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TEXTILE TECHNOLOGY

Evaluation of Cotton Stickiness via the Thermochemical Production of Volatile Compounds

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ABSTRACT

Insect honeydew contamination of cotton lint can interfere with carding, roving, and spinning processes at the mill, and thus presents a major concern for the textile industry. Several methods exist for the detection of insect honeydew on cotton lint, but none have proven to be sufficiently reliable, cost effective, and rapid enough to be used as an online screening method. The objective of this study was to determine whether production of volatile compounds resulting from the heating of honeydew-contaminated cotton can be utilized to quantify the level of contamination. A set of 17 cotton samples with varying levels of whitefly honeydew contamination were heated to 180°C under a stream of air. Honeydew present on the cotton underwent thermochemical degradation with concomitant production of the compound 5-hydroxymethyl-2-furaldehyde (HMF). HMF is volatile at 180°C and was collected from the gas phase using a fiber coated with an adsorbent material and subsequently quantified using gas chromatography. Results indicate that the level of HMF production from honeydew-contaminated cotton correlates with the stickiness level as measured by the sticky cotton thermodetector ($R^2 = 0.77$) and with sugar levels as measured by both high performance anion exchange chromatography ($R^2 = 0.73$) and by the glucose oxidase enzyme method ($R^2 = 0.74$). This work is a feasibility study for the development of a potentially rapid, cost effective, and portable method for the detection of sticky cotton based on the release and subsequent measurement of volatile compounds.

It is widely accepted that the primary cause of cotton stickiness is the presence of hygroscopic sugars on the surface of the cotton fibers. These sugars may originate from the plant as a consequence of cotton plant physiology or from insects in the form of honeydew excreted by phloem-feeding insects. The cotton aphid (*Aphis gossypii* Glover) and silverleaf whitefly (*Bemesia argentifoli* Bellows & Perring) are responsible for most cases of cotton stickiness (Sisman and Schenek 1984). Because of the relationship between insect derived sugars and cotton stickiness, a variety of methods have been developed to measure the sugar content of cotton, many of which have been included in a comprehensive survey of sugar test methods (Brushwood and Perkins 1993).

Of the available methods to test for sugar, high performance anion exchange chromatography (HPAEC) is perhaps the most effective for both the identification and quantification of the individual sugars present. The time it takes to analyze a single sample (30 minutes) and the prohibitive cost of the equipment are major drawbacks of employing HPAEC as a screening method for stickiness on cotton. An enzymatic method involving the use of glucose oxidase to convert glucose levels into an amperometric reading has been demonstrated as a reliable method for determining the extent of total sugars, as well as sugar content attributable to insect honeydew contamination (Gamble 2001). The enzymatic method, like HPAEC and other sugar analysis methods, suffers from the inability to provide the rapid results needed for on-line screening of sticky cotton.

Previous research has demonstrated that trehalulose and melezitose, the primary oligosaccharides comprising whitefly honeydew, in addition to other constituent sugars including glucose, fructose, maltose, and sucrose are subject to thermochemical degradation at sufficiently high temperatures (Gamble 2002). One of the common products of sugar degradation is 5-hydroxymethyl-2-furaldehyde (HMF), a compound that is volatile at the temperatures required to induce thermochemical degradation of sugars. The purpose of this work is to determine whether HMF, as well as other volatile compounds, produced as a result of the thermochemical degradation of all sugars present on contaminated

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cotton can be collected, measured and calibrated against the amount of surface sugars present as measured by HPAEC and the glucose oxidase methods. These sugars may be present as plant metabolic sugars, as well as insect honeydew sugars. If such a calibration can be demonstrated, it could provide a basis for the development of a method for the detection of sticky cotton based on the production and measurement of volatile compounds. Such a method could potentially be utilized at the heating tower of the cotton gin for continuous monitoring of volatiles produced, and provide a rapid and cost effective alternative to methods currently employed.

