The *Journal of Cotton Science 13:221–226 (2009)*
http://journal.cotton.org, © The Cotton Foundation 2009

TEXTILE TECHNOLOGY

Regional, Varietal, and Crop Year Variations of Metal Contents Associated with the Separate Structural Components of Upland Cotton (*Gossypium hirsutum*) Fiber

Gary R. Gamble*

ABSTRACT

Though the presence of metal cations in raw cotton fiber has been well documented in previous studies, little information exists in the literature regarding the relative proportions of these metals in or on the different structural components of the fiber. Such information may prove useful in attempts to increase the processing efficiency of the various stages involved in the conversion of lint into finished fabric. The purpose of this study is twofold: (1) attempt to delineate the relative proportions of 8 different metals present as water soluble salts on the surfaces of the fiber, as crosslinking agents within the pectin component of the fiber, and as complexed cations within the cellulose matrix, and (2) determine differences in metal contents due to regional, varietal, or environmental effects. Two cotton varieties were grown in three growing locations across the cotton belt over two consecutive crop years. Each of the 12 samples were subjected to water extraction, scouring, and finally acid digestion, with the three solutions subsequently analyzed for metal content. Results indicate that different metal profiles exist in the different structural components of the fiber, and that these metal contents may be affected by environmental conditions and fiber maturity.

Metal cations are present as salts, or complexes, either on the surfaces of the cotton fiber or contained within the chemical matrices of the various structural components of the fiber, including the primary and secondary cell walls. These cations may contribute to a number of issues associated with yarn processing, fabric production, bleaching and dyeing processes. The presence of salts on the outer fiber surface and in the lumen have been associated with a possible beneficial effect to yarn quality and processing efficiency due to their anti-static properties (Gamble, 2006). In the dyeing of cotton fabrics the presence of calcium and magnesium salts in the dye bath are known to interfere with dyeing quality (Cook, 1991) due to their ability to form insoluble complexes with sulfonate groups present on most dyes and surfactants (Rodriguez, et al., 2001). Copper, iron and aluminum have been demonstrated to contribute to yellowness of finished denim goods (Rucker, et al., 1992). Though many of the interfering metals are introduced via external sources, such as hard water or metallic processing equipment, a substantial amount is native to the cotton lint itself. Previous work (Brushwood and Perkins, 1994) has shown that the most abundant metals naturally occurring on cotton fiber are potassium, calcium, magnesium, and sodium. Other metals observed at a much lower relative concentration are iron, copper, manganese, zinc, nickel, silicon, cobalt, and aluminum (Rezic and Steffan, 2006). Some of these metals, such as calcium and potassium, are essential for the normal development of the cotton fiber. Potassium is present primarily as a malic acid salt (Dhindsa, et al., 1975), providing turgor pressure within the lumen of the developing fiber. Once the open boll is exposed to weathering, this form of potassium may be easily solubilized and washed away (Domelsmith and Berni, 1984). Calcium has been shown to be abundant in the pectin comprising the primary cell wall of cotton (Wartelle, et al, 1995), and in this form is not likely to be affected by weathering due to the fact that the complex formed between the pectin and calcium renders the calcium insoluble in water. An efficient alkaline scouring process results in solubilization of pectin, and thereby the calcium associated with it. Following removal of waxes, pectins, and proteins during alkaline scouring, the remaining fiber is composed almost entirely of cellulose.

Little published information exists regarding the presence of metal cations within this cellulose structure, though several reports (McCaffrey and Santokhi, 1999; Goto-Doshida, et al., 2003) indicate that a substantial quantity of Ca^{2+} and Mg^{2+} remains

G.R. Gamble, USDA-ARS, Cotton Quality Research Station, P.O. Box 792, Clemson, SC 29633
*Corresponding author: gary.gamble@ars.usda.gov

associated with the fiber. Because the presence of these metals in the fiber after the scouring preparation for dyeing could potentially affect dye uptake, one goal of the current study is to establish not only the total metal content of the raw fiber, but to determine whether these metals are present as soluble salts, as pectate complexes within the primary cell wall, or as bound cations within the secondary cell wall. In addition, a previous study (Brushwood, 2005) has suggested that metal content may vary as a result of growing conditions, growing region, or cotton variety. Information regarding dependence of metal content on these variables may provide textile operations with the ability to better predict and control processing efficiency. In this study two varieties of cotton grown in three different growing regions within the U.S. cotton belt over the course of two growing seasons were analyzed for metal content with the secondary goal of providing preliminary evidence for elucidating the role of growth variables in metal content differences.

