3 replicate 1.0 g sample per cotton. Empty weighing bottles were also subjected to the OD treatments to measure the value of a blank weighing bottle error.

Water Content by Karl Fischer Titration

Karl Fischer Titration is a procedure specific for water in cotton and has a recovery of 99.99% (Montalvo, Von Hoven, and Cheuk, 2011; Cheuk et al., 2011). Measurements were made following the OD1 conditioning procedures for the 0.1 g samples (GBTTR). 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.

Experimental Design

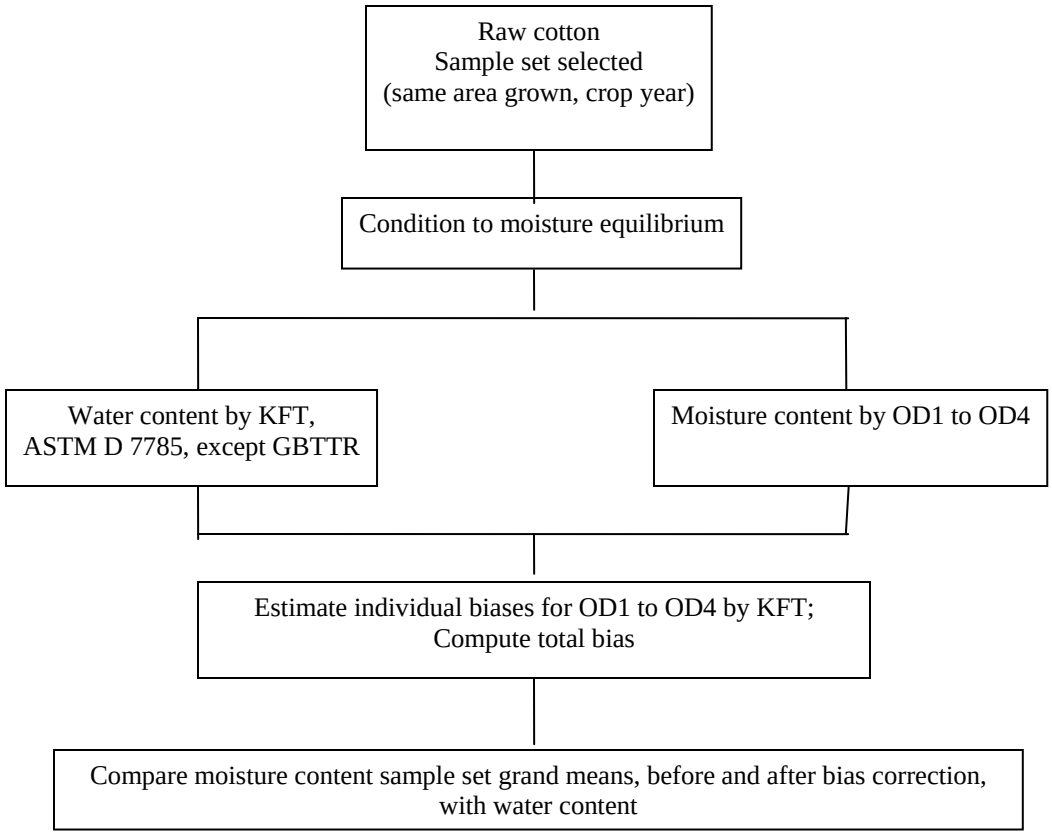

Figure 1. Experimental Design

Bias Estimation

The estimates of the biases that occur during all oven drying conditions were made on mechanically cleaned, scoured and bleached commercially available cottons. To estimate ambient air exposure, samples in KFT vials were removed from the MCO in a non-conditioned room and capped after 10 sec, 20 sec, 30 sec, to simulate the time required to place caps on a large number of weighing bottles; the water contents were 0.42, 0.44 and 0.50 for the 10, 20, 30 sec intervals. Simulation of residual water was carried out by placing the KFT vials in an oven, immediately capping them within the oven and measuring the remaining water via KFT, 0.30% water content was found.

Biases attributed to particulate matter, oxidation, and conditioning were all measured in previous research (Montalvo, et al., in press). Particulates were estimated when 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). With the use of air as a carrier gas, the particulate matter was estimated (Montalvo et al., in press). The error due to oxidation is estimated by the consumption of water during thermo-oxidative degradation of cotton in a sealed KFT vial at 105°C (Montalvo et al., in press). Conditioning errors occur with small fluctuations in humidity that occur even within a textile testing conditioned laboratory.