MATERIALS AND METHODS

Cotton Samples. Cotton samples exhibiting a range of whitefly honeydew contamination were obtained from the Western Cotton Research Laboratory, USDA-ARS. A limited quantity (~8 grams) of each cotton sample was available. The fact that the samples were ginned at ambient temperature made them ideal for use in this study. Since the samples experienced no prior heat history, degradation of the sugars due to thermochemical reactions during ginning was avoided. The criterion used to identify samples exhibiting a wide range of stickiness potential was the measurement provided by the sticky cotton thermodetector (IRCT, Montpellier, France). Operation of the thermodetector has been described (Brushwood and Perkins 1993). Results from 17 samples chosen based on this criterion ranged from 1 to 70 sticky counts, indicating potential stickiness ratings ranging from non-sticky to extremely sticky.

Sugar Analysis by the Glucose Oxidase Electrode. A single 1.0-gram sub-sample of each of the 17 cotton samples was weighed and subsequently extracted with 20 parts (w/w) cold, deionized water. The extraction procedure consisted of wetting the cotton through agitation, followed by a period of 30 minutes during which time the sample was periodically reagitated. The resulting extract was analyzed for glucose content using a Yellow Springs Instrument Co. Model 2700 Bioanalyzer (Yellow Springs, OH). An aliquot of 8.0 ml of the remaining extract was brought to 0.4 N HCl by addition of 2.0 ml of a 2.0 N solution of HCl. The resulting solution was subsequently heated to 95°C for 2 hours in a sealed glass vial in order to insure that no evaporation occurred. These conditions ensure that nearly complete hydrolysis of all oligosaccharides occurs without a concomitant degradation of glucose. The solution was then cooled to room temperature and neutralized by the addition of 2 ml of a 2.0 N solution of NaOH. The resultant hydrolyzed solution was then analyzed for glucose content using the bioanalyzer described above, and the concentration reading (ppm) multiplied by a factor of 1.5 to account for dilution using the acid and base solutions. Results are reported in ppm relative to the weight of the cotton sample. Two measurements are reported based on this analysis. Total glucose following hydrolysis (HG) provides an indication of total sugar content due to both plant and insect origin. The initial glucose measurement preceding hydrolysis was subtracted from the final measurement following hydrolysis and the resultant quantity, ΔG, provides an indication of total oligosaccharide content due primarily to insect honeydew contamination (Gamble 2001).

High Performance Anion Exchange Chromatography. Separate 1.0-gram sub-samples were similarly extracted in cold, deionized water, and an aliquot of 0.5 ml was analyzed for the individual sugars glucose, fructose, trehalulose, sucrose, melezitose and maltose using high performance anion exchange chromatography (HPAEC). Chromatography was performed on a Dionex DX-500 (Dionex Corp., Sunnyvale, CA) using pulsed amperometric detection. Two Dionex Carbopac PA-1 (4 x 250 mm) columns were connected in series and elution was carried out at 0.75 ml/min using 200 mM NaOH as the mobile phase and a sigmoidal gradient of 0 to 500 mM NaOAc. Results of the 6 primary constituent sugars found on the whitefly honeydew-contaminated cottons are reported in ppm relative to the weight of the cotton sample. The HPAEC chromatograms each exhibited a sugar profile consistent with previous observation on whitefly honeydew (Brushwood 1998). In general, trehalulose is the most prevalent sugar, accounting for between 15 to 56% of the total extract, followed by fructose (8-40%), glucose (1-36%), and melezitose (1-30%). Sucrose and maltose make up a relatively small proportion (0-10% and 0-5%, respectively). The ratio of melezitose to trehalulose ranged from 0.27 to 0.67, with an average value over all 17 samples of 0.49, consistent with previous reports on whitefly honeydew (Brushwood 1998).

