MOISTURE IN COTTON BY THE KARL FISCHER TITRATION REFERENCE METHOD

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Abstract

Moisture is a critical parameter that influences many aspects of cotton fiber from harvesting and ginning to various fiber properties. Because of their importance, reference moisture methods that are more accurate than the existing oven drying techniques and relatively easy to generate results are necessary. One such method is the Karl Fischer Titration technique, which is based on the chemical reaction between water, iodine and sulfur dioxide in a non-aqueous medium. A mechanical burette containing iodine is used to titrate the amount of moisture in a sample. Used in 126 ASTM reference methods, KFT is popular because of its precision, its small sample size and simple sample preparation, as well as its ability to measure water with a high degree of accuracy. In this paper, cotton fiber moisture is measured in 13 cottons by fully automated KFT instrumentation that uses a novel oven design to extract moisture in solid samples, a dry sweep gas to transport the released moisture to the titration cell, and software to detect the end point. Analysis time is about 5 minutes per specimen. The measured moisture levels across all samples, compared to the mechanical convection oven drying method, was 0.43 % lower with a pooled standard deviation about half that of the oven procedure.

Introduction

A comprehensive review of reference methods for moisture in cotton in eleven countries that represent all six continents revealed that almost all of the methods are based on oven drying (Montalvo and Von Hoven, 2008a). In each method, all of the weight loss is attributed to moisture. Research has shown that weight change by oven drying in air may also be due to other factors (Montalvo and Von Hoven, 2008b; Montalvo et al., 2008) such as other volatiles, oxidation of impurities in cotton, oxidation of the cellulose in the fiber, and other physical processes (e.g., blowing high velocity air through raw cotton may remove dust and trash particles). These other factors tend to inflate the measured value of moisture in cotton by the oven drying technique. Thus, there is a need for more accurate reference methods for moisture in cotton.

The trend in the oven drying procedures has been to improve precision by increasing sample size. For example, the Chinese national standard method, GB/T6102.1, (Montalvo and Von Hoven, 2008a) uses a 50 g sample. Ideally, an improved reference method for moisture in cotton should also be more precise and therefore allow for smaller samples analyzed with better precision.

In this country, there are no national standard methods for moisture in cotton. The voluntary reference methods (ASTM 2495 and ASTM 2654) and the more detailed procedure by Shepherd (1972) are most often cited in the literature (Montalvo and von Hoven, 2008a) and were developed for cotton ginning research. Both methods do not require preconditioning of the sample and are intended for "point" sampling at a specific location in the fiber processing. Oven drying is at 105 to 110^{o}C from 1 to 5 hours. There are no voluntary reference methods based on preconditioning prior to oven drying. An improved reference method for moisture in cotton should allow for reduced analysis time and permit the measurement on conditioned and non-conditioned cottons.

In searching for a modern reference method to measure moisture in cotton that is: (a) more accurate and precise with smaller samples analyzed, and (b) allows for measurements on fibers conditioned to moisture equilibrium or sampled during processing, Karl Fischer Titration (Karl Fischer Titration, 2008) is an attractive option. The fundamental principle behind it is the Bunsen reaction in which water is consumed by an oxidation reaction involving iodine and sulfur dioxide. Karl Fischer discovered that this reaction could be modified for the determination of water in a non-aqueous system using an alcohol as the solvent, and an organic base as the buffering agent. Since water and iodine are consumed in equal amounts in the reaction, the volume of titrating reagent (iodine) quantify the water in the sample (Karl Fischer Titration Basics, 2008). Platinum electrodes are used to detect the end point. There is broad application of the KFT method in industry – 126 ASTM reference methods currently in use that employ KFT technology, ranging form D1123 to determine the water in engine coolant to

D1348 test methods for moisture in cellulose, to D1045 methods for testing plasticizers. Some other ASTM methods utilize the Karl Fischer coulometric titration method for trace levels of moisture in industrial products. In the latter procedure, iodine is generated at the anode.

The objectives of this paper are: (1) obtain cottons from the Agricultural Marketing Service (AMS) that represent a wide range in crop year, micronaire and mechanical processing (i.e., cleaned and raw), (2) obtain a bleached and scoured cotton as the control fibers, (3) determine moisture contents of all cottons by the standard oven drying methods using both gravity convection ovens (GCO) and mechanical convection ovens (MCO), (4) determine moisture contents by the Karl Fischer Titration method (KFT), and (5) compare results.