MATERIALS AND METHODS

Cotton samples. Two varieties of cotton were each grown in three different growing regions (Texas high plains, Georgia, and Mississippi delta) in the U.S. cotton belt over two different growing seasons. For the three growing regions boll opening occurs in September and October with the harvest normally taking place from mid-October to the first or second week of November. September and October rainfall amounts (National Weather Service, http://www.srh.noaa.gov) are presented in Table 1 for both the 2001 and 2002 crop years over all three growing locations. The 2002 crop year experienced relatively large amounts of rainfall compared to the 2001 crop year in each of the three growing locations.

Micronaire. Duplicate measurements of micronaire were performed on each sample by high volume instrumentation (HVI) according to standard test methods (ASTM 1997).

Maturity ratio. Each sample was tested for maturity ratio (MR) on an Advanced Fiber Information System (Uster, Knoxville, TN) with five replications of 3000 fibers.

Water Extraction. Duplicate water extractions were performed on each of the 12 different cotton samples by adding 20 ml aliquots of deionized water to one gram of the fiber and agitating in order to remove soluble salts. The fiber was filtered off and the process was repeated until the resultant extract exhibited no salt content as indicated by conductivity. The aliquots were consolidated and condensed down to 45 ml. The solution was then brought to a volume of 50 ml by addition of 5 ml 50% nitric acid for analysis by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES).

Scouring. The resultant water extracted fiber samples were subsequently scoured in order to remove the wax and pectin components. The scouring process consisted of placement of the extracted fiber sample in 20 ml of a 1% (w/w) solution of tetrabutylammonium hydroxide (TBAH) (Aldrich Chemical Co., Milwaukee, WI). The solution was then heated to 80°C and maintained at this temperature with constant agitation for 45 minutes. The fiber was removed and the resultant scour solution was neutralized using nitric acid, resulting in the precipitation of the pectin fraction, and diluted to 45 ml using deionized water. To this solution was then added 5 ml 50% nitric acid for analysis by ICP-OES.

Table 1. Metal contents (ppm on weight of cotton) of water extract, scour solution and acid digest of cotton samples (2 varieties grown in 3 growing regions) compared by 2 crop years.[z]

	Crop year	Ca	K	Na	Mg	Fe	Zn	Rainfall (in)	mic	Maturity Ratio
extract	**2001**	**361.2**	**4940.0 a**	**61.4 a**	**247.7 a**	**7.4**	**17.2 a**	**5.2 b**	**3.83**	**0.89**
	2002	**331.1**	**3099.1 b**	**41.6 b**	**166.0 b**	**7.6**	**11.2 b**	**11.6 a**	**4.12**	**0.89**
			P<0.001	**P=0.036**	**P=0.028**		**P=0.045**	**P=0.010**		
scour	**2001**	**652.9**	**5.8**	**NA**	**76.7 a**	**0.0**	**7.9**	**5.2 b**	**3.83**	**0.89**
	2002	**530.6**	**0.0**	**NA**	**57.0 b**	**0.7**	**3.7**	**11.6 a**	**4.12**	**0.89**
					P=0.008			**P=0.010**		
digest	**2001**	**453.2**	**7.5**	**27.9**	**206.7**	**12.1**	**10.3**	**5.2 b**	**3.83**	**0.89**
	2002	**491.0**	**2.6**	**24.0**	**195.6**	**14.5**	**6.2**	**11.6 a**	**4.12**	**0.89**
								P=0.010		

[z] Means within a column followed by the different letters are significantly different according to Duncan's New Multiple Range test. Means within a column followed by no letters are not significantly different.

