UNDERSTANDING WATER CONTENT DATA IN COTTONS EQUILIBRATED TO MOISTURE EQUILIBRIUM

J. Montalvo
T. Von Hoven
Southern Regional Research Center
New Orleans, LA
R. Byler
U.S. Cotton Ginning Laboratory
Stoneville, MS
James Knowlton
AMS Cotton Program
Memphis, TN

Abstract

The accurate measurement of moisture in cottons conditioned to moisture equilibrium and understanding the data are prerequisites to the development of applications of the data. In this study, moisture is measured by Karl Fischer Titration, which is highly selective for water in cotton; the results are referred to as water content. The main locations of water in raw cotton are the botanical trash, other non-cellulosic materials and the fiber's cell wall. To aid in understanding the data in samples conditioned to moisture equilibrium, water is directly measured in the raw material, mechanically cleaned lint, and scoured and bleached fibers. The contribution of the water in the trash and in the non-cellulosic substances to the total level in raw cotton is estimated from differences in the observed readings. The contribution of the water in the main constituent (cellulose) of the fiber's cell wall to that in raw cotton is taken as the water concentration in the purified fibers. The ranges of water contents were dramatically different for two sample sets investigated. In one set, water content for the cottons with the same growing conditions showed little dependence on micronaire. Additionally, this set showed smaller ranges as well as consistent values for the directly measured and estimated entities. The other set revealed a complex relationship with micronaire and inconsistent values for the water entities. This study indicates that extraneous materials in the sample matrix can limit the range of water content in raw and mechanically cleaned cotton. When cotton samples are from one growth area and a recent crop year, the range of water content is minimized and better understood.

Introduction

The critical nature of moisture is well known and expressed by Mayfield et al. (2011) as "… the most important single factor affecting fiber quality during ginning." Gins use drying equipment in order to facilitate seed removal and fiber cleaning with minimum damage. Also, moisture is sometimes added just prior to baling to restore moisture that was removed early in the ginning process. There is a clear understanding that drying the seed cotton in the gin reduces moisture content during ginning.

Standard conditioning of cotton fibers to moisture equilibrium at 70^{o} F and 65 % RH is set forth as the fiber testing conditions (specifically, as specified in ASTM 1776, 2008). Cotton researchers have recognized that moisture has a significant effect on strength, length, and micronaire measurement results yet little is understood of moisture content data in cottons equilibrated to moisture equilibrium. For example, how does the location of moisture in the various components of raw cotton (trash, other non-cellulosics, and the fiber's cell wall) influence the moisture equilibrium process? Do growth area, crop year and cultivar influence the results? Also, do the botanical trash and other non-lint material in raw cotton have an impact on the total moisture content?

Previous research has indicated that at moisture equilibrium, with cottons from the same growth area and crop year, different levels of cleaning of raw cotton produced cottons with little change in water content across the range of micronaire values (Von Hoven, et al., 2012). In that paper, moisture was analyzed by Karl Fischer Titration (KFT, ASTM D7785, 2012) and reported as water content rather than moisture content by standard oven drying (ASTM D2495, 2007). The KFT technique is highly selective for water. All weight loss in the oven drying procedure is attributed to moisture even though other components of the raw fiber may also be lost in drying, so not all of the weight loss is from the water.

To help understand how to interpret water content results at moisture equilibrium, a similar study is presented in this paper, with cottons from different growth areas and crop years. The different crop years would provide for comparing fresh to aged cotton results. Also, mathematical models are derived to study the amount of water in the three main components of raw fiber: botanical trash, non-cellulosics (substances removed by scouring and bleaching) and the fiber's cell wall. Next, experimental methods are developed to separate raw cotton into the three components, condition all samples to moisture equilibrium, then measure water contents by KFT. Once the data are produced, the amounts of water in the extraneous materials are compared to the total water content of raw fibers, as well as influence of growth area, variety, crop year and aging in the cotton warehouse. This is a preliminary report of water content in raw fiber components as measured by KFT.