Material and Methods

Two sets of cotton samples were obtained from the AMS; one set was produced in 2001 and the other in 2007 (Table 1). Each set was made up of six cottons that represented a range of micronaires from about 5.5 to 2.5. The control cotton was a set of cotton balls that had been scoured and bleached and readily available at commercial retailers nationwide.

For the standard oven drying tests, two laboratory ovens were used and placed side by side (Table 2). One was the Curtin Mateson Equatherm D 1580 gravity convection oven with an approximate capacity of 72.75 liters and a flow rate of approximately 0.25 liter/second. The other oven used was the Yamato DKN 600 mechanical convection oven with a 150 liter capacity and a mean flow rate of approximately 1.3 liters/second.

Cotton samples of approximately 1.0 gram were used for this study and these samples were conditioned to standard textile testing conditions for at least 24 hours. A set of six 1-gram samples was used in a test run for each cotton in each of the two ovens. Using gloved hands, the 1-gram samples were placed in a pre-weighed 45 ml glass weighing bottle, covered with the bottle cap, and then reweighed with the conditioned cotton sample inside. Next, the opened weighing bottles were placed in a cylindrical wire basket for both ovens, and then placed in the respective ovens. The oven temperature used was 105^{o}C for both ovens. Next, samples were removed after 24 hours and were immediately capped with the accompanying bottle top; the number 1 top went on the number 1 bottle and the number 2 top was placed on the number 2 bottle and so on. Table 2 illustrates the oven drying times and temperatures. When removed from the oven as quickly as possible, the capped weighing bottles were placed in mini-desiccators (one bottle per desiccator) and allowed to cool one hr. This procedure was followed until all samples were removed from the oven. A mini-desiccator consists of an 8-oz Kerr Quilted Crystal jelly jar containing indicating Drierite and a layer of metal gauze on top of the desiccant. The gauze prevented the weighing bottle from coming in direct contact with the desiccant.

Next, the desiccators were moved into the conditioned lab and allowed to acclimate for 15 minutes. Once the samples were acclimated, the weighing bottles were reweighed to determine the oven dry weights. Mean moisture content (%) and standard deviation from the six replicates were calculated from the weight loss data. As a final step, the bottles were opened with a custom built weighing bottle opener, the cottons were removed and the weighing bottles wiped clean so they could be used in the next run.

For all the runs, the operator followed a quality control procedure (Montalvo and Von Hoven, 2008b). To monitor the balance weights over time, an empty weighing bottle was used. If the weight deviated, the balance must be checked. For monitoring the conditioned environment, an open weighing bottle containing approximately 1-gram sample was used. Again, if the weight deviated, the conditions in the lab must be checked.

The second phase of this study involved the new moisture reference method that we are developing, based on Karl Fischer Titration. This procedure uses a Metrohm 774 oven sample processor at 150^{o}C, with a 35 glass vial carousel, an 800 Dosino with a mechanical burette, an 801 stirrer, an 803 Ti stand for the titration cell with platinum electrode, and the Tiamo 1.2 titration software. Hydranal composite 5K was used as the titration reagent and Hydranal medium K the solvent in the titration cell. For each cotton sample analyzed, three 0.1 gram replicates that had been subjected to standard textile testing conditions for at least 24 hours were used. These samples were placed in the sample vial and crimped closed in the conditioned air right before KFT testing. The samples were then placed on the KFT carousel and run between two sets of three blank vials, one set prior to the cottons, and one set after. The blanks serve as a quality control measure. The fully automated instrument analyzed all samples for %

moisture. In this process each vial is heated, in turn for about 5 minutes, under a stream of dry nitrogen flowing through the cotton sample that is contained in the sealed vial thus, removing the released water and transporting it to the titration cell. Mean moisture content and standard deviation were calculated from these replicates per cotton. More detailed information on the KFT procedure will be presented elsewhere.

Table 1. Cotton samples used in study

Sample Name	Details	Number of cottons
Control	Cotton balls scoured and bleached	1
2001 Crop year	Source- AMS cottons; mic 5.50-2.56	6
2007 Crop year	Source- AMS cottons; mic 5.45-2.54	6

Table 2. Standard oven drying parameters

Method	Oven Temp (^{o}C)	Sample test time	Sample size (g)	Number of reps
Gravity convection oven	105	24 hours	1.0	6
Mechanical convection oven	105	24 hours	1.0	6

Results and Discussion

Sample Set Means

Table 3 depicts mean moisture contents and differences with respect to the KFT results. The 2001CY and 2007 CY sample set means are across all six samples in each set. The KFT values (7.11 and 7.18%) are in close agreement and less than the oven drying means. Also, the MCO values (7.58 and 7.59%) are essentially the same. However, the two GCO values (7.74 and 7.37%) differ by 0.37.