Microwave Digestion. Digestion of the scoured and rinsed cotton fibers was performed on a Microwave Accelerated Reaction System (CEM Corporation, Matthews, NC). A 0.5 g sample of fiber was predigested in 2 ml 50% nitric acid for 15 minutes. Subsequently, 20 ml of deionized water was added and the sample sealed in a Teflon pressure vessel. The temperature of the vessel was ramped to 205ºC over a 15 minute period and held at this temperature for an additional 15 minutes. Samples were then diluted to 25 ml for analysis by ICP-OES.

ICP-OES. The resultant extraction, scour, and digest solutions were analyzed for calcium, potassium, sodium, magnesium, iron, nickel, copper and zinc on a Liberty Series II (Varian, Inc., Palo Alto, CA) ICP-OES spectrometer.

Statistics. All linear regressions were performed using SigmaPlot 8.0 (SPSS Science, Chicago IL). T-tests and ANOVA were performed using SigmaStat 3.0 (SPSS Science, Chicago IL).

RESULTS AND DISCUSSION

Metal contents of the water extract, scour solution and acid digest of 12 cotton samples (two varieties grown in three separate growing regions) are compared by two consecutive crop years in Table 1. An analysis of metal contents in the water extract indicates potassium, calcium, and magnesium to be the most abundant followed by sodium, zinc, and iron. Copper and nickel were at or below the limits of detection and are not shown. Statistical analysis of the extract further indicates significant differences in potassium, magnesium, sodium, and zinc between the two crop years. These differences appear to be related to comparatively different rainfall amounts over the two crop years, with year 2 having a substantially higher total over the three growing regions. The apparent effect of this higher rainfall is to decrease the amounts of soluble salts present on the fiber surface. By far the most abundant cation present in the form of water soluble salts is potassium. Figure 1 shows the relationship between potassium content as a function of rainfall for both crop years. Though the coefficient of correlation (R^2 = 0.53) does not indicate a strong relationship, it is sufficient to suggest a trend, with potassium content decreasing with increasing rain amounts. Metal contents comprised by the scour solutions in Table 1 include a relatively high proportion of calcium, associated with the pectin removed by treatment with tetrabutylammonium hydroxide. Magnesium and zinc also appear to be associated with structural components removed by scouring, though only in the case of magnesium is a statistically significant difference between crop years observed. The resultant scoured fiber was digested in nitric acid, and as seen in Table 1 this solution also exhibits relatively high amounts of calcium and magnesium, with lower amounts of sodium, iron, zinc and potassium also present. Though no statistically significant differences were observed between crop years for this solution, the results lend evidence that even following the scouring process, substantial quantities of Ca^{2+} and Mg^{2+} remain associated with the fiber. This behavior has been observed in previous work (McCaffrey and Santokhi, 1999; Goto-Doshida, et al., 2003), and though the nature of the binding mechanism remains uncertain, at least two possibilities exist: (1) the scouring process does not remove all of the pectin and the cations associated with it, or (2) the cations are incorporated in the cellulose structure itself. Pure cellulose is known to exhibit a very low binding capacity at acidic pH (Lehrfeld, 1996), but at the high pH associated with scouring, the Ca^{2+} and Mg^{2+} present in the cellulose component might be expected to remain bound.

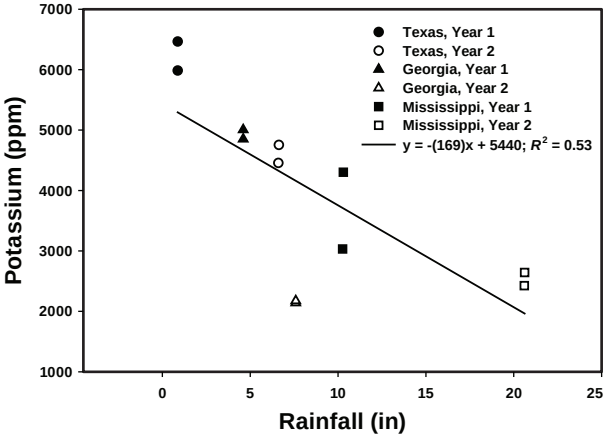

Figure 1. Potassium content (ppm on weight of cotton) in water extract of cotton samples (two varieties grown in three locations over two crop years) as a function of rainfall amount on open bolls prior to harvest.

