The *Journal of Cotton Science 19:603–612 (2015)*
http://journal.cotton.org, © The Cotton Foundation 2015

TEXTILE TECHNOLOGY

Botanical Trash Mixtures Analyzed with Near-Infrared and Attenuated Total Reflectance Fourier Transform Spectroscopy and Thermogravimetric Analysis

Chanel Fortier*, James Rodgers, and Jonn Foulk

ABSTRACT

Botanical cotton trash mixed with lint reduces cotton's marketability and appearance. During cotton harvesting, ginning, and processing, trash size reduction occurs, thus complicating its removal and identification. This trash causes problems by increasing ends down in yarn formation and thus processing efficiency. The Uster® High Volume Instrument (HVI) and Shirley Analyzer are extensively used to determine trash levels in cotton lint, but they do not specifically identify its origin. This study was performed to determine the potential for recognizing differences between botanical cotton trash mixtures via near-infrared (NIR) spectroscopy and attenuated total reflectance-Fourier transform infrared (ATR/FT-IR) spectroscopy, and thermogravimetric analysis (TGA). A "proof of concept" was demonstrated that showed the promise of NIR and ATR/FT-IR spectroscopy along with TGA to be employed to identify binary mixtures of botanical cotton trash. In the case of the ATR/FT- IR results, the leaf and seed coat mixtures in the presence of cotton yielded the lowest accuracy of the trash mixtures. This might have arisen from the presence of noncellulosics in the samples.

Cotton quality measurement of trash comingled with lint is important because it can affect its later use in yarn and fabric, as well as its profitability. Conventional methods to determine trash content, such as the Uster® High Volume Instrument (HVI) and Shirley Analyzer, give information on the amount of trash present, but the identities of the trash components present are not specified.

Recently, understanding how to classify foreign matter comingled with cotton has been the aim of many researchers. Previous classification of cotton trash has been successfully carried out employing cluster analysis, neural networks, and visible image analysis (Siddaiah et al., 2006, 2009; Whitelock et al., 2009; Xu et al., 1999). Having a better understanding of trash identity could improve textile processing efficiency. Specifically, the development of methods for improved trash removal based on specific trash types at various stages of cotton processing would be advantageous. Thus, there is interest in identifying the types of trash present with cotton using a technique that is fast, accurate, and reproducible.

Near-infrared (NIR) spectroscopy meets these requirements because it is has been used previously to study textiles, particularly cotton, due to its speed, accuracy, precision, nondestruction of samples, and user friendliness (Montalvo and von Hoven, 2004; Rodgers and Beck, 2009; Rodgers and Ghosh, 2008; Taylor, 1980). The NIR spectral region encompasses 800 to 2500 nm (4000-12500 cm^{-1}) where the regions are defined as first, second, and third overtones or combination bands. The overtone NIR bands refer to vibrational transitions appearing in the NIR region that correspond to the fundamental vibrational frequencies in the mid-infrared region. The NIR combination bands correspond to stretching and deformation of mid-infrared fundamental bands**.** The primarily used NIR spectral region encompasses 1100 to 2500 nm. The primary absorbencies observed in the NIR spectral region are for the chemical species CH_i, NH_i, and OH (Perkampus, 1993). Also, NIR spectroscopy offers the flexibility of multiple sampling systems (e.g., fiber optic probe, rotating sphere) and the option of analyzing different size samples (pepper, powder) and large, raw cotton trash samples. Recently, NIR has been used to identify pure botanical trash components such as hull, leaf, seed coat, and stem with the overall prediction accuracy being greater than 98% (Fortier et al., 2010). Moreover, pure field trash components were identified uniquely using NIR spectroscopy (Fortier et al., 2012).

C. Fortier* and J. Rodgers, USDA-ARS-Southern Regional Research Center, Cotton Structure and Quality, 1100 Robert E. Lee Boulevard, New Orleans, LA 70124; and J. Foulk, USDA-ARS-Cotton Quality Research Laboratory, P.O. Box 792, Clemson, South Carolina 29633
*Corresponding author: chanel.fortier@ars.usda.gov

Fourier-Transform mid-infrared (FT-MIR) spectroscopy, commonly known as Fourier Transform infrared (FT-IR) spectroscopy, is a branch of vibrational spectroscopy and is a primary method that yields structural information about the chemical makeup of a sample. Group absorption frequencies defined by wavelength regions over the range of 400 to 4000 cm^{-1} can be used to get qualitative information about the functional groups in a sample. Recently, attenuated total reflection (ATR) FT-IR accessories have been used widely. The ATR accessory greatly simplifies or removes sample preparation compared to traditional FT-IR samples employing KBr pellets. Briefly, the ATR accessory operates on the principle that a highly reflective crystal such as diamond or germanium is used as the internal reflective element (IRE). This IRE has a higher index of refraction compared to the sample. This higher refractive index of the IRE results in internal reflection and generation of an evanescent wave into the sample. However, this evanescent wave limits the depth from which the spectrum of the sample occurs from. As a result of this limitation, species buried deeper than a micron within a sample might go undetected. In the present study, this disadvantage could strongly affect the results. It is important to have the sample and IRE in close contact, usually accomplished with a high pressure clamp and a homogeneous sample surface (Mirabella, 1993).

The ATR/FT-IR spectroscopy technique has been applied previously to study cotton trash often found comingled with cotton lint such as grass and plant parts, as well as other organic (including sugars), synthetic, and inorganic materials using the development of a spectral database (Fortier et al., 2010; Himmelsbach et al., 2006; Loudermilk et al., 2008). Recently, comparable research was carried out employing NIR spectroscopy on textiles (Church and O'Neil, 1998; Church et al., 1998). Moreover, ATR/FTIR spectroscopy also was applied to identify cotton trash collected in a rotor (Foulk et al., 2004), and to explain the effect of heat treatment and size reduction on cotton trash (Allen et al., 2007). Dust found in a cotton rotor instrument tends to be not easily identified. Thus, the small powder-size trash (0.177 mm standard diameter) and pepper-size trash (0.841 mm standard diameter) were chosen to assess these methods' ability to uniquely identify trash mixtures present with cotton when only a small amount of trash is found. Although ATR/FT-IR is a surface measurement and is limited in the depth of the measurement, this preliminary study has the potential to be scaled up once identifying spectral bands can be determined.