As expected, the moisture content of the control sample by GCO and MCO oven drying are nearly identical because the fibers had been scoured and bleached.

The grand means across the 13 samples is noteworthy. The GCO and MCO oven values are identical (7.49%) and their differences with respect to the KFT results (0.43%) are the same and significant. The KFT sensor is more specific for water than the gravimetric approach in the laboratory oven method, hence the lower moisture contents. There are several physical processes that occur during oven drying in both the laboratory ovens (Montalvo et al., 2008). These processes may influence weight loss. Therefore, the greater specificity of the Karl Fischer method is needed, coupled with the inert gas nitrogen as the sweep gas makes it a more ideal method for moisture in cotton.

Individual Sample Differences

The individual sample differences between the oven drying methods and KFT are illustrated by the bar graphs in Figure 1. For the control cotton, the higher GCO and MCO results compared to the KFT is not explained in these preliminary results. Scouring and bleaching removed the volatiles present in raw cotton. However, the weight change by oven drying in air may also be due to other factors (Montalvo and Von Hoven, 2008b; Montalvo et al., 2008) such as oxidation of the cellulose in the fiber.

Note the larger differences for the cleaned and aged cottons (2001 CY). Aging may stabilize the oven values by oxidation. By contrast, the newer raw cottons may have undergone oven drying processes that resulted in smaller weight loss. There are other differences in the data: 2001 CY, GCO – KFT > MCO – KFT and 2007 CY, GCO – KFT < MCO – KFT. Drying at 16 versus 24 hrs gave essentially the same results.

Line plots of the individual sample means (Figure 2) reveal that the 2001 CY MCO data tracks the KFT values quite well. The minimum point in each plot occurred with the “C” cotton (4.54 micronaire) and the maximum value with the “D” cotton (4.02 micronaire).

Moisture Repeatability

The two different test methods, laboratory ovens and KFT, used different sample sizes as well as different numbers of replicates; the laboratory oven methods six 1 gram samples while KFT only three 0.1 gram samples. Figure 3 demonstrates that despite the smaller sample size and fewer reps, the precision, based on the standard deviations, is better for the KFT values than the oven values. In fact, the KFT pooled standard deviation is approximately half that of the oven values as seen in Figure 3. Note also that the KFT repeatability is best for the mid-micronaire cottons which include most of the cottons produced in this country.

Link Between KFT and MCO

We envision that the KFT reference method for moisture in cotton will also be used to calibrate the moisture measuring instruments. As a first application of this concept, we calibrated the MCO moisture data for the 12 crop year cottons with the corresponding KFT data. The calibration equation was then used to correct the moisture content of the control sample that had been determined by drying in the MCO. Finally, the corrected MCO value was compared with the actual KFT. Results of % moisture are as follows: MCO and KFT, respectively (see Table 3). 7.30 and 6.89; and corrected MCO by calibration equation, 6.90.

Table 3. Moisture content (%) by KFT and oven drying procedures

Sample	KFT	GCO	MCO	GCO-KFT	MCO-KFT
Control	6.89	7.36	7.30	0.47	0.41
2001 CY	7.11	7.74	7.58	0.63	0.47
2007 CY	7.18	7.37	7.59	0.19	0.41
Grand Means	7.06	7.49	7.49	0.43	0.43