Volatile Compound Production and Collection. Duplicate 1.0-gram sub-samples of each cotton sample and samples of individual sugars were

heated to 180°C under a stream of air for three hours using a Thermal Desorption Sample Collection System (Scientific Instruments Services, Ringoes, NJ). Glucose, fructose, maltose, melezitose, sucrose, and 5-hydroxymethyol-2-furaldehyde (HMF) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO), and trehalulose was obtained as a 95% syrup from Mitsui Sugar Co. (Japan). The resultant air stream was subsequently passed over a Solid Phase Microextraction (SPME; Supelco, St. Louis, MO) fiber coated with 100 mm polydimethylsiloxane adsorbent. Though sugar degradation has been shown to proceed at a more rapid rate as a result of increased temperature (Gamble 2002), 180°C represents the maximum temperature to which cotton is heated at the cotton gin in order to avoid concomitant degradation of the fibers. Because of the potential utilization of this technique as a gin-based screening method, the production of volatiles must be demonstrated at temperatures of ≤180°C. Each sample was heated for 3 hours in order to insure a quantitative degradation of all sugars present on the surface of the fiber. Although 3 hours is unrealistic in terms of a screening method, this study attempts to preliminarily determine whether a correspondence exists between total volatile production and total surface sugars. Assuming such a relationship is shown to exist, any screening method developed as a result would likely rely on the rate of volatile production from a known quantity of cotton rather than total volatile production.

Gas Chromatography. At the end of the volatile collection period, the SPME fiber was desorbed directly onto a Hewlett-Packard 5890 Gas Chromatograph (Agilent Technologies, Palo Alto, CA) equipped with an Ultra-2 column. The sample was introduced by splitless injection at 250 °C. The injection port was equipped with a 0.75 mm I.D. deactivated glass liner for small volume SPME injections. The column temperature was ramped from 40 °C to 250 °C in 10 minutes and held at 250 °C for 10 minutes. Peak detection was by flame ionization at 250 °C. Hydrogen at a flow rate of 0.45 ml/min was used as the carrier gas. Peak quantification was performed by integrated area, and results for the duplicate samples averaged.

Statistics. All regressions and analyses of standard error were performed using SigmaPlot 5.0 (SPSS Science, Chicago, IL). Multivariate analyses were performed using release 8.00 of SAS for Windows (SAS Institute, Inc., Cary, NC).

RESULTS AND DISCUSSION

The gas chromatogram of pure 5-hydroxymethylfuraldehyde (HMF) adsorbed onto the SPME fiber at room temperature shows a primary response at t = 7.0 minutes (Figure 1). Secondary responses observed at t = 5.8 and t = 4.8 minutes are due to the degradation of HMF in the injection chamber and exhibit approximately 10% of the integrated area compared to the t = 7.0 minutes peak. A decrease in injection temperature results in a decrease in this secondary peak, but in spite of this it was determined that a 250 °C injection temperature was optimal for desorption of all components arising from the heating of cotton samples. The peak at t = 11.8 minutes is due to a contaminant from the injection port septum.

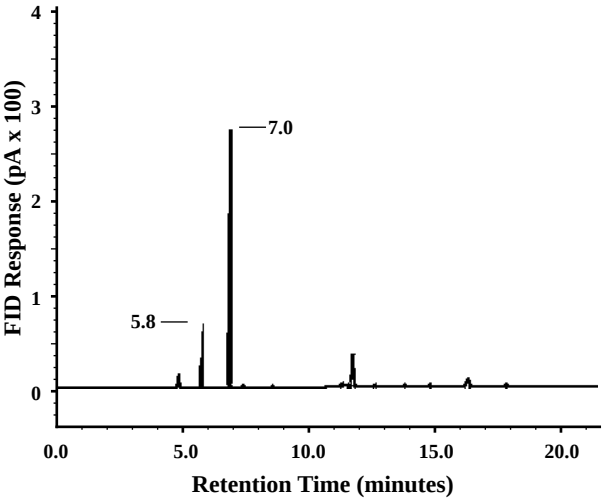

Figure 1. Gas chromatogram of 5-hydroxymethyl-2-furaldehyde (HMF) heated at 180°C under a stream of air for 3 hours using flame ionization detection (FID). pA=pico-amperes.