Fundamentals

In generating the mathematical models to describe the water content in the various components of raw cotton a series of equations were derived. In these equations, W = water content (%), t = total, raw = lint cotton before processing, mc = mechanically cleaned, sb = scoured and bleached, tr = trash, nc = non-cellulosics, pf = purified fiber, F = mass fraction, and EW = estimated water content. The non-cellulosic chemicals of cotton are usually located in the cuticle of the fiber; these chemicals consist of protein, wax, sugar, and electrolytes.

The water contents of the raw fiber, the mechanically cleaned, and the scoured and bleached fiber are all measured directly by KFT, where as the contribution of the water in the trash, non-cellulosics and cell wall to the total water content are estimated from the measured values. The total water content (%) in the raw fiber (Eq. 1) may be expressed as the sum of the water content in each of the above three components of raw cotton multiplied by the respective mass fraction.

In this paper, the symbols for the directly measured parameters by KFT are: the water content (%) of the raw fibers (W_{raw}), mechanically cleaned (W_{mc}), and the scoured and bleached fibers (W_{sb}). The symbols for the estimated contribution of each term in Eq. 1 to the total water content in raw fibers are: water content in the trash (EW_{tr}), non-cellulosics (EW_{nc}), and the purified cell wall by scouring and bleaching (EW_{pf}), Eqs. 2 to 4.

$$W_t = W_{raw} = F_{tr}W_{tr} + F_{nc}W_{nc} + F_{pf}W_{pf} \quad (1)$$

$$F_{tr}W_{tr} \approx EW_{tr} = \left| W_{raw} - W_{mc} \right| \quad (2)$$

$$F_{nc}W_{nc} \approx EW_{nc} = \left| W_{mc} - W_{sb} \right| \quad (3)$$

$$F_{pf}W_{pf} \approx EW_{pf} = W_{sb} \quad (4)$$

Note that the contribution of the first term to the water content in Eq. 1 is estimated (EW_{tr}) as the absolute value of the difference between the water contents in the raw and mechanically cleaned fibers (Eq. 2). The contribution of the second term is approximated (EW_{nc}) as the absolute value of the difference between the water contents in the mechanically cleaned, and scoured and bleached fibers (Eq. 3). The absolute value difference is used rather than the real value difference (positive or negative) because we are assuming in this preliminary paper that other possible moisture absorption processes are not occurring (e.g., additional water taken up by the cell wall after removal of non-cellulosics).

Finally, the contribution of the last term to the water content in Eq. 1 is approximated (EW_{pf}) as the water content in the scoured and bleached fiber (Eq. 4) since F_{pf} is close to 1. The estimated water contents of the extraneous material (EW_{tr} and EW_{nc}) give a synopsis of the two sets of cottons examined in this study.

Materials and Methods

The flow chart in Figure 1 provides a visual outline of this study. It highlights the experimental approach to estimate water content values of the trash (EW_{tr}), non-cellulosics (EW_{nc}), and purified fibers (EW_{pf}) based on the directly measured KFT values for the raw cotton (W_{raw}), mechanically cleaned (W_{mc}), and scoured and bleached fibers (W_{sb}).

Cottons and Gin-Drying Treatments

Two sets of cottons were used in this study. The first was a set of 12 from 2009 in the same growing area with a micronaire range of 3.5 to 4.7. To achieve this micronaire range, five cultivars were grown in Stoneville, MS with two possible defoliation dates. These cottons were subjected to standard gin processing with dryer 1, Cylinder Cleaner (CC), stick machine, (SM), dryer 2, Cylinder Cleaner (CC), Extractor-Feeder/Gin Stand (EFGS), one lint cleaner. The two possible dryer settings were 32.2°C, 90°F (Low) and 82.2°C, 180°F (High), respectively. Each of the 12 bags was ginned separately (Table 1). The other set was a set of six AMS samples comprised of different areas grown, crop years, and an unknown number of cultivars with a micronaire range of 2.7 to 5.5.

Cleaning Treatments of the Lint Samples

For both sets of cottons, there were three levels of cleaning in this study: none, mechanically cleaned, and scoured and bleached. Mechanically cleaning the samples involved passing one hundred gram cotton fiber samples through the Shirley Analyzer two times. Additionally, for the AMS cottons, Table 2, the Shirley waste trash was hand carded over a clean, white surface while allowing the waste to fall on the prepared surface. Trash particles and entrained fibers were collected and separated with the aid of forceps, carefully removing the botanical trash for water content measurement by KFT.