Thermogravimetric analysis (TGA) is a common analytical technique that yields information on the change in analyte mass with temperature, which can signify a change in sample composition, thermal stability, or kinetic parameters for chemical reactions in the sample. Weight losses or gains can be caused by chemical reactions or physical transitions such as desorption, vaporization, sublimation, or drying (Turi, 1981). TGA formerly has been used to study textiles (Easson et al., 2011; Faughey et al., 2000; Sammartino et al., 2010). Abidi and co-workers evaluated cotton quality using TGA to study the structural changes of cotton fibers during their development (Abidi et al., 2008). In addition, cotton fiber micronaire, maturity, and fineness have been studied using TGA (Abidi et al., 2007).

The aim of this study is to determine the feasibility of using NIR and ATR/FT-IR spectroscopy, as well as TGA, to analyze binary mixtures of botanical trash with cotton. Specifically, trash mixtures of known composition were prepared and analyzed in the absence and presence of cotton.

MATERIALS AND METHODS

Cotton and Trash Samples. All cotton samples were bleached cotton balls bought commercially. The trash samples originated from Mississippi, South Carolina, and New Mexico and were composed of nine varieties. The trash mixtures were analyzed as raw ("as is"), powder-sized samples (with a 0.177-mm standard diameter created using an 80 mesh and Wiley mill), and pepper-sized samples (with a 0.841-mm standard diameter created using a 20 mesh and Wiley mill).

NIR Analysis. Trash samples composed of binary combinations of hull, leaf, seed coat, and stem were initially run on the Bruker NIR MPA bench top instrument (Bruker Optics, Billerica, MA) using the rotating cup accessory and rotating macrosampling integrating sphere. Raw samples were run in the absence of cotton lint. In addition, pure pepper-sized samples of hull, leaf, seed coat, and stem were used to compose the binary trash mixtures as follows. Five concentrations by weight were prepared: 50:50, 75:25, 25:75, 20:80, and 80:20. Pure trash samples were mixed and then placed in glass vials, making sure each mixture was centered in the bottom of the vials. Next, a commercially bought cotton ball was placed on top of the mixtures. Samples of the bottom of the glass vials were run on the Bruker MPA benchtop NIR spectrometer using the rotating integrating sphere microsampling method. Five replicates were run for each mixture, turning the glass vial each time before the measurement was taken. A total of 32 scans with a resolution of 8 cm^{-1} were collected. Samples were averaged and baseline corrected using the Bruker OPUS software (v. 6.5). The calibration set was composed of the binary mixtures having the composition of 50:50, 75:25, and 25:75. The prediction set was composed of binary trash mixtures of 50:50, 20:80, and 80:20. Bruker OPUS IDENT software was used to develop NIR spectral libraries. Average samples in the prediction set were identified based on their spectral similarity to mixtures in the calibration set.

ATR/FTIR Analysis. For ATR/FT-IR measurements, a Vertex 70 FT-IR spectrometer (Bruker Optics, Billerica, MA) fitted with an ATR accessory with a ZnSe ATR crystal was used. In addition, a mid-infrared ceramic source, a KBr beam splitter, and a deuterated triglycine sulfate detector were employed. High purity nitrogen was utilized to minimize water and carbon dioxide bands. As the measurements were taking place, a low flow of positive pressure of the high purity nitrogen was applied. The resolution was 8 cm^{-1} and 32 scans were collected for the background and samples. Powder-sized binary trash mixtures having a composition of 50:50 by weight in the absence and presence of cotton were prepared, with the binary mixture sample size being 10 mg in total for mixtures of hull and leaf, hull and seed coat, hull and stem, leaf and seed coat, leaf and stem, and stem and seed coat. Five replicates were run for binary trash mixture samples in the absence of cotton. Samples were averaged and baseline corrected. In some cases, derivative math preprocessing was employed. A single measurement was made for trash mixtures in the presence of cotton, using two methods to measure the cotton-trash mixtures. First, a cotton ball was placed on top of the binary trash mixture and the samples were taken for a surface measurement of the binary trash mixtures on cotton (step 1). Next, the binary trash mixtures were mixed in a circular motion under the cotton ball without picking up the cotton ball and the samples were taken for a measurement of the cotton comingled with the binary trash mixtures (step 2).

TGA. Binary trash mixtures and individual trash component samples were run using a TA Instruments Q500 TGA (New Castle,DE) equipped with an evolved gas analysis (EGA) furnace. Using ultra-high purity nitrogen gas, a flow rate of 90 mL/min to the sample and 10 mL/min to the balance was maintained. The trash samples were weighed to contain 4 to 8 mg and were then were placed directly into sample pans, with no further sample preparation required. Next, samples were run using the ramp method of 10 °C/min from room temperature to 600 °C.

A principal component analysis (PCA) was carried out on the TGA data to show the effect of a computerized discrimination method. The sample names were: hull and seed coat, hull and leaf, hull and stem, leaf and stem, leaf and seed coat, and stem and seed coat.

RESULTS AND DISCUSSION

NIR Spectroscopy. Initially, large, raw, binary botanical trash mixtures were run on the NIR instrument in the absence of cotton. The calibration and prediction set were composed of binary mixtures of stem and seed coat, hull and seed coat, hull and stem, leaf and stem, leaf and seed coat, and hull and leaf. Representative first derivative spectra of the binary mixtures are shown in Fig. 1. Slight differences over the spectral range of 4450 to 4350 cm^{-1} are associated with CH stretching and bending frequencies. Table 1 shows the result summary for the NIR identification of raw trash mixtures in the prediction set. As can be observed, the NIR technique was used to identify botanical trash mixtures with greater than 95% accuracy.