Trehalulose and melezitose, the two most prevalent saccharides present in whitefly honeydew, were heated at 180 °C under a stream of air and the resultant volatile thermochemical degradation products collected on the SPME fiber. The chromatograms of these volatile degradation products for trehalulose and melezitose (Figures 2 and 3, respectively) show peaks at t = 7.0 minutes, identified in both cases as HMF. The secondary peak at t = 5.8 minutes is also observed in both cases. In addition, trehalulose produces a third major peak upon thermochemical degradation, observed at t = 6.4 minutes. This component has yet to be identified, but is nevertheless used in addition to the peak at t = 7.0 minutes as a mea-

sure of trehalulose in this work. Chromatograms for glucose and fructose (not shown) are similar to melezitose. This is not unexpected in that melezitose initially thermally decomposes to its constituent monosaccharides (Gamble 2002), which subsequently undergo degradation to HMF. Trehalulose, by contrast, appears to undergo direct degradation to HMF and the unidentified component at t = 6.4 minutes (Gamble 2002).

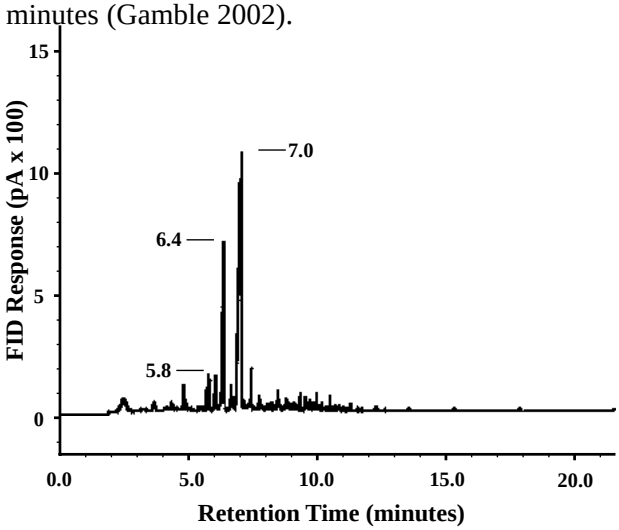

Figure 2. Gas chromatogram of volatile products from the thermochemical degradation of trehalulose heated at 180°C under a stream of air for 3 hours using flame ionization detection (FID). pA=pico-amperes.

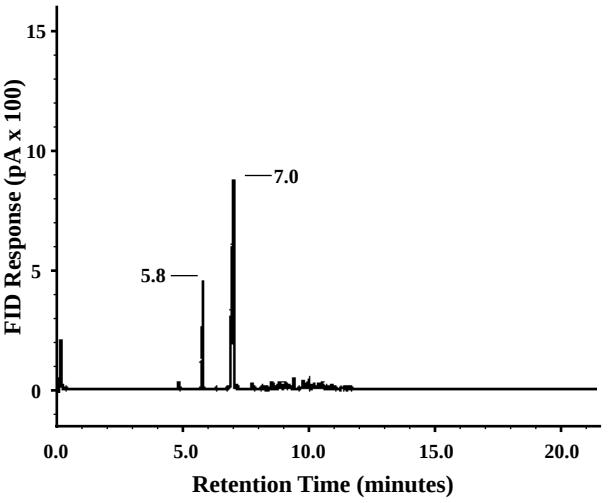

Figure 3. Gas chromatogram of volatile products from the thermochemical degradation of melezitose heated at 180°C under a stream of air for 3 hours using flame ionization detection (FID). pA=pico-amperes.

The gas chromatogram obtained by heating honeydew-contaminated cotton is more complex than for the individual sugars or HMF (Figure 4). In addition to the peaks observed for HMF, there are many response peaks observed between 7.0 and 15.0 minutes. These peaks are due primarily to the presence of volatile compounds arising from non-sugar components of the cotton fiber, including waxes, organic acids, and proteins. The response peaks at t = 7.0 and 6.4 minutes are nevertheless easily distinguishable from the background.