Results and Discussion

The discrepancies between the oven drying and Karl Fischer results are due to the fact that the oven moisture test method (sensor measures weight loss) is nonspecific for water and not all of the water is removed in oven drying. Figure 2 shows the differences between the grand mean moisture content of the oven drying methods and KFT water content before any corrections were made. In this context, grand mean refers to the mean across the 12 cottons at fixed OD practice. Better agreement is sought by estimating the changes in the amount of water remaining in the samples when oven drying in conditioned air, unexplained variance in relative humidity in room conditioning or changes in the extent of sample oxidation, which may vary with maturity.

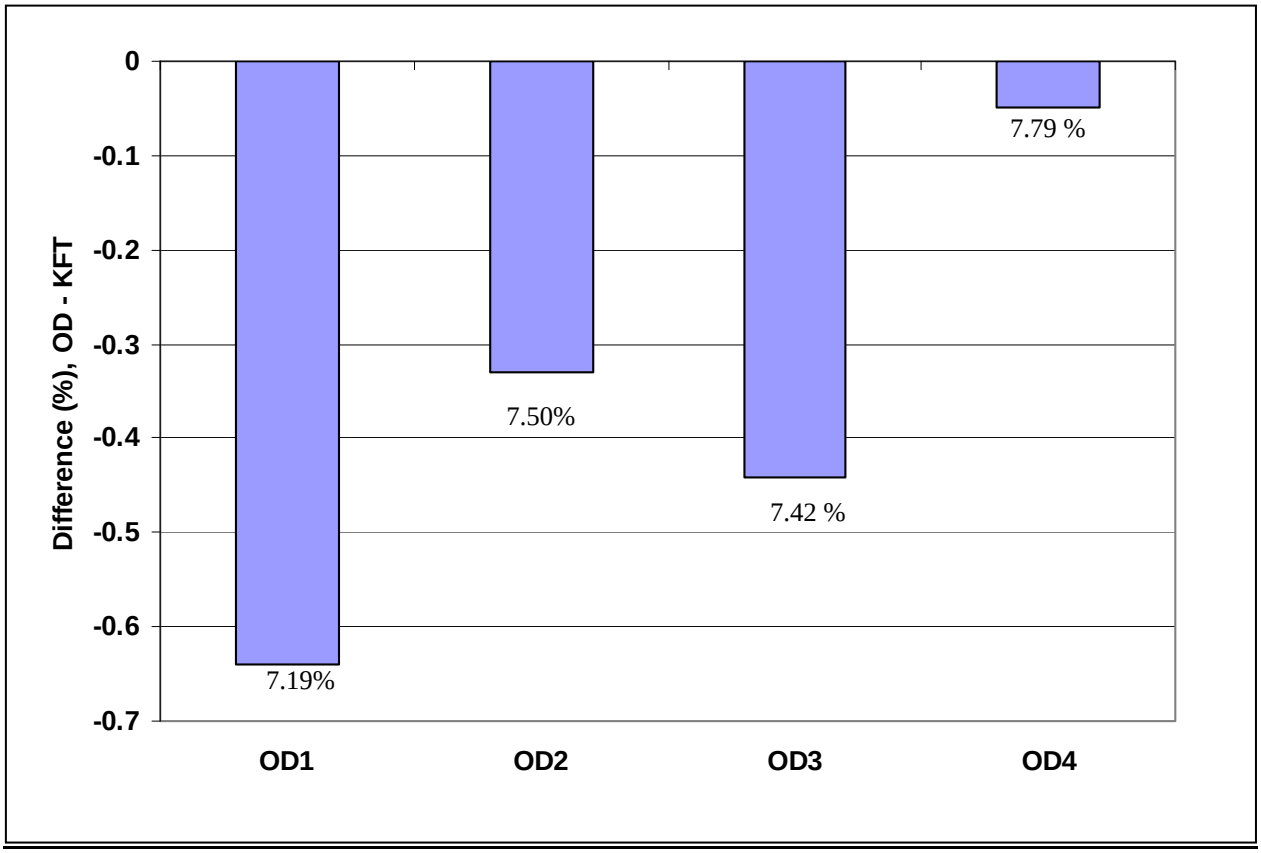

Figure 2. Grand Mean Difference: Equilibrium Moisture and Water Content (before correction) 7.83% water content by KFT; OD1 and OD2 textile testing room conditions with gravity convection oven; OD3 and OD4 normal conditioned room with mechanical convection oven

The KFT value is corrected for its blank value, Table 4. To correct the oven drying methods, the simple algebraic sum of the estimated biases was subtracted from the measured values. After correction, agreement between OD methods and KFT was much better. In fact, after bias correction there are no statistically significant differences between KFT values and OD1, OD2 and OD3. Significant differences are present between the corrected OD4 and KFT values. Table 4 also shows the sum of the absolute values of all the biases, demonstrating how significant the biases may be if they were all in the same direction.