To remove the non-cellulosics and natural color of the cottons, samples were scoured and bleached. Three grams of each raw cotton 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.

Conditioning Systems

Following standard textile testing conditions, a conditioning room set to 70°F and 65% relative humidity was used. 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). The glove box also contained a fan to circulate air, a balance, and a thermometer; the thermometer was connected to a digital recorder placed outside the box. All cotton samples, raw and processed, were conditioned to moisture equilibrium for 24 hrs in the glove box.

Water Content by Karl Fischer Titration

Following the standard period for conditioning 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 (ASTM, 2012; Montalvo et al., 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.

Water content was measured by Karl Fischer Titration (KFT) (Montalvo et al., 2011). In practice, the specimen tested is placed in a glass container, sealed with a septum 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.

In more detail, the Karl Fischer samples were conditioned, weighed, placed in vials, and capped while in the glove box. Following the outline of Figure 1, 0.1g samples were conditioned in a glove box with a final weight determination taken just prior to KFT testing. 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

MS Cottons

The MS cottons were analyzed by KFT within a year of harvest. Mean values for the directly measured water parameters in the MS set of cottons (Table 1) were ($W_t = W_{raw}$ = 7.83 %, W_{mc} = 7.69 %, and W_{sb} = 8.10 %). The scoured and bleach samples had the highest water contents, followed by the raw fibers and lastly by the mechanically cleaned fibers. The corresponding water content ranges for the same parameters (Table 2 and Figure 2) are relatively small ($W_t = W_{raw}$ = 0.37 %, W_{mc} = 0.30 %, and W_{sb} = 0.28 %). Note the increased variability of all KFT directly measured water contents in the micronaire range 3.8 to 4.57 (Figure 2). However, most of the values within a sample treatment are not significantly different (Von Hoven et al., 2012).

As predicted by modeling (Montalvo and Von Hoven, 2012), the water content in all 12 mechanically cleaned cottons should be slightly less than that in the raw material (i.e., $W_{mc} < W_{raw}$). Models were developed as a function of the mass fraction of trash removed in cleaning, and the water contents in the trash and cleaned cottons. The experimental values for the MS cottons compared well with the predicted difference in W_{raw} and W_{mc}. The water content in the botanical trash is greater than in the raw cotton. Consequently, W_{mc} must be less than W_{raw}.

Mean values for the contribution of the estimated water parameters in the MS set of cottons to the water content in raw cotton (Table 1) were (EW_{tr} = 0.14 %, EW_{nc} = 0.40 %, and $W_{sb} = EW_{pf}$ = 8.10 %). The corresponding water content ranges for the same estimated parameters (Table 2 and Figure 2) is relatively small (EW_{tr} = 0.21 %, EW_{nc} = 0.41 %, and EW_{pf} = 0.28 %). Unfortunately, the W_{sb} points lie above the $W_{raw} = W_t$ line (Figure 2) rather than below the W_{mc} line. This is explained as follows. For every molecule of water removed in the non-cellulosics as a result of scouring and bleaching, more than one molecule of water is absorbed on the new active sites associated with the purified fiber. Research has shown scouring and bleaching removes the waxy coating on the fiber, as well as other impurities and exposes more fibrils to the conditioned atmosphere (Goynes et al, 1984; Wakelyn et al, 2007). Thus, W_{nc} by Eq. 3 is biased; ideally, no water would be absorbed by the new active sites. Nonetheless, the contribution of the estimated water content in the extraneous matter to that in the raw cotton can be expressed as ($EW_{tr} + EW_{nc}$) << ($EW_{pf} = W_{sb}$); most of the water is in the purified fibers.