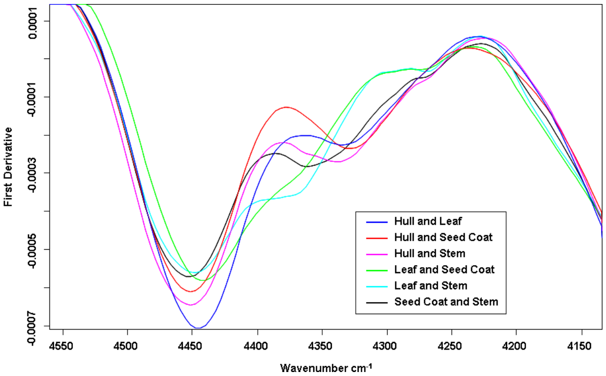

Figure 1. Representative NIR first derivative spectra of raw binary trash mixtures in the absence of cotton.

Table 1. NIR identification of raw trash mixtures in the prediction set in the absence of cotton

	%Correct	Number of Samples
Hull and Leaf	100.00%	3
Hull and Seed Coat	80.00%	5
Hull and Stem	100.00%	3
Leaf and Seed Coat	100.00%	5
Leaf and Stem	100.00%	3
Stem and Seed Coat	100.00%	5
Total	95.83%	24

As a follow-up study, pepper-sized binary trash mixtures in the presence of cotton were analyzed using NIR spectroscopy. Initially, one library encompassing all of the mixtures was created. Unfortunately, the accuracy of this method was hindered by the similar spectra of the binary trash mixtures. Thus, four separate libraries for hull, leaf, seed coat, and stem had to be created to improve the identification accuracy. Table 2 shows a representative hull mixture study by NIR. The data suggest that when hull component ratios in the binary mixtures are above 50%, the accuracy of the NIR identification routine is diminished in the presence of leaf and stem. The other binary trash libraries, where the common trash component was leaf, seed coat, and stem, yielded modest results and, therefore, are not shown. These results suggested that the averaging effects on NIR spectra and small trash particle size in the presence of large amounts of cotton presented a limitation in the identification of binary mixtures. Thus, ATR/FT-IR spectroscopy was investigated because it yields sharper spectral bands compared to NIR spectroscopy.

Table 2. Representative NIR identification of pepper hull mixtures in the prediction set

Component Ratio- 50:50	%Correct	Total Samples
Hull and Leaf	80%	10
Hull and SC	70%	10
Hull and Stem	60%	10
Component Ratio- 20:80	%Correct	Total Samples
Hull and Leaf	85%	13
Hull and SC	77%	13
Hull and Stem	77%	13
Component Ratio-80:20	%Correct	Total Samples
Hull and Leaf	46%	13
Hull and SC	77%	13
Hull and Stem	31%	13

ATR-FTIR Spectroscopy. Next, ATR-FTIR spectroscopy on a Bruker Vertex FTIR fitted with an ATR accessory by Pike Technologies was explored for its feasibility of determining the identification of powder-size binary trash mixtures, first in the absence of cotton. A calibration set composed of three different binary trash batches was created as shown in Table 3, with the remaining batches used in the prediction set as shown in Table 4. Figure 2 shows representative ATR/FT-IR spectra of the cotton and binary trash mixtures applying vector normalization preprocessing. Over the spectral range of 3200 to 3300 cm^{-1}, the cotton spectrum appears as a doublet versus the singlet observed for the binary trash mixtures. This peak is associated with the OH functional group. Also, a peak at 1730 cm^{-1} is present in the trash spectra and absent from the cotton spectrum. This peak is associated with the carbonyl functional group. Over the range of 1500 to 1000 cm^{-1}, there are distinctive spectral bands for both binary trash mixtures and cotton. The CH vibrations, over the spectral region of 1500 to 1420 cm^{-1}, have overlapping contributions from many different sources and might require further data treatment or physical extractions to specifically identify spectral peaks (Foulk et al., 2004). The bands in the 1160 to 1000 cm^{-1} range represent the CO stretching frequency and the COH and COC functional groups associated with carbohydrates (Foulk et al., 2004). In the case of binary mixture determination in the absence of cotton, the ATR-FTIR spectroscopy technique yielded greater than 95% accuracy as shown in Table 5.

Table 3. Calibration set for powder samples

Batch a	Batch b	Batch c
SC Hull	SC Hull	NM Hull
SC Seed Coat	MS Seed Coat	SC Seed Coat
SC Leaf	NM Leaf	SC Leaf
SC Stem	SC Stem	SC Stem

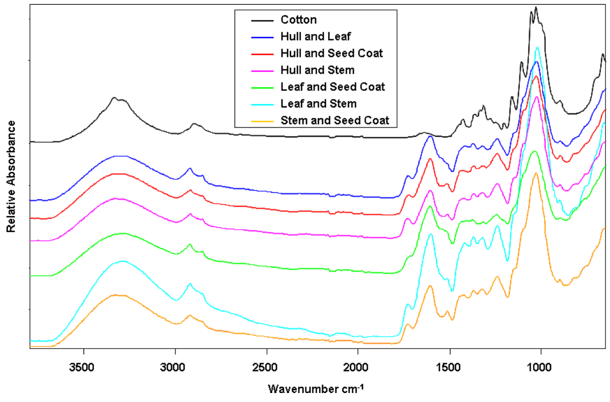

Figure 2. ATR/FT-IR representative absorbance spectra of clean cotton and binary trash mixtures in the absence of cotton.