Metal contents of the water extract, scour solution and acid digest of 12 cotton samples (two varieties grown in two consecutive crop years) are compared by the three growing regions in Table 2. Analysis of the water extract indicates that the cottons grown in Texas over the two crop years have a significantly higher proportion of potassium and magnesium than the Georgia or Mississippi growing regions. This may

in part be due to a lower rainfall amount, as discussed previously, but the Texas cottons also exhibited a lower micronaire and maturity ratio than the other growing regions. Previous work (Gamble, 2003) has shown that the amounts of soluble salts, as measured by conductivity of the water extract, are negatively correlated with micronaire due to a higher surface to volume ratio of lower micronaire cottons. Figure 2 shows the behavior of soluble potassium content as a function of micronaire. The correlation ($R^2 = 0.55$) is large enough to observe a general trend. When potassium content is correlated simultaneously with both rainfall and micronaire (not shown) via the two dimensional linear equation

$$z = z_o + ax + by$$

where z is potassium content, x is micronaire, and y is rainfall, a coefficient of correlation of R = 0.69 is achieved, indicating that soluble salt content (in this case potassium salts) is dependent upon both of these variables.

A similar argument based upon maturity differences is proposed to explain the relatively higher proportion of calcium present in the scour solution of the Texas cotton (Table 2). In this case, calcium content is a function of the amount of pectin present before scouring. The pectin content of cotton fiber has been demonstrated to be inversely correlated with maturity/micronaire (Gamble, 2003). The relationship between calcium present in the scour solution and micronaire is shown in Figure 3. The acid digest solution of the scoured fiber (Table 2) also

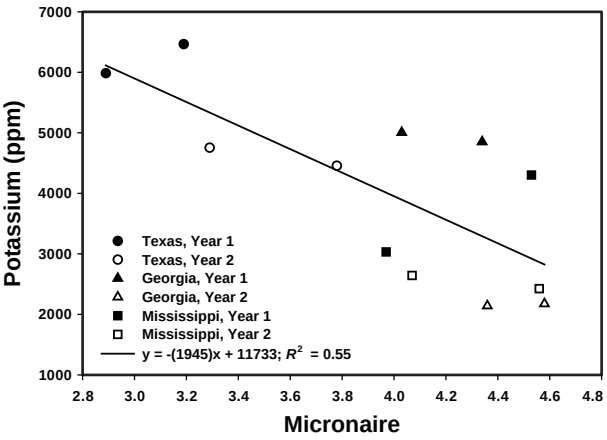

Figure 2. Potassium content (ppm on weight of cotton) in water extract of cotton samples (two varieties grown in three locations over two crop years) as a function of micronaire.

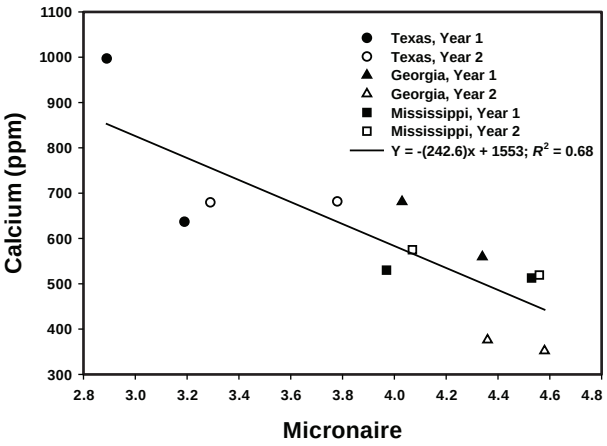

Figure 3. Calcium content (ppm on weight of cotton) in scour solution of cotton samples (two varieties grown in three locations over two crop years) as a function of micronaire.