Note: Tentative KFT data pending method validation

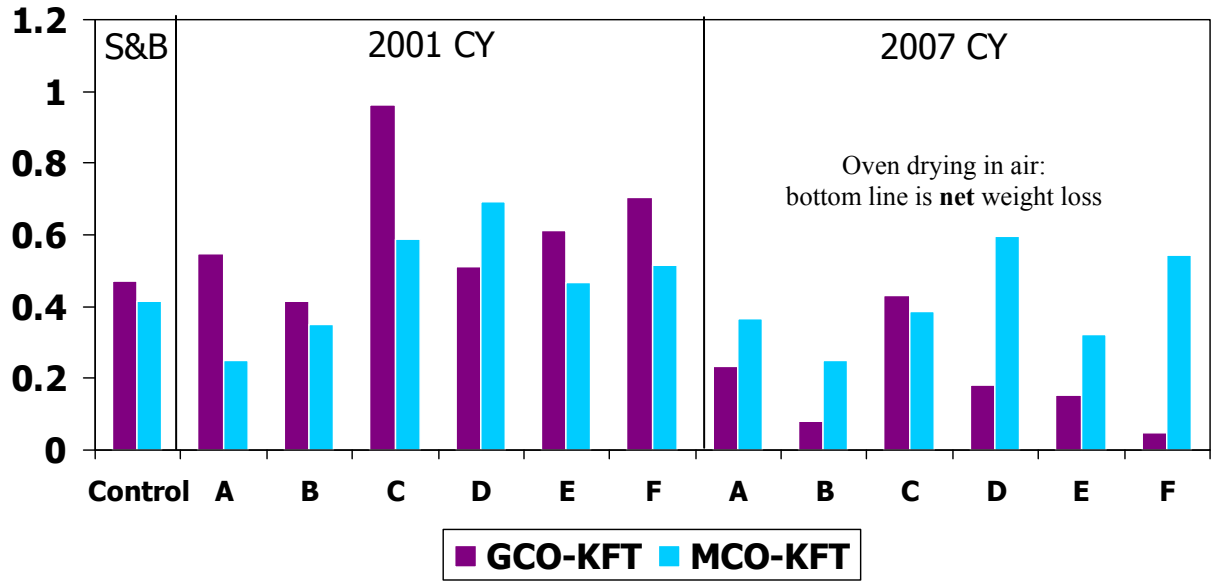

Figure 1. Individual sample differences between moisture content by the oven drying methods and KFT. Sample labels A to F represent decreasing microinaire values in each set of crop year samples.

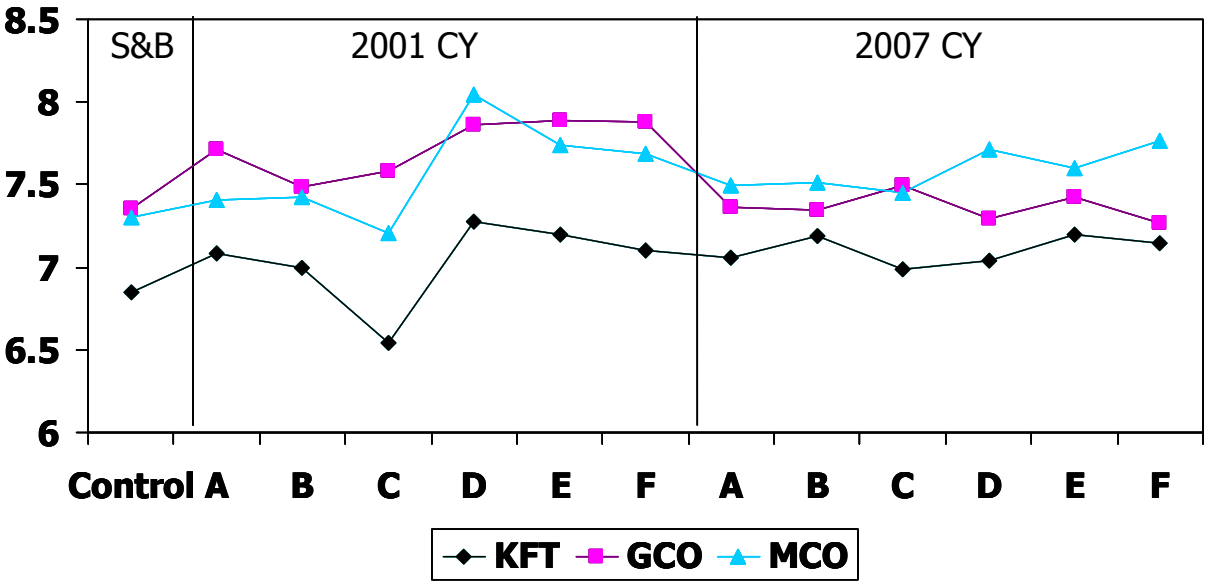

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Figure 2. Line plots of moisture data.