Table 4. Prediction set for powder samples

Batch d	Batch e	Batch f
NM Hull	SC Hull	MS Hull
NM Leaf	NM Seed Coat	NM Seed Coat
NM Seed Coat	NM Leaf	SC Leaf
NM Stem	SC Stem	SC Stem
Batch g	**Batch h**	**Batch i**
NM Hull	SC Hull	SC Hull
SC Seed Coat	SC Seed Coat	NM Seed Coat
SC Leaf	SC Leaf	MS Leaf
MS Stem	NM Stem	SC F Stem
Batch j		
NM Hull		
SC Seed Coat		
SC Leaf		
NM Stem		

Table 5. ATR FTIR identification by cotton trash types for powder samples without cotton

Prediction Set	Powder Samples	
	%Correct	Number of samples
Hull and Leaf	100.00	35
Hull and Seed Coat	97.14	35
Hull and Stem	97.14	35
Leaf and Seed Coat	85.71	35
Leaf and Stem	97.14	35
Stem and Seed Coat	97.14	35
Total	95.71	210

Next, binary mixtures in the presence of cotton were prepared using either step 1 or step 2 as described in Materials and Methods. Using step 1, a calibration set composed of the three batches shown in Table 3 in the presence of cotton was created with the remaining batches being included in the prediction set as shown in Table 4. Figure 3 highlights the representative second derivative spectral differences of cotton and trash mixtures in the presence of cotton. The cotton spectra were observed to have bands different from the trash mixture spectra applying vector normalization, but the trash spectra were similar under these conditions. Thus, a top-down method was used to create the calibration set. First, the cotton spectra were separated from the spectra of the trash mixtures using vector normalization preprocessing. Next, the trash mixtures were included in a sublibrary where second derivative math and vector normalization preprocessing were applied. As depicted in Fig. 3, the cotton spectrum is uniquely different from the trash mixtures in the presence of cotton over the spectral range of 1730 to 1600 cm^{-1}. Over the same spectral range, the trash mixtures in the presence of cotton can be uniquely identified. The spectral range of 1730 to 1600 cm^{-1} includes the CO stretching band at 1730 cm^{-1} and adsorbed water at 1633 cm^{-1}. In the case of binary mixture determination in the presence of cotton (step 1), the ATR/FT-IR spectroscopy technique yielded greater than 90% accuracy as shown in Table 6.

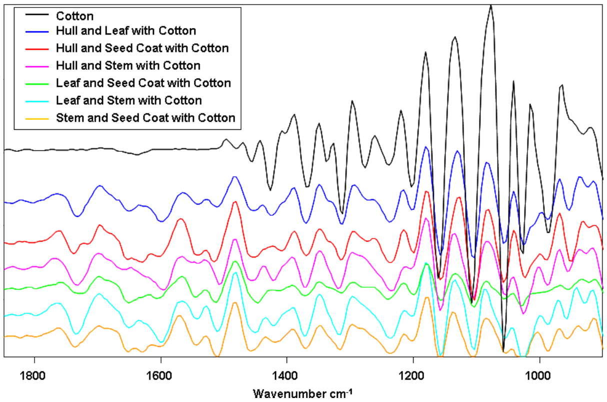

Figure 3. ATR/FT-IR representative second derivative spectra of clean cotton with binary trash mixtures in the presence of cotton.

Table 6. ATR FTIR identification by cotton trash types for powder samples with cotton (Step 1)

Prediction Set	Powder Samples	
	%Correct	Number of samples
Hull and Leaf	85.71	7
Hull and Seed Coat	100.00	7
Hull and Stem	100.00	7
Leaf and Seed Coat	71.43	7
Leaf and Stem	100.00	7
Stem and Seed Coat	85.71	7
Total	90.48	42

Next, the step 2 method was used to disperse the trash further into the cotton ball. A calibration set composed of three batches in the presence of cotton under these conditions was created with the batches shown in Table 3 with the remaining batches being included in the prediction set shown in Table 4. Table 7 reveals that this method resulted in greater than 83% accuracy. The spectra for each binary trash group type might be slightly different for different batches due to their natural origin and differences in amounts of non-cellulosic components such as waxes, color, and phenolics (Himmelsbach, 2006). This might have lead to some of the misidentifications in the prediction sets in the absence and presence of cotton, particularly for the identifications of the leaf and seed coat mixtures, which were determined with the lowest accuracy in all ATR/FT-IR studies. Although this program yielded highly accurate results, the small sample size (6 mm in diameter) and depth of penetration of the ATR crystal (typically on the order of 0.5 to 2 µm) could be viewed as a limitation of the ATR/FT-IR spectroscopic method. The two methods (step 1 and step 2) reveal the accuracy and potential to identify binary trash spectra when the trash is on the surface versus when the trash is embedded in the cotton sample. Even when the trash is embedded in the cotton, the accurate identification of the trash mixtures exceeds greater than 80%.

Table 7. ATR FTIR identification by cotton trash type for powder samples with cotton (Step 2)

Prediction Set	Powder Samples	
	%Correct	Number of samples
Hull and Leaf	100.00	7
Hull and Seed Coat	71.43	7
Hull and Stem	100.00	7
Leaf and Seed Coat	57.14	7
Leaf and Stem	85.71	7
Stem and Seed Coat	85.71	7
Total	83.33	42

TGA. First, pure samples of hull, leaf, seed coat, and stem were analyzed using TGA as shown in Fig. 4. The data below 100 °C represented unbound water loss and decomposition of fatty acids/esters, and thus, were not shown to simplify data presentation and analysis. All of the thermograms gave distinct thermal decomposition characteristics. The decomposition characteristics are given in Table 8 with the corresponding first derivative thermograms shown in Fig. 5.