AMS Cottons

The AMS cottons represent aged fibrous material; the oldest cotton was grown in 1999. There were five different crop years produced in three growing regions. The samples were analyzed at SRRC in the fall of 2012. Whereas the set of MS cottons produced consistent values across the micronaire range (Figure 2) the AMS cottons yielded complex patterns over a wider range of micronaire (Figure 3). All ranges of water content parameters are dramatically larger for the AMS compared to the MS cottons. Also, there is much more overlap of water contents; no clear separation exists for the various measures of water. A limited interpretation of the AMS data follows.

Mean values for the directly measured water parameters in the AMS set of cottons (Table 3) were ($W_t = W_{raw}$ = 7.69 %, W_{mc} = 7.77 %, and W_{sb} = 7.68 %). The scoured and bleach samples had the highest water contents in only three of the six cottons. Generally, water content in the mechanically cleaned fibers was equal to or greater than that in the raw cottons. This was unexpected, since the water level in the trash (Figure 3, secondary *y*-axis) is greater than in the raw cottons. Perhaps this is due to the aging of the cottons so that when mechanically cleaned additional sites are opened to which water can bond. The corresponding water content ranges for $W_t = W_{raw}$, W_{mc} and W_{sb} (Table 3 and Figure 3) are larger than with the MS cottons ($W_t = W_{raw}$ = 0.71 %, W_{mc} = 0.50 %, and W_{sb} = 1.19 %).

Mean values for the contribution of the estimated water parameters in the AMS set of cottons to the water content in raw cotton (Table 3) were (EW_{tr} = 0.10 %, EW_{nc} = 0.24 %, and $W_{sb} = EW_{pf}$ = 7.68 %). The corresponding water content ranges for the same estimated parameters (Table 2 and Figure 3) varies from small to large (EW_{tr} = 0.23 %, EW_{nc} = 0.39 %, and EW_{pf} = 1.19 %). Note the close agreement between the MS and AS cottons (Table 2) for EW_{tr} and EW_{nc}; in contrast, EW_{pf} is greater in the AMS cottons.

Of particular interest are the data for the two AMS cottons that came from the same growing area and crop year, and represented by the first (2.72 Mic) and last (5.49 Mic) points in Figure 3. Results are very similar: mean values averaged across W_t and W_{mc} (2.72 Mic, 7.91 % and 5.49 Mic, 7.77 %); mean values averaged across W_t, W_{mc}, and W_{sb} (2.72 Mic, 7.82 % and 5.49 Mic, 7.82 %). To confirm these results, the two raw cottons were analyzed for water content by oven drying in nitrogen (Montalvo et al., 2011): mean difference in results was 0.0056 % water.

Note that for the points in the micronaire range 3.51 to 4.5, there seems to be a correlation with micronaire, with increasing micronaire a decrease in water content is seen. Also noteworthy is that at Mic 4.5 and 5.02, $W_{sb} < W_{mc}$, so that the estimated values for the non-cellulosics water content, EW_{nc} (4.5 Mic, 0.25 % water and 5.02 Mic, 0.46 % water), may not be influenced significantly by additional water absorption on the purified cellulose.

Dependence of Water Content on Micronaire

There are conflicting trends in the data regarding correlation of micronaire with water content. For the MS cottons with the same area grown and crop year, there were no significant correlations of W_t, W_{mc} or W_{sb} with micronaire (Figure 2). For the two AMS cottons with the same area grown and crop year, results are similar, in spite of a wide difference in micronaire; confirmation by oven drying in nitrogen produced equivalent results. For the three AMS cottons with different area grown and crop years, the apparent correlation of micronaire with the various water contents must be due to the fact that those are the only data points in the plot space with those specific attributes of area grown and crop year.

Conclusions

The understanding of water content data in cottons conditioned to moisture equilibrium was enhanced by analyzing two very different sample sets. One set was made up of fresh samples of raw cotton from the same area grown and crop year; the other had aged samples of raw material that were grown in different areas and crop years. To tease apart underlying trends in the data, the cottons were mechanically cleaned, and scoured and bleached. All materials were analyzed by standard Karl Fischer Titration. Additionally, the contribution of water content in the botanical trash and non-cellulosic chemicals in the fiber was estimated from the observed readings.

