VALIDATION STUDIES OF KARL FISCHER REFERENCE METHOD FOR MOISTURE IN COTTON

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Abstract

With current international standard oven drying (*SOD*) techniques lacking precision and accuracy statements, a new standard reference method is needed. Volumetric Karl Fischer Titration (KFT) is a widely used measure of moisture content. The method is used in many ASTM methods, 14 NIST SRMs, and testing labs that run 24 hours a day, seven days a week. In this study, validation of the method's ability to quantify the water in cotton fibers is explored and cotton is distilled to confirm the presence, if any, of non-aqueous volatiles. Results on three cottons investigated demonstrate high selectivity by the KFT technique for measuring water over the interferences in cotton. Also, the release of non-aqueous volatiles in cotton by *SOD* was confirmed by distillation. This can explain most of the variance between standard oven drying and KFT results.

Introduction

In techniques to measure moisture in cotton, such as standard oven drying (Shepherd, 1972), all of the weight loss is attributed to moisture. An exhaustive literature review (Montalvo and Von Hoven, 2008a) showed that most international standard methods involve oven drying in which volatile organic molecules and even particulate matter may be released when the water is evaporating. Oxidation of impurities or even the cellulose may occur (Montalvo and Von Hoven, 2008b; Montalvo et al., 2010; Cheuk and Montalvo, 2010; and Cheuk et al., 2010).

Because it is widely used and lauded for its selectivity for water, easy sample preparation, small sample size, rapid measurement and of course, excellent accuracy and precision, volumetric Karl Fischer Titration (KFT) is a viable option for measuring moisture content of cotton fibers. The technique involves a two-stage chemical reaction in which iodine is reduced and the amount is in proportion to the water titrated. Modern technology has provided better reagents and fully automated instruments, resulting in reduced labor cost and small cost for reagents.

The food industry cites the high selectivity of KFT to water compared to interfering substances. In contrast, weight loss by oven drying of food can include free water, crystalline water, volatiles, as well as decomposition of other compounds (Isengard, 1995). At an oven temperature of 105^{o}C, the measured water content of rice was higher than KFT measurements (Vassileva and Quetel, 2008). However, it was found that weight loss of the rice as measured in an oven at 85^{o}C, closely matched that found by KFT, suggesting that perhaps only water is being released at the lower temperature.

The objectives of this paper are to determine the selectivity of the KFT method to water in cotton relative to interfering materials and to demonstrate the visual confirmation and quantification of non-aqueous volatiles by distilling large samples of cotton at 105^{o}C.

Material and Methods

Cottons

Three cottons were used for this study, the control and two raw cottons. One of the raw cottons was produced in 2001 and the other in 2007 (Table 1), both with mid range micronaires, and identified as 2001 C and 2007 C. The control was a set of commercially available, scoured and bleached cotton balls. All samples were conditioned to standard textile testing conditions for at least 24 hours prior to testing.

Table 1. Cotton samples used in study

Sample Identification	Details
control	cotton balls scoured and bleached
2001 C	source- AMS; mic 4.5
2007 C	source- AMS; mic 4.5

Volumetric Karl Fischer Titration

Water Content in Cotton (*WCR*). The 0.1 g specimens were weighed to the nearest 0.1 mg, placed in the Karl Fischer glass vials and immediately crimped with septum caps. The sealed samples were then placed into Mason jars that had been acclimated in the conditioned lab. The samples were then encapsulated in the jar until testing to maintain the environment. Details regarding the KFT method are described in Table 2. Prior to KFT analysis of cotton samples, blank vials were run for quality control measures. During testing, the vial is lowered into a 150°C oven for approximately 5 minutes while dry nitrogen (< 20 ppb water) is bubbled into the vial at 60 mL per minute. The water is released from the cotton in the vial and transported into the titration cell by the carrier gas. From the volume of Karl Fischer reagent consumed, the percentage of moisture in the cotton is calculated, after correction for atmospheric moisture in the blank vials. Immediately after KFT analysis an *in vitro* NIR spectrum was taken through the bottom wall of the vial to confirm complete removal of water (Table 3). NIR spectra were generated with the Bruker MPA using OPUS 5.0 software. Three replications of each cotton sample in its sealed vial were generated and averaged. The samples were deemed dry if there was no visible peak in the spectrum at 1940 nm.