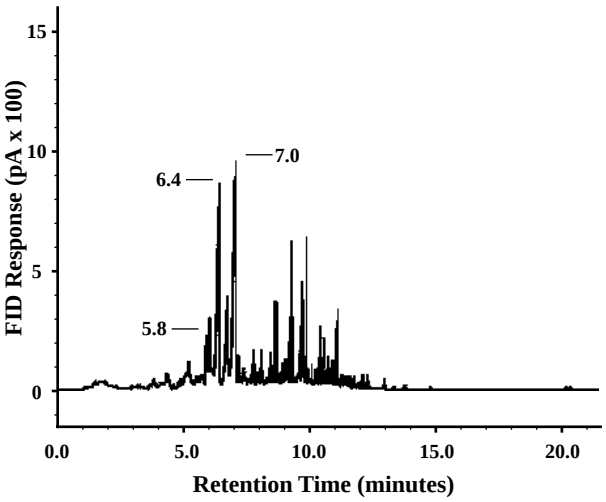

Figure 4. Gas chromatogram of volatile products from the thermochemical degradation of whitefly honeydew on contaminated cotton lint heated at 180°C under a stream of air for 3 hours using flame ionization detection (FID). pA=pico-amperes.

The coefficients of determination for linear regressions between SCT counts, total sugars measured by HG, total sugars measured by HPAEC, the combined integrated areas of the gas chromatographic peaks at t = 6.4 and 7.0 minutes, and also with the individual sugars as measured by HPAEC and total oligosaccharide content as measured by DG are shown in Table 1. A high degree of correlation (R^2 = 0.95) is found between total sugars as measured by HG and HPAEC, despite the fact that HG measures nearly 52% of the total sugars relative to HPAEC, as determined from the slope of the linear regression (not shown). This discrepancy is due to the fact that whitefly honeydew has a large proportion of fructose and trehalulose, which is a disaccharide of fructose and glucose base units. Fructose is not accounted for in the HG measurement, but the fact that the two total sugar measurements correlate well indicates that the fructose base sugar unit may be present in a roughly constant proportion with the glucose base sugar unit in the case of whitefly honeydew.

Table 1. Coefficients of determination (R^2) between thermodetector sticky counts (SCT) and sugar measurements obtained by the glucose oxidase electrode (HG), anion exchange chromatography (HPAEC), and gas chromatography (GC)

Sugar(s) and method of measurement[z]	Coefficients of determination (R^2)			
	Sticky spots (by SCT)	HG (by glucose electrode)	Total sugar (by HPAEC)	δ6.4 + δ7.0 (by GC)
Glucose	0.08	0.20	0.27	0.15
Fructose	0.45	0.54	0.68	0.57
Trehalulose	0.59	0.92	0.88	0.63
Sucrose	0.33	0.30	0.38	0.35
Melezitose	0.56	0.90	0.92	0.62
Maltose	0.49	0.65	0.57	0.42
Total sugars	0.64	0.95	1.00	0.73
Total sticky spots (by SCT)	1.00	0.66	0.64	0.77
HG (by glucose electrode)	0.66	1.00	0.95	0.74
ΔG (by glucose electrode)	0.66	0.99	0.93	0.72
δ6.4 + δ7.0 (by GC)	0.77	0.74	0.73	1.00

[z] Measured by anion exchange chromatography unless otherwise noted.