There were dramatic differences in water contents in the two sample sets, attributed to aging effects and growing characteristics. Extraneous material influences the range of water content in the raw and mechanically cleaned cottons. Conditions such as the area grown and crop year also influences results, but the range of water content is minimized for samples grown in a single area and crop year. At fixed area grown and crop year, micronaire does not appear to influence the results based on the limited studies to date. To our knowledge, this is the first reported attempt to estimate the relative amounts of water in the trash in raw cotton, the other non-cellulosic substances, and the fiber's cell wall.

Disclaimer

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Table 1. Results for the twelve MS Cottons: 1 growing areas, 1 crop year, 5 varieties.

MIC	Cultivar	Defol	Heat	W_t (%)	W_{mc} (%)	W_{sb} = EW_{pf} (%)	EW_{tr} (%)	EW_{nc} (%)
3.47	STV4554B2RF	early	low	7.79	7.65	8.09	0.14	0.44
3.69	STV4427B2RF	early	low	7.84	7.73	8.00	0.11	0.27
3.80	PHYTO485	late	high	7.82	7.73	8.24	0.09	0.51
3.81	PHYTO485	late	low	8.01	7.76	8.21	0.25	0.45
4.03	DP164B2RF	late	high	7.74	7.49	8.17	0.25	0.68
4.06	DP164B2RF	late	low	7.75	7.62	8.12	0.13	0.50
4.14	FM960BR	late	high	7.64	7.60	7.96	0.04	0.36
4.14	FM960BR	late	low	7.80	7.67	7.99	0.13	0.32
4.57	STV4427B2RF	late	low	7.94	7.79	8.08	0.15	0.29
4.60	STV4427B2RF	late	high	7.86	7.72	8.03	0.14	0.31
4.63	STV4554B2RF	late	high	7.92	7.78	8.09	0.14	0.31
4.70	STV4554B2RF	late	low	7.89	7.76	8.16	0.13	0.40
Mean values				7.83	7.69	8.10	0.14	0.40

Table 2. Water content ranges in the MS and AMS sample sets.

Range (%)	MS	AMS
W_t	0.37	0.71
W_{mc}	0.30	0.50
W_{sb}	0.28	1.19
EW_{tr}	0.21	0.23
EW_{nc}	0.41	0.39
EW_{pf}	0.28	1.19

Table 3. Results for the six AMS Cottons: 3 growing areas, 5 crop years, unknown number of cultivars.

Mic	Sample	W_t (%)	W_{mc} (%)	W_{sb} = EW_{pf} (%)	EW_{tr} (%)	EW_{nc} (%)
2.72	Gu	7.90	7.91	7.66	0.01	0.25
3.51	CM	8.06	8.02	8.25	0.04	0.27
3.98	Dm	7.64	7.71	7.78	0.07	0.07
4.50	BM	7.35	7.59	7.34	0.24	0.25
5.02	Im	7.53	7.52	7.06	0.01	0.46
5.49	Au	7.65	7.88	7.99	0.23	0.11
Mean values		7.69	7.77	7.68	0..10	0.24