Table 2. Karl Fischer Titration Specifications

Sample processor	Metrohm 774 oven
Electronic buret	800 Dosino
Vial and sample size	6 mL and 0.1 g
Oven/sweep gas	150°C/ N_2 at 60 ml/min
Cell solution	Hydranal Medium K
Titrating reagent	Hydranal Composite K
Software	Taimo 1.2
Test Time	5 min
Replicates/cotton	3
Sequential samples	5 in vessel solvent

Equivalent Water Content of Interferences (*EWCI*). Cotton samples were pre-dried by low temperature distillation (Table 3) in order that the equivalent water content of interferences *(EWCI)* could be measured by KFT. By definition, *EWCI* is the extent to which the KFT method responds to the interfering volatiles in pre-dried cotton and expressed as equivalent water content (%). This drying technique was carried out in an oven at a mild temperature (50°C) to minimize removal of non-aqueous volatiles. In a sealed and vented KFT vial containing 0.1 g cotton, dry nitrogen (preheated to 50°C in a heat exchanger in the oven) was injected into the fibers at 60 mL/min for at least 12 hours. To ensure the sample was free of moisture, NIR spectra were taken and confirmed complete removal of water.

Selectivity (*S*). The selectivity *(S)* of the KFT method for water in cotton relative to any interfering volatile material was calculated by the following formula (Montalvo et al., 2009)

$$S = (WCR - EWCI)/EWCI \quad (1)$$

where *WCR* = water content in cotton, % and *EWCI* = equivalent water content of interferences, %.

Table 3. Low Temperature Distillation Modified to Pre-dry Karl Fischer Samples for Selectivity Studies

Instrument system	Bruker (NIR) MPA
Vial and sample size	6 mL (KFT) and 0.1 g
Oven/sweep gas	50°C/N_2 at 60mL/min
Test Time	overnight
End Point	no H_2O peak - 1940 nm validate KFT (*WCR*) and KFT (*EWCI*)
Air exchange rate	6 sec

Cotton Distillation at 105°C

Fifty gram samples were distilled at 105°C in an all glass apparatus with dry (< 20 ppb water), compressed air as the carrier gas to allow for visual confirmation of non-aqueous volatiles and quantification of the material (Cheuk and Montalvo, 2010).

Results and Discussion

In order to validate the KFT reference method for water in cotton, ongoing comparability studies at SRRC include: Low Temperature Distillation (LTD) with an inert gas at a temperature less than 105°C; KFT selectivity (*S*) measurements of water relative to interferences; and distillation at 105°C. The LTD method under nitrogen at 75°C has produced weight loss (water) values within 01% of the KFT values (Cheuk et al., 2010). The results below demonstrate high *S* values and mass balances based on standard oven drying, water content by KFT and non-aqueous volatiles by distillation.

KFT Selectivity *(S)*

Do the non-aqueous volatiles in cotton produce chemical interferences in the KFT titration reaction with the iodine reagent? Typically, interfering chemicals take longer to react with KFT reagents than moisture to react with KFT reagents, but still have an adverse effect on the accuracy of the results.

Moisture selectivity in cotton (*S*) was calculated by Equation 1. It is the difference between the water content reported by KFT (*WCR*, %) and the equivalent water content of interferences divided by the equivalent water content of interferences (*EWCI*, %). Note that *EWCI* is measured on cotton that was pre-dried at 50°C and expressed as equivalent water content.