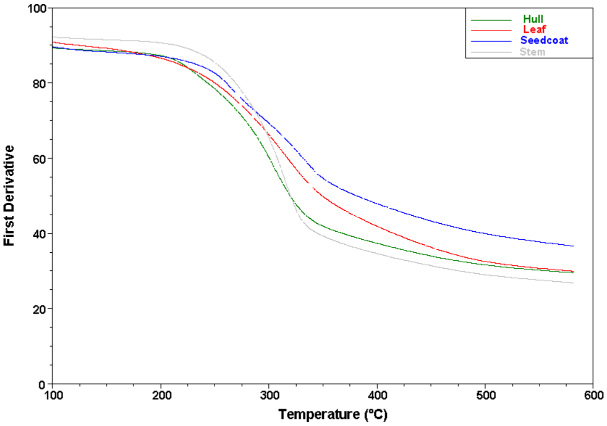

Figure 4. Representative TGA thermograms of pure botanical trash components in the absence of cotton.

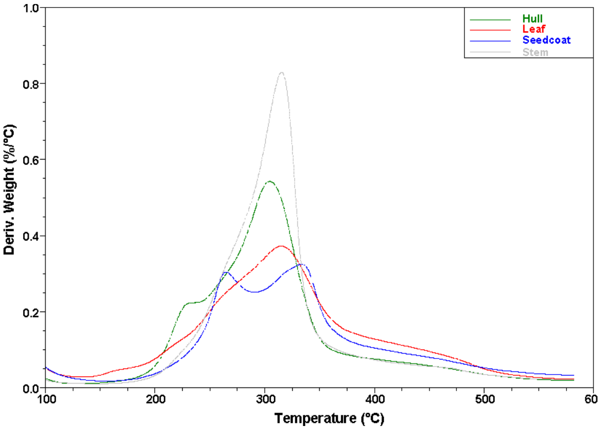

Figure 5. Representative TGA first derivative thermograms of pure trash components in the absence of cotton.

The three representative curves for each pure trash component, the original thermogram (TG), and the first and second time derivatives of the original thermogram, (DTG, and D^2TG) respectively, were used to find the decomposition parameters with the example curves given for stem represented in Fig. 6.

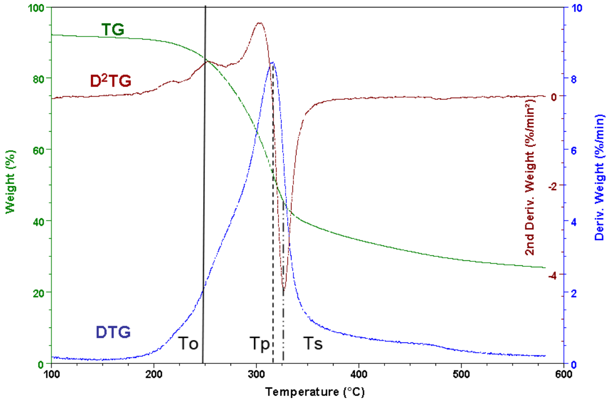

Figure 6. Determination of decomposition characteristic parameters of pure trash components using stem as an example. TG = original thermogram, DTG = first time derivative thermogram. And D^2TG = second time derivative thermogram.

The decomposition parameters of the pure trash components are given in Table 8. The onset temperatures (T_O) were found by extrapolating the slope of the first time derivative in correspondence with the first local maximum in the second time derivative curve and down to the zero level of the first derivative axis (Gronli et al., 2002). The peak temperatures (T_P) are represented by the maximum decomposition temperature for the first time derivative (Gronli et al., 2002). The shift temperatures (T_S) were found by extrapolating the slope of the first time derivative curve corresponding to the local minimum in the second time derivative curve in this region and down to the zero level of the first time derivative axis and also signifies the beginning of the final "tailing" region of the first time derivative indicating the completion of cellulose decomposition (Yao et al., 2008). Weight losses corresponding to the onset temperature (WL_o), the peak temperature (WL_p), and the shift temperature (WL_s), also were determined (Table 8) (Yao et al., 2009). In addition, the residues corresponding to weight losses at the final temperature, 580 °C, were found.

Table 8 depicts the onset temperatures for the four trash components in the range of about 200 ± 15 °C with the highest value occurring for seed coat. Hull had the highest weight loss at the onset temperature, signifying that it had the fastest initial decomposition compared to the other trash components. In the region of the peak temperatures where the highest decomposition rate occurred, the highest weight loss was observed for stem trash signifying its thermal instability compared to the other trash types, whereas seed coat required the highest peak temperature and highest residue suggesting it was the most thermally stable in this region as shown in Fig. 5. Also, recognizable from the first time derivative thermograms in Fig. 5 is that seed coat and hull trash samples have multistep decompositions with both having a shoulder peak represented in the temperature range of 200 to 275 °C, suggesting the presence of proteins, pectins, and hemicelluloses, as determined previously for developing cotton fibers (Hartzell-Lawson and Hsieh, 2000). Their similar chemical make-up also was observed previously by near-infrared spectroscopy (Fortier, 2010). The weight losses occurring at the peak temperatures above 300 °C were most likely due to cellulose decomposition (Yao et al., 2009). The seed coat had the highest residue amount of all of the trash components. The differences in thermogravimetric properties of the pure trash components are thought to be due to differences in noncellulosic and cellulosic content.