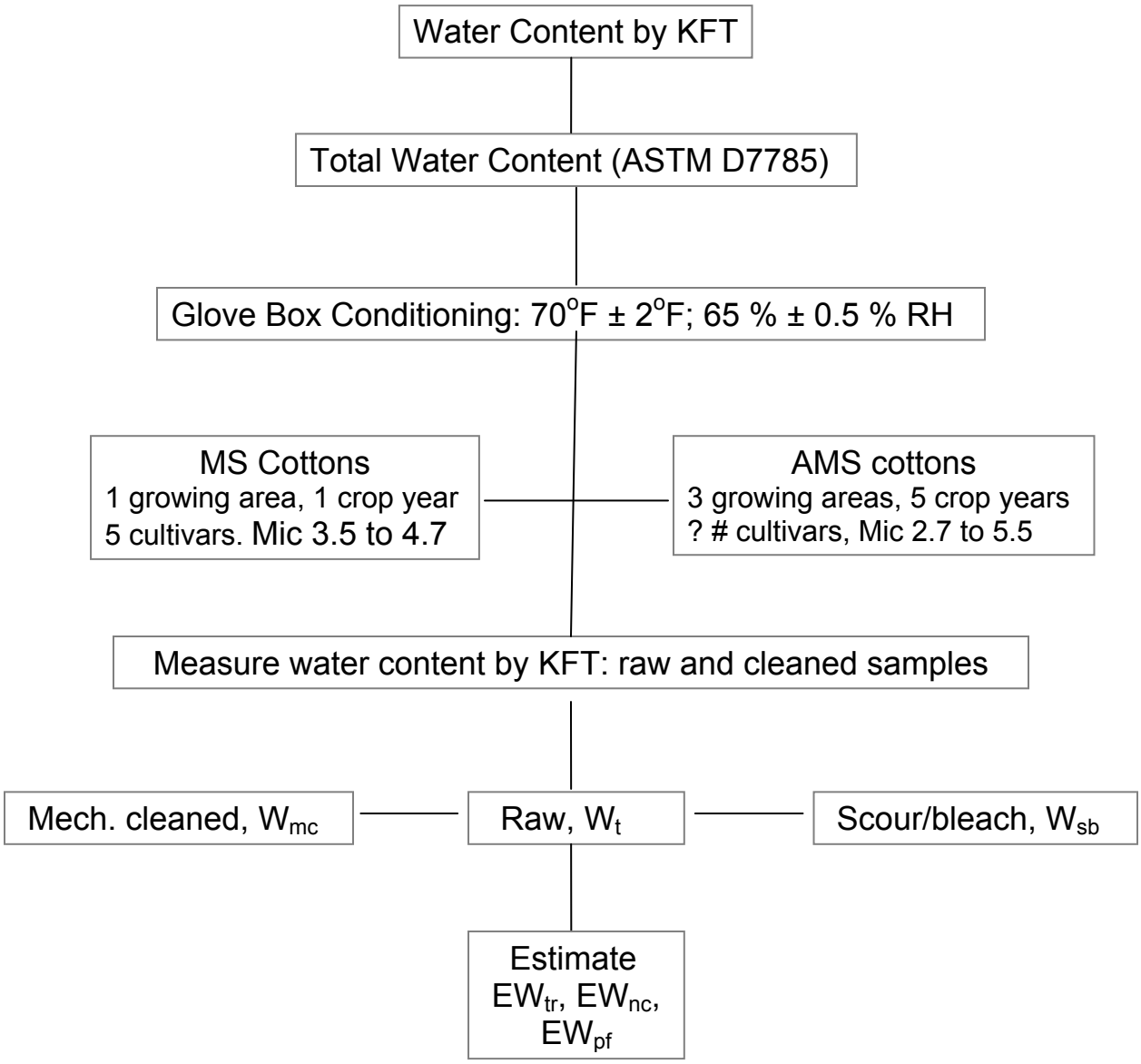

Figure 1. Flowchart of water content measurements.