Sugar measurements are not as widely utilized for screening sticky cotton as are the mechanical screening methods, including the sticky cotton thermodetector, a method widely used in the textile industry for screening sticky cotton. This wide acceptance is due in part to the relative speed of the method, taking approximately 5 minutes per sample. The High Speed Thermodetector, an automated derivative of the thermodetector, is even faster. Due to this wide usage, the acceptance of any new screening method is partially contingent upon its ability to provide results comparable with the sticky cotton thermodetector. Figure 5 shows a comparison of thermodetector counts with the combined integrated area of the gas chromatographic peaks at t = 7.0 and 6.4. The correlation in this case (R^2 = 0.77) is higher than for any of the other variables, including HG (R^2 = 0.66) and total sugars by HPAEC (R^2 = 0.64). A stepwise multivariate analysis using SCT counts as the dependent variable resulted in a 4-variable model with R^2 = 0.84, where the combined gas chromatographic peaks were the best predictor of sticky counts (F = 12.06, P = 0.0046). The next 3 variables were glucose, fructose, and DG, each exhibiting F values close to 1.00 and P values > 0.100.

A comparison of total saccharide content (as measured by HG) with the combined integrated area of the gas chromatographic peaks at t = 7.0 and 6.4 minutes for the 17 honeydew-contaminated cotton samples is shown in Figure 6. There is a good correlation (R^2= 0.74) between the measurements, indicating that measurement of HMF released as a result of thermochemical degradation is potentially an alternative method for determination of sugar contamination on cotton lint. A comparison of total sugar, as measured by HPAEC, with the combined integrated area of the gas chromatographic peaks at

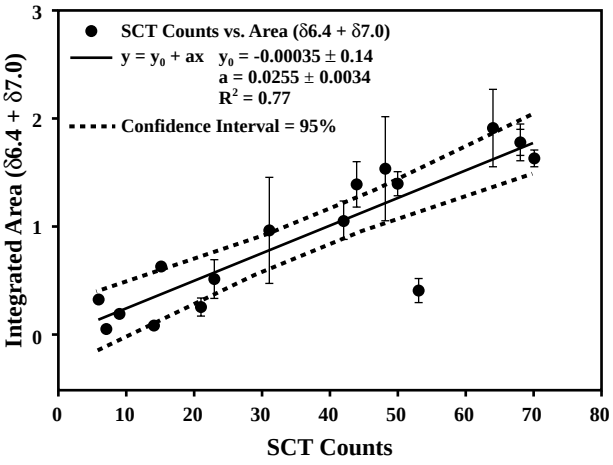

Figure 5. Comparison of the combined integrated areas of the t = 6.4 and t = 7.0 peaks in the gas chromatograms of 17 whitefly honeydew-contaminated cottons with sticky cotton thermodetector (SCT) counts. Bars indicate standard error.

t = 7.0 and 6.4 minutes is shown in Figure 7. The correlation between the measurements is also high in this case (R^2 = 0.73), and serves to corroborate the potential utility of the HMF measurement as an alternative to direct sugar measurements.

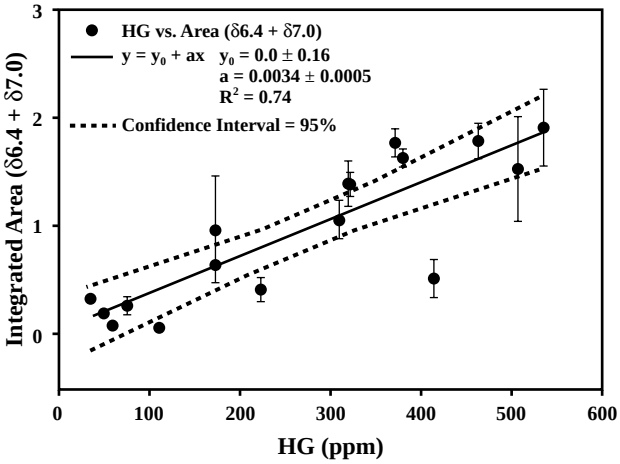

Figure 6. Comparison of total sugar content on cotton lint as measured by total glucose following hydrolysis (HG) with the combined integrated areas of the t = 6.4 and t = 7.0 peaks in the gas chromatograms of 17 whitefly honeydew-contaminated cottons. Bars indicate standard error.