Six representative binary trash mixtures in the absence of cotton (50:50) were prepared (hull and leaf, hull and seed coat, hull and stem, leaf and seed coat, leaf and stem, and stem and seed coat) then analyzed by TGA as shown in Fig. 7. The decomposition parameters are shown in Table 9. The similarity in the TGA thermograms led to application of derivative math to the binary mixture data. The leaf and seed coat binary mixture had the highest weight loss at the onset temperature signifying that it had the fastest initial decomposition compared to the other trash mixtures. The hull and stem binary mixture was observed to have the highest weight loss at the peak temperature signifying that it was the most thermally unstable in this region. As can be observed from the first time derivative thermograms in Fig. 8, the peaks at 264.50 °C are due to the presence of seed coat in mixtures with stem, hull, and leaf. Also, in Fig. 8, the peak at 226.80 °C signifies the presence of hull in mixtures with stem, leaf, and seed coat. Both sets of shoulder peaks are thought to be due to the proteins, pectins, and hemicelluloses stemming from the hull and seed coat trash components in the mixtures. The observation that the hull and seed coat mixture in Fig. 7 had the highest remaining residue is not surprising because this mixture was more complex requiring multistep decomposition and, thus, decomposed to a lesser degree relative to the other mixtures having fewer components.

Table 8. Decomposition characteristics of pure trash components including onset temperatures (T_o), peak temperatures (T_p), shift temperatures (T_s), and corresponding weight losses and residues

Trash Type	T_o(°C)	WL_o(%)	T_p(°C)	WL_p(%)	T_s(°C)	WL_s(%)	Residue (%)
Hull	**211.26**	**13.65**	**304.07**	**42.40**	**336.60**	**55.74**	**29.55**
Leaf	**192.74**	**12.89**	**315.16**	**39.24**	**344.00**	**48.77**	**29.97**
Seed Coat	**213.00**	**13.53**	**335.40**	**41.20**	**355.39**	**46.37**	**37.05**
Stem	**198.42**	**9.27**	**316.64**	**47.26**	**334.40**	**58.16**	**26.87**

Table 9. Decomposition characteristics of binary trash mixtures without cotton including onset temperatures (T_o), peak temperatures (T_p), and shift temperatures (T_s) with corresponding weight losses and residues

Trash Mixtures	T_o(°C)	WL_o(%)	T_p(°C)	WL_p(%)	T_s(°C)	WL_s(%)	Residue (%)
Hull and Leaf	**189.48**	**12.83**	**309.02**	**40.06**	**370.64**	**56.07**	**31.33**
Hull and Seed Coat	**187.32**	**12.29**	**309.90**	**38.28**	**381.53**	**53.99**	**35.91**
Hull and Stem	**194.89**	**10.12**	**313.43**	**45.43**	**342.18**	**58.45**	**28.01**
Leaf and Seed Coat	**188.86**	**15.33**	**318.27**	**40.86**	**365.17**	**52.99**	**31.80**
Leaf and Stem	**195.03**	**13.18**	**318.27**	**44.50**	**337.37**	**52.70**	**29.10**
Stem and Seed Coat	**196.26**	**9.65**	**320.73**	**43.51**	**348.46**	**53.26**	**31.33**

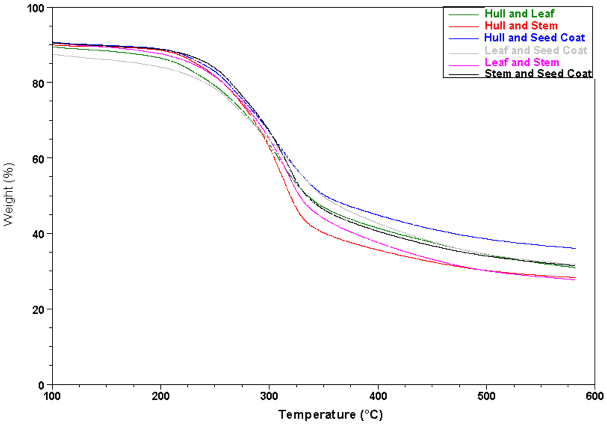

Figure 7. Representative TGA thermograms of binary trash mixtures in the absence of cotton.

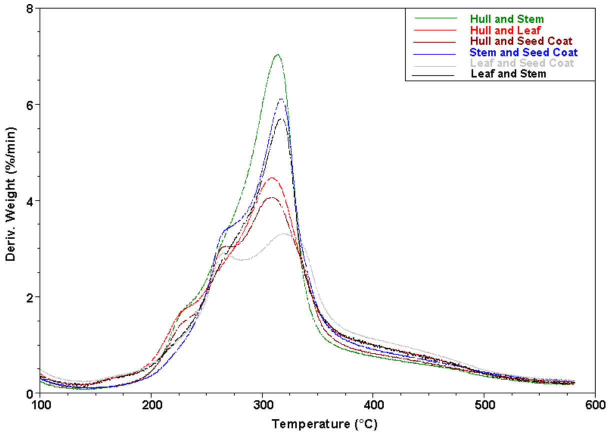

Figure 8. Representative TGA first derivative thermograms of binary trash mixtures in the absence of cotton.

Next, the decomposition characteristics of binary trash mixtures with cotton are listed in Table 10. Once again the hull and seed coat trashes had the highest residue with hull and stem having the lowest residue in the presence of cotton. Thus, TGA can be used to discriminate between pure botanical trash samples and binary trash mixtures in the presence of cotton when small sizes of trash mixture are under study.

Fig. 9 depicts that hull and stem in the presence of cotton degrades the fastest compared to the other combinations. In contrast, hull and seed coat in the presence of cotton degrades the slowest suggesting a more complex chemical makeup. Fig. 10 depicts the trash mixtures in the presence of cotton when applying the first derivative. Based on this figure, it appears that many of the mixtures have multi-step degradation. As was observed with the trash mixtures without cotton, mixtures including seed coat and hull showed multi-step degradation suggesting the presence of hemicellulose and cellulose.

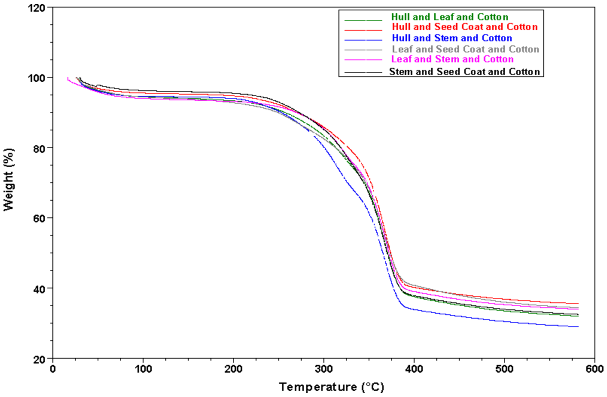

Figure 9. Representative TGA thermograms of trash mixtures in the presence of cotton.