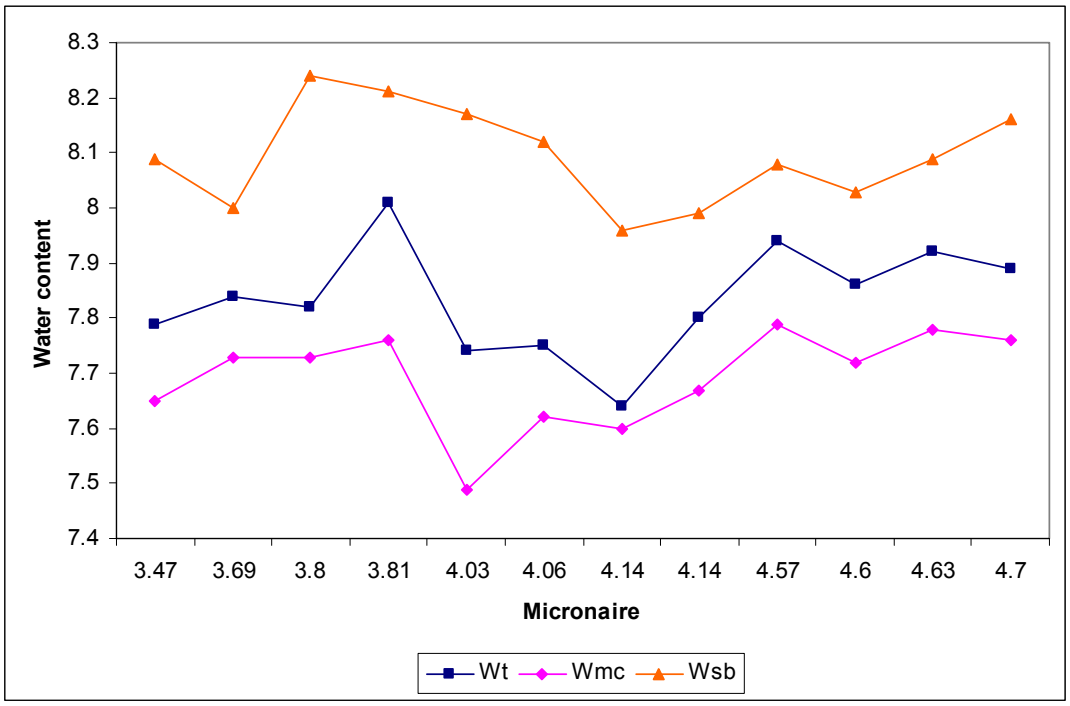

Figure 2. Water contents (%) in twelve MS cottons as measured by KFT. 3.

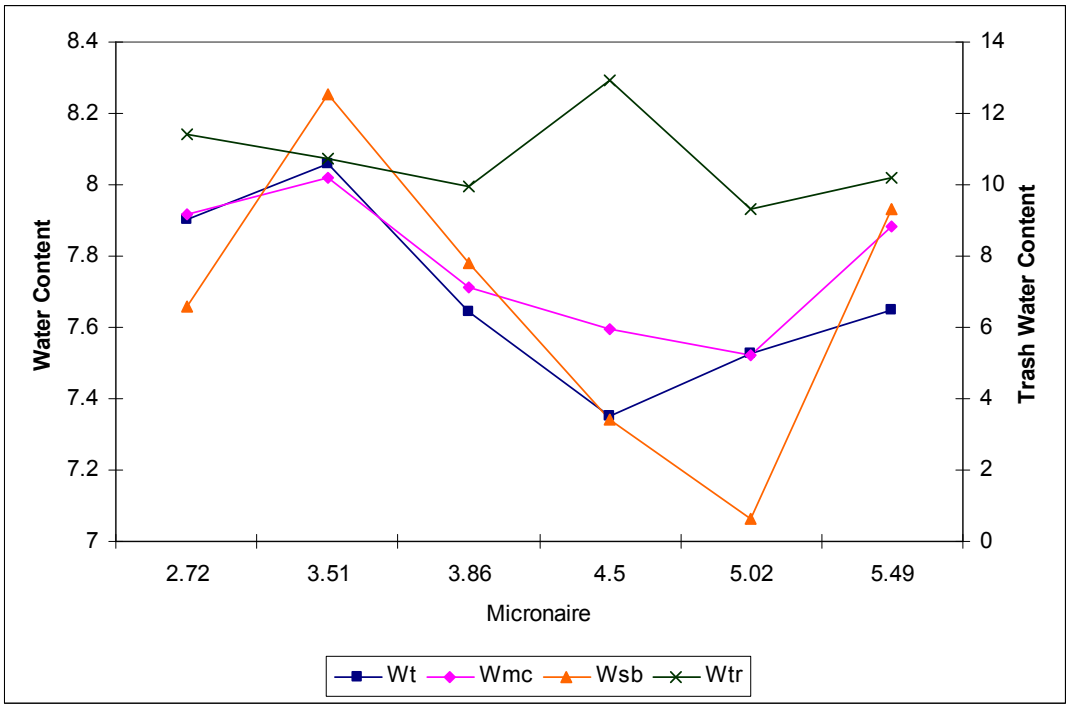

Figure 3. Water contents (%) in six AMS cottons as measured by KFT. Primary *y*-axis scale (Wt, Wmc, and Wsb); secondary *y*-axis scale (Wtr).