Typically the water content reported by KFT (*WCR*) is about 7% and the desired accuracy is 0.1 %. Let the equivalent water content of interferences (*EWCI*) be half the desired accuracy or 0.05%. The target selectivity is therefore

$$S = (WCR - EWCI)/EWCI = (7 - 0.05)/0.05 \geq 139. \quad (2)$$

Note in Figure 1 the dependence of *S* on *EWCI* at fixed *WCR* = 7 %. As *EWCI* increases, the selectivity value approaches zero. Conversely, as *EWCI* approaches zero, the selectivity increases to the point that the method is specific for moisture in cotton.

Selectivity results for the three cottons analyzed are also included in the text box in Figure 1. The *WCR* values varied from 6.50 % to 7.06 %; *EWCI* varied from 0.017 % to 0.033 %. The calculated *S* values for the cottons represent the mean of three replications: control, (6.803 – 0.01667)/0.01667 = 407; 2001 C cotton, (6.53 – 0.025)/0.025 = 260; and 2007 C cotton (7.06 – 0.03333)/0.03333 = 211. All selectivity values exceed the target of 139, indicating the ability of the KFT method to measure water at high selectivity for moisture over the interferences.

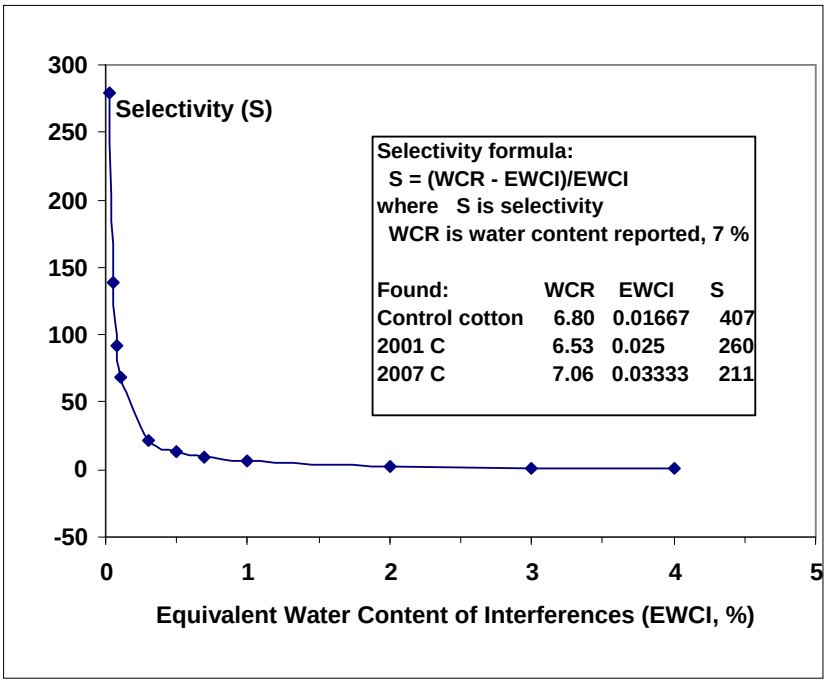

Figure 1. Water selectivity by KFT versus equivalent water content of interferences at fixed *WCR* = 7 %.