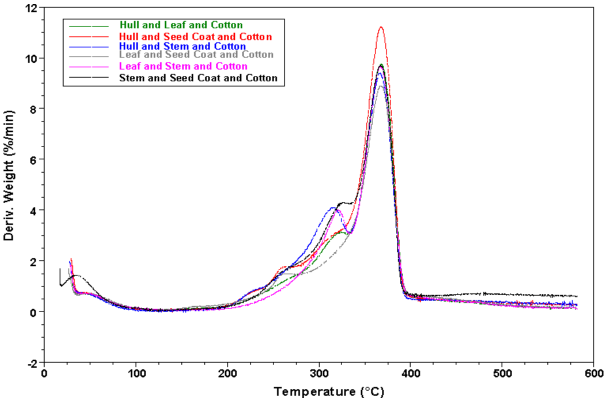

Figure 10. First derivative thermograms of trash mixtures in the presence of cotton.

Table 10. Decomposition characteristics of binary trash mixtures with cotton including the onset temperatures,(To), peak temperatures (Tp), and shift temperatures, (Ts) with corresponding weight losses and residues

Trash Mixtures	T_0(°C)	WLo(%)	Tp(°C)	WLp(%)	Ts(°C)	WLs(%)	Residue (%)
Hull and Leaf	209.09	6.94	369.41	49.25	385.10	60.29	32.14
Hull and Seed Coat	197.68	5.26	368.82	44.88	393.71	59.43	35.80
Hull and Stem	188.41	5.88	366.56	51.02	381.13	62.49	29.06
Leaf and Seed Coat	145.23	6.11	370.84	47.85	384.94	57.02	34.06
Leaf and Stem	208.35	7.01	369.50	47.48	391.65	60.38	34.15
Stem and Seed Coat	192.93	4.44	366.81	46.70	386.95	60.71	17.08

Fig. 11 depicts the PCA score plot carried out on the TGA zero-order data; the seed coat-containing mixtures appeared highly influenced by principal component 1. In contrast, two of the three stem-containing mixtures were highly influenced by principal component 2. This gives credence to the stem mixtures being more easily degraded in contrast to the seed coat mixtures. As for the validation variance, 98% of the model is explained by principal component 2 and 90% of the model is explained by principal component 1. For the calibration variance, principal component 1 described 95% of the model and principal component 2 described 99% of the model.

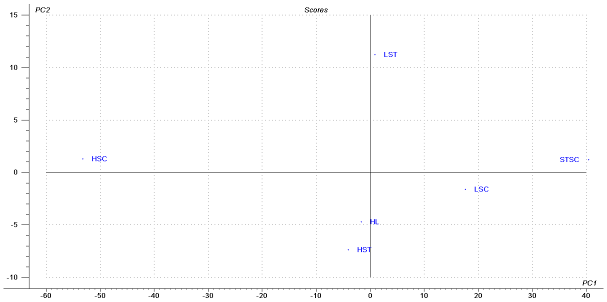

Figure 11. Principal component analysis of TGA binary mixtures. The sample names are: hull and seed coat (HSC), hull and leaf (HL), hull and stem (HST), leaf and stem (LST), leaf and seed coat (LSC), and stem and seed coat (STSC).

In conclusion, a program was implemented using NIR and ATR/FT-IR spectroscopy as well as TGA to identify binary mixtures of botanical trash in the absence and presence of cotton. Botanical binary trash mixture components consisting of large size hull, seed coat, stem, and leaf in cotton were studied by NIR spectroscopy. The large raw trash mixtures in the absence of cotton yielded highly accurate results, with greater than 95% correct identifications. However, the use of NIR spectroscopy to analyze powder-sized binary trash mixtures was not as successful, probably due to the averaging effect of this technique. ATR/FT-IR spectroscopy on powder-size binary trash mixtures gave highly accurate results in the absence (95%) and presence of cotton (90% and 83%). Notably, the leaf and seed coat mixture had a lower accuracy than the other binary trash mixtures. This might be due to the effect of noncellulosics, which was not determined in the current study. The fact that the origins of the samples (Mississippi, South Carolina, and New Mexico) were different did not play a major role in the correct prediction of binary mixture types as evidenced by the NIR and ATR/FTIR prediction set results. When comparing the large sample volume of NIR to that of the small sample required for ATR/FTIR, the ATR/FTIR technique yielded superior classification results. TGA was successfully used to identify individual trash components as well as binary trash mixtures in the absence and presence of cotton proving the feasibility of this method to qualitatively identify pure trash components and binary trash mixtures. The PCA analyses of the TGA data just further described the differences in binary trash mixtures in the presence of cotton.

ACKNOWLEDGMENTS

The authors wish to acknowledge the outstanding work of Sarah Lillis, Nicholas Saybe, Karl Jackson, and Jade Smith for preparing the samples and acquiring the NIR, ATR/FT-IR, and TGA data.

DISCLAIMER

The use of a company or product name is solely for the purpose of providing specific information and does not imply approval or recommendation by the United States Department of Agriculture to the exclusion of others.

REFERENCES

Abidi, N., E. Hequet, L. Cabrales, J. Gannaway, T. Wilkins, and L. Wells. 2008. Evaluating cell wall structure and composition of developing cotton fibers using Fourier Transform infrared spectroscopy and thermogravimetric analysis. J. Appl. Polym. Sci. 107:476–486.