Table 2. Metal contents (ppm on weight of cotton) of water extract, scour solution and acid digest of cotton samples (2 varieties grown over 2 consecutive crop years) compared by 3 growing regions.[z]

	region	Ca	K	Na	Mg	Fe	Zn	Rainfall (in)	mic	Maturity Ratio
extract	T	397.5	5415.1 a	45.9	313.1 a	5.8 b	16.6	3.8 b	3.28 b	0.86 b
	G	323.4	3539.1 b	41.9	178.6 b	4.6 b	13.0	6.1 b	4.33 a	0.90 a
	M	319.4	3098.1 b	75.1	128.4 b	12.2 a	13.0	15.4 a	4.28 a	0.90 a
			P<0.001		P<0.001	P<0.001		P=0.007	P=0.001	P<0.001
scour	T	748.8 a	0.0	NA	67.4	0.0	10.4	3.8 b	3.28 b	0.86 b
	G	492.1 b	21.3	NA	78.9	0.0	3.4	6.1 b	4.33 a	0.90 a
	M	534.3 b	3.2	NA	53.8	1.9	3.5	15.4 a	4.28 a	0.90 a
		P= 0.002						P=0.007	P=0.001	P<0.001
digest	T	556.4 a	5.0	36.7	225.4 a	15.7	13.8 a	3.8 b	3.28 b	0.86 b
	G	379.6 b	5.5	17.7	208.0 a b	10.0	5.4 b	6.1 b	4.33 a	0.90 a
	M	483.1 a b	4.4	22.5	156.7 b	14.6	6.1 b	15.4 a	4.28 a	0.90 a
		P<0.001			P=0.014		P=0.013	P=0.007	P=0.001	P<0.001

[z] **Means within a column followed by the different letters are significantly different according to Duncan's New Multiple Range test. Means within a column followed by no letters are not significantly different.**

indicates that the lower micronaire Texas cottons contain a higher proportion of calcium, magnesium and zinc. As discussed previously, this may be due to the incomplete removal of the pectin component, and therefore the metals associated with it, during the scouring process. If, on the other hand, the remaining metals are directly associated with the cellulose component, then the dependence upon maturity suggests that immature fibers may have a higher amorphous-to-crystalline cellulose ratio than more mature fibers, since amorphous cellulose exhibits more potential binding sites for divalent cations.

Though a number of regional differences are observed in the metal contents of the extract, scour, and digest solutions, these differences can be attributed to either rainfall conditions or maturity differences, which may themselves be possibly attributed to regional environmental conditions during the growing season. It cannot be demonstrated from the present results whether regional soil differences may contribute to observed differences in metal content in the extract, scour, or digest solutions. In order to accomplish this, cotton samples must be grown under identical environmental conditions but in separate soil types. This is most easily accomplished under greenhouse management, and will be the subject of future investigation.

Metal contents of the water extract, scour solution and acid digest of 12 cotton samples (cotton grown in three separate growing regions over two crop years) are compared between two varieties in Table 3. In this case, very little difference in metal content is observed between the varieties, and similarly no difference is seen with micronaire, maturity ratio, or rainfall. Based upon these results, metal content does not appear to be affected by variety of upland cotton. These results should be interpreted cautiously, however, since only two varieties were utilized in this study. A more comprehensive study, utilizing a much larger number of upland cotton varieties grown under identical environmental conditions, must be undertaken in order to establish conclusively that metal content is unaffected by variety.

CONCLUSION

Analysis of metal contents of cotton fiber was performed on two varieties of cotton grown in three growing regions of the U.S. cotton belt over two crop years. Sequential analysis of water soluble cations, cations removed during scouring, and cations solubilized as a result of acid digestion reveals: (1) that the proportion of water soluble cations, primarily K^+, is affected by the amount of rainfall experienced by the open bolls prior to harvest as well as by fiber maturity, (2) that the quantity of Ca^{2+} present in the scour solution is directly and negatively correlated with fiber maturity, and (3) that substantial amounts of Ca^{2+} and Mg^{2+} remain present in the post-scoured fiber, with an indication that lower maturity cottons retain higher levels than more mature cottons. Each of these observations is potentially applicable to one or more of the multiple stages involved in the processing of raw lint into finished fabric.