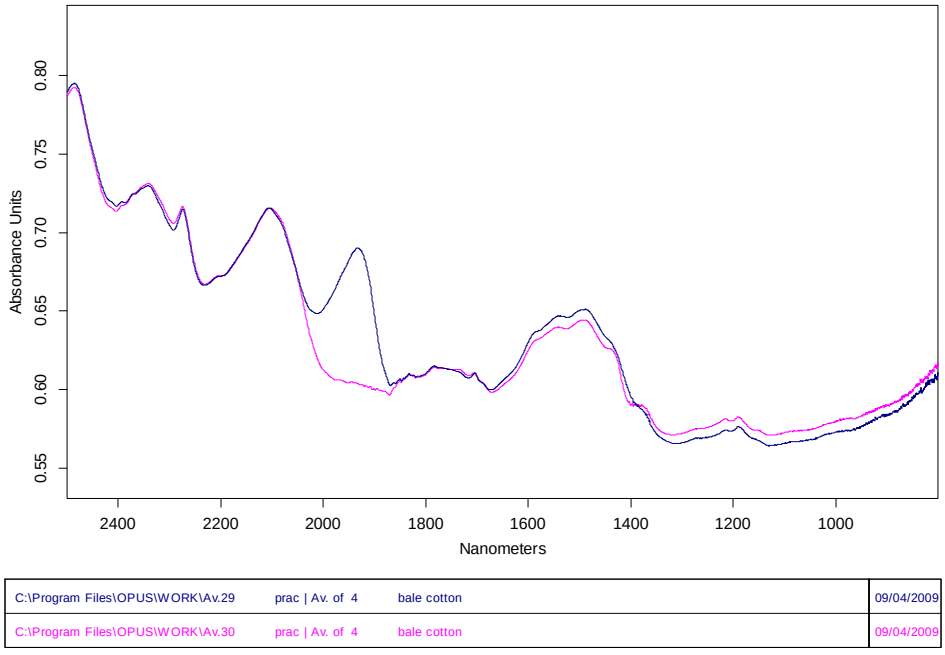

Figure 2. NIR spectrum of control cotton before (blue) and after pre-dry (pink)

Cotton Distillation at 105°C

The distillation of 50 grams of cotton (105°C, in dry air) in an all glass apparatus allows for the visualization and quantification of the non-aqueous volatiles, thus explaining the difference between the standard oven drying and KFT techniques. The volatiles provide a piece to the puzzle to the true measurement of water in cotton. The non-aqueous volatiles were deposited in the glass apparatus in significant amounts (Table 4). Non-aqueous volatiles residue was clearly visible on the inside walls of the apparatus.

The proposed mass balance equation to link standard oven drying, Kart Fischer Titration and distillation results is described by Equation 3

$$SOD - WCR = NAV \quad (3)$$

where *SOD* = weight loss by standard oven drying, %; *WCR* is water content, % by KFT and *NAV* = mass of non-aqueous volatiles by distillation, %. The target mass balance for the experimental data is given by Equation 4.

$$(SOD - WCR) - NAV = 0.0 \pm 0.1\%. \quad (4)$$

For the three cottons investigated, control: (7.28 - 6.90) – 0.33 = 0.05%, 2001 C: (7.02 - 6.59) – 0.57 = -0.14%, 2007 C: (7.56 – 7.05) – 0.38 = 0.13%. The control cotton is well below the target value, while the 2001 C and 2007 C cottons are very close to the target value.

Table 4. Results by Standard Oven Drying, Karl Fischer Titration and Non-aqueous Volatiles by Distillation

	Standard oven drying (*SOD*, %)	**Karl Fischer Titration (*WCR*, %)**	**Non-aqueous volatiles (*NAV*, %)**
Temperature	105°C	150°C	105°C
Carrier gas	air	N_2	air
Size (g)	1	0.1	50
Property	Weight loss	Water content	Weight loss
Control	7.28	6.90	0.33
2001 C	7.02	6.59	0.57
2007 C	7.56	7.05	0.38

Conclusions

The selectivity of the oven evaporation-Karl Fischer Titration reference method to measure the water content of cotton relative to volatile interferences exceeds the target value. Evidently the speed of this chemical reaction method minimizes the effects of the slower side reactions in the titration cell that can occur with the volatiles present in cotton. It is also automated, very easy to run with simple sample preparation, and is repeatable. Future plans include submitting a draft standard method to ASTM as well as single laboratory precision data for a set of cottons run by KFT. The authors also plan to educate potential users through workshops and collaborations. In order to complete the submission to ASTM, round robins will be conducted.

Distillation of large samples of cotton at 105°C in dry air allowed for the visual confirmation of non-aqueous volatiles in cotton. The synthetic pathways of the non-aqueous volatile material in cotton are a complex issue and will be reported elsewhere. However, recent studies (Cheuk et al., 2010) suggest oxidation is occurring and volatile oxidation products are produced.

References

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