Abidi, N., E. Hequet, and D. Ethridge. 2007. Thermogravimetric Analysis of cotton fibers: Relationships with maturity and fineness. J. Appl. Polym. Sci. 103:3476–3482.

Allen, A., J. Foulk, and G. Gamble. 2007. Preliminary Fourier-Transform infrared spectroscopy analysis of cotton trash. J. Cotton. Sci. 11:68–74.

Church, J., and J. O'Neill. 1999. The Detection of Polymeric Contaminants in Loose Wool and Cotton by NIR Spectroscopy. Vib. Spectrosc. 19:285–293.

Church, J., J. O'Neill, and A. Woodhead. 1998. The detection of fibrilated polymeric contaminants in wool and cotton yarns by NIR spectroscopy. Appl. Spectrosc. 52(8):1039–1046.

Easson, M., B. Condon, M. Yoshioka-Tarver, S. Childress, R. Slopek, J. Bland, T-M Nguyen, S. Chang, and E. Graves. 2011. Cyanuric chloride derivatives for cotton textile treatment-synthesis, analysis, and flammability testing. AATCC Rev. 11(6):60–66.

Faughey, G., S. Sharma, and R. McCall. 2000. Determining fiber fineness in flax using derivative thermogravimetric analysis, scanning electron microscopy, and airflow methods. J. Appl. Polym. Sci. 75:508–514.

Fortier, C., J. Rodgers, M.S. Cintrón, X. Cui, and J. Foulk. 2010. Identification of cotton and cotton trash components by Fourier Transform near-Infrared spectroscopy. Tex. Res. J. 81:230–238.

Fortier, C., J. Rodgers, J. Foulk, and D. Whitelock. 2012. Near-Infrared classification of cotton lint, botanical and field trash. J. Cotton Sci.16:72–79.

Foulk, J., D. McAlister, D. Himmelsbach, and E. Hughs. 2004. Mid-infrared spectroscopy of trash in cotton rotor dust. J. Cotton Sci. 8:243–53.

Himmelsbach, D. J. Hellgeth, and D. McAlister. 2006. Development and use of an attenuated total reflectance/Fourier Transform infrared (ATR-FTIR) spectral database to identify foreign matter in cotton. J. Agric. Food Chem. 54:7405–7412.

Gronli, M., G. Varhegyi, and C. Di Blasi. 2002. Thermogravimetric analysis and devolatilization kinetics of wood. Ind. Eng. Chem. Res. 41:4201–4208.

Hartzell-Lawson, M.M., and Y-L. Hsieh. 2000. Characterizing the noncellulosics in developing cotton fibers. Textl. Res. J. 70:810-819.

Loudermilk, J.B., D.S. Himmelsbach, F.E. Barton, 2nd, J.A. De Haseth. 2008. Novel Search Algorithms for Mid-Infrared Spectra Library of Cotton Contaminants. Appl. Spectrosc. 62(6):661–670.

Mirabella, Jr., F. 1993. Internal Reflection Spectroscopy. Marcel Dekker, New York, NY.

Montalvo, J., and T. Von Hoven. 2004. Analysis of cotton. near-infrared spectroscopy in agriculture. p. 671–728 *In* C. Roberts et al. (eds.). Near-Infrared Spectroscopy in Agriculture. American Society of Agronomy, Agronomy Monogr. No. 44, Madison, WI.

Perkampus, H. 1993. Encyclopedia of Spectroscopy. Wiley-VCH Verlagsgesellchaft mbH, Weinheim, Germany.

Rodgers, J., and K. Beck. 2009. NIR characterization and measurement of the cotton content of dyed blend fabrics. Tex. Res. J. 79:675–686.

Rodgers, J., and S. Ghosh. 2008. NIR Analysis of Textiles. p. 485–520 *In* D. Burns and E. Ciurczak (eds.). Handbook of Near-Infrared Analysis, 3rd ed. CRC Press, Boca Raton, FL.

Sammartino, L., M. Aranguren, and M. Rebredo. 2010. Chemical and mechanical characterization of two South-American plant fibers for polymer reinforcement: Caranday palm and phormium. J. Appl. Polym Sci. 115:2236–2245.

Siddaiah, M., E. Hughs, M. Lieberman, and J. Foulk. 2006. Trash measurements in ginned cotton. p.1923-1937 *In* Proc. Beltwide Cotton Conf., San Antonio, TX. 3-6 Jan. 2006. Natl. Cotton Counc. Am., Memphis, TN.

Siddaiah, M., D. Whitelock, M. Lieberman, S. Hughs, and S. Grantham. 2009. Categorization of extraneous matter in cotton using machine vision systems. p.1211-1216 p. *In* Proc. Beltwide Cotton Conf., San Antonio, TX. 5-8 Jan. 2009. Natl. Cotton Counc. Am., Memphis, TN.

Taylor, R. 1980. Cotton trash and contamination measurements for quality classification using near infrared reflectance. p.259-262 Proc. Beltwide Prod. Res. Conf., St. Louis, MO. 6-10 Jan. 1980. Natl. Cotton Counc. Am., Memphis, TN.

Turi, E. 1981. Thermal Characterization of Polymeric Materials. Academic Press, New York, New York.

Whitelock, D., M. Siddaiah, E. Hughs, and E. Barnes. 2009. Effects of lint cleaning on lint trash particle size distribution. p.514-520 *In* Proc. Beltwide Cotton Conf., San Antonio, TX. 5-8 Jan. 2009. Natl. Cotton Counc. Am., Memphis, TN.

Xu, B., and C. Fang. 1999. Clustering analysis for cotton trash classification. Textl. Res. J. 69:656–662.

Yao, F., Q. Wu, and D. Zhou. 2009 Thermal decomposition of natural fibers: Global kinetic modeling with nonisothermal thermogravimetric analysis. J. Appl. Polym. Sci. 2:834-842.