Table 3. Metal contents (ppm on weight of cotton) of water extract, scour solution and acid digest of cotton samples (grown in 3 separate growing regions over 2 crop years) compared by 2 varieties.[z]

	variety	Ca	K	Na	Mg	Fe	Zn	Rainfall (in)	mic	Maturity ratio
extract	FM832	333.2	3926.7	61.7 a	215.0	6.8	11.5	8.4	3.77	0.89
	FM966	360.3	4112.4	41.2 b	198.7	8.2	16.9	8.4	4.16	0.90
				P=0.030						
scour	FM832	639.9	0.0	NA	63.7	0.0	7.2	8.4	3.77	0.89
	FM966	543.6	3.6	NA	69.9	1.0	4.3	8.4	4.16	0.90
digest	FM832	477.8	1.8	17.9	224.6 a	14.2	8.4	8.4	3.77	0.89
	FM966	466.4	8.3	33.9	176.0 b	12.4	8.9	8.4	4.16	0.90
					P=0.012					

[z] Means within a column followed by the different letters are significantly different according to Duncan's New Multiple Range test. Means within a column followed by no letters are not significantly different.

REFERENCES

American Society for Testing and Materials (ASTM). 1997. Standard test method for micronaire reading of cotton fibers (D1448-97). *In* Annual Book of ASTM Standards. Vol. 07.01. ASTM, West Conshohocken, PA.

Brushwood, D.E., H.H. Perkins.1994. Determining the metal content of cotton. Textile Chemist and Colorist. 26(3):32-35.

Brushwood, D.E. 2002. metals in domestic and non-domestic cottons and their frictional properties. AATCC Review. 5:20-24.

Brushwood, D.E. 2005. Predicting yarn processing performance from the non-cellulosic content of raw cottons. Textile Res. J. 75:1-5.

Cook, F.C., 1991. Environmentally friendly: More than a slogan for dyes. Textile World 141(5): 84-89.

Domelsmith, L.N, R.J. Berni. 1984. Potassium:A new marker for washed cotton. Textile Res. J. 54(3):210-214.

Gamble, G.R. 2003. Variation in surface chemical constituents of cotton (Gossypium hirsutum) fiber as a function of maturity. J. Agric. Food Chem. 51: 7995-7998.

Gamble, G.R. 2006. The Influence of Surface Electrolyte and Moisture Content on the Frictional Behavior of Cotton Fiber. J. Cot. Sci. 10:61-67.

Goto-Doshido, S., M. Saito, M. Nagayama. 2003. Effects of calcium present in fabric and in washing liquor on detergency. J. Oleo Science 52: 73-82.

McCaffrey, S., G.K. Santokhi. 1999. The preparation of cotton knit goods. J. Soc. Dyers and Colourists 115:167-172.

Rezić, I., I. Steffan. 2007. ICP-OES determination of metals present in textile materials. Microchemical J. 85: 46-51.

Rodriguez, C.H., L.H. Lowery, J.F. Scamehorn, J.H. Harwell. 2001. Kinetics of precipitation of surfactants.1. Anionic surfactants with calcium and with cationic surfactants. J. Surfactants and Detergents 4(1):1-14.

Rucker, J.W., H.S. Freeman, W.N. Hsu. 1997. Evaluation of factors contributing to the light-induced yellowing of whitewashed denim. 1. Identification of extractable organics and metal ions. Textile Chemist and Colorist 24(9):66-71.

Dhindsa, R.S., C.A. Beasley, I.P. Ting. 1975. Osmoregulation in cotton fiber-accumulation of potassium and malate during growth. Plant Physiol. 56(3):394-398.

Wartelle, L.H., Bradow, J.M., Hinojosa, O., Pepperman, A.B., and Sassenrath-Cole, G. 1995. Quantitative cotton fiber maturity measurements by X-ray fluorescence spectroscopy and advanced fiber information system. J. Agric. Food Chem. 43:1219-1223.