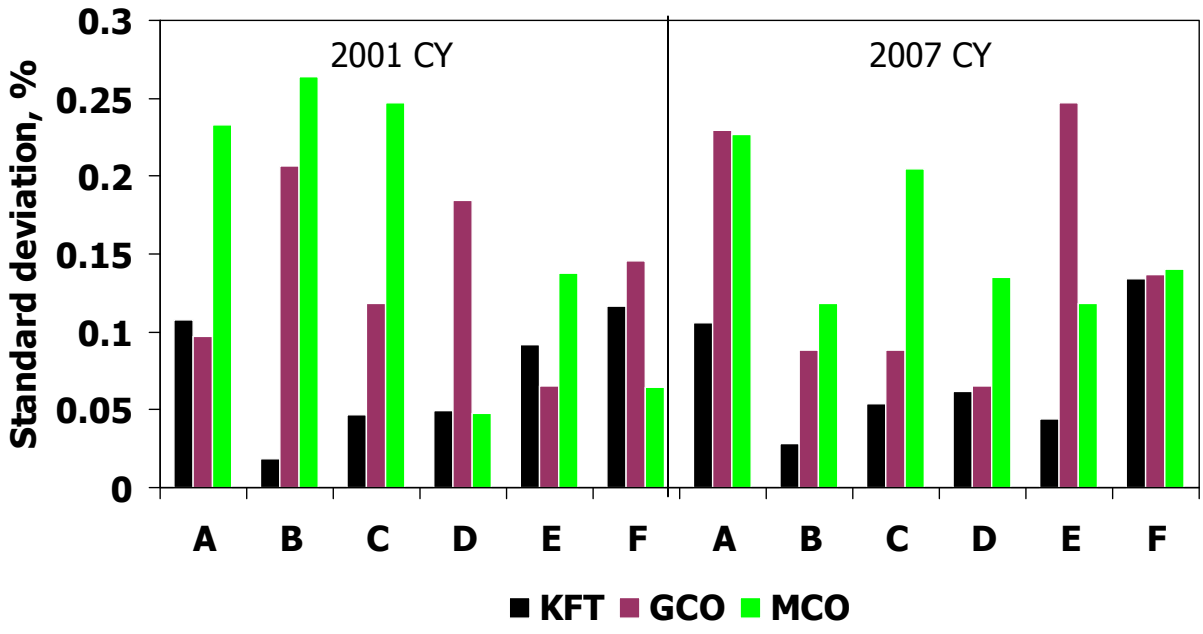

Figure 3. Standard deviation of mean moisture content. Replicates per cotton: Ovens, 6 reps; KFT, 3 reps. Sample labels A to F represent decreasing micronaire values in each set of crop year samples.

Conclusions

Cotton fiber moisture is a very important aspect of cotton harvesting and processing affecting many important properties such as length, strength and uniformity. A reliable, convenient, rapid, precise and accurate means of measuring is desirable. The Karl Fischer Titration reference method for moisture in cotton offers all these advantages compared to the oven drying procedures. This fully automated instrumentation isolates moisture from the fiber matrix by its oven module, transports the released moisture by a dry, inert sweep gas into the titration cell and titrates the moisture. Platinum electrodes detect the end point and the software calculates the moisture content in the sample. The 150^{o}C oven temperature ensures that the total moisture in the fiber is released for titration. Due to the fast chemical reaction between moisture and the iodine titrating reagent, and the formulation of the solvent and titrant to suppress side reactions from other volatiles, the electrochemical sensor is highly selective for water.

With its automation, non-prohibitive cost for reagents and supplies, ease of use and small sample consumption, the more accurate data produced by KFT makes it a welcome candidate as a modern reference method for moisture in cotton. Work is ongoing to document sensor specificity for moisture, validate and optimize the KFT draft procedure presented in this paper, and submit the reference method to ASTM.

References

ASTM D2495-01. 2006. "Standard Test Method for Moisture in Cotton by Oven-Drying." Annual Book of ASTM Standards. Vol. 7.01 Section 7. Textiles I. p. 610-614.

ASTM 2654-89a. 1997. "Standard Test Method for Moisture in Textiles." Annual Book of ASTM Standards. Vol. 7.01 Section 7. Textiles I. p. 693-702.

"Karl Fischer Titration ." http://www.astm.org/Standard/index.shtml. Date referenced 19 Nov 2008.

"Karl Fischer Titration Basics." http://www.emdchemicals.com/analytics/literature/KF_Titration_Basics.pdf. Date referenced 19 Nov 2008.

Montalvo, J. G., Jr. and T. M. Von Hoven. 2008a. Review of Standard Test Methods for Moisture in Lint Cotton. Journal of Cotton Science, Vol 12. p. 33-47.

Montalvo, J. G., Jr. and T. M. Von Hoven. 2008b. Moisture in Cotton by Oven Drying. Proc. 2008 Beltwide Cotton Confs., National Cotton Council, p. 1511-1517.

Montalvo, J. G., Jr., T. M. Von Hoven. J. Smith, T. North, D. Francois and A. Schindler. 2008. Reference Methods for Moisture in Lint Cotton: Fundamentals and Applied. Presented to the Cotton Structure and Quality Stakeholders Meeting, Southern Regional Research Center, SRRC, Sept. 2008.

Shepherd, J. V. 1972. "Standard Procedures for Foreign Matter and Moisture Analytical Tests Used in Cotton Ginning Research." Agriculture Handbook No. 422. p. 1-13.