Table 4. Raw Cotton Grand Means (%) at Moisture Equilibrium

	KFT	OD1	OD2	OD3	OD4
Bias calculation summary: E_{tot} (%) = - e_{rsw} – e_{aae} + e_{bwb} + e_{pic} ± e_{oxd} ± e_{con} (rsw= residual water, aae = ambient air exposure, bwb = blank weighing bottle, pic = particulate matter in cotton, oxd = oxidation, con = conditioning ; ox and con errors may be ± depending on drying conditions					
Algebraic sum		-0.61	-.030	-0.27	-0.13
Absolute value sum		0.89	0.72	0.66	0.59
Before Correction (blank value, KFT)	7.83 0.10	7.19	7.50	7.42	7.79
After correction	7.73	7.80	7.80	7.69	7.92

As one example of bias estimation, the residual water and ambient air exposure biases are represented graphically as a function of time in Figure 3. This figure demonstrates how the bias increases with the amount of time the dried sample vials are exposed to room air, in a very linear fashion, proving that exposure time should be dramatically limited, if not eliminated, since the very dry cottons are quick to pick up what ever water is in the air. Of course, the bigger problem is the residual water which probably varies for raw, ginned, and scoured and bleached.

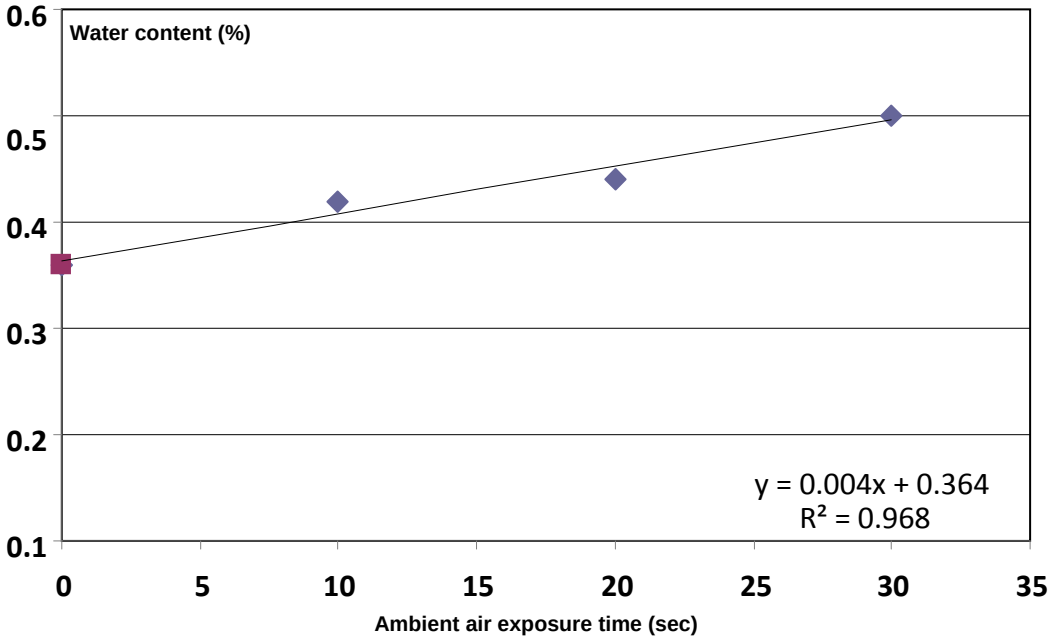

Figure 3. Example Bias Estimates of Ambient Air Exposure (AAE, 10, 20 30 sec) on Residual Water (RSW, 0 sec).

Conclusions

There are many reasons that differences in measured values at moisture equilibrium will occur between weight loss as measured by oven drying techniques and water content as measured by KFT. These differences, or biases, were estimated by varying oven drying techniques, ovens and specialty conditioning, and demonstrating that these biases can indeed be tracked, quantified and suppressed. After an algebraic summation of OD biases is applied to the data, the corrected values are no longer significantly different compared to KFT. The summed absolute values of OD biases demonstrate the possible extent of the biases; the mass fraction of moisture content due to water is a function of all the biases. Additional possible biases may exist, such as crop year and area grown. Because the weight loss by oven drying and water content by KFT agreed after correction, some standardization of the oven drying techniques may be of help to determine equilibrium moisture content by oven drying. Information on the biases observed at moisture equilibrium allows better use of equilibrium moisture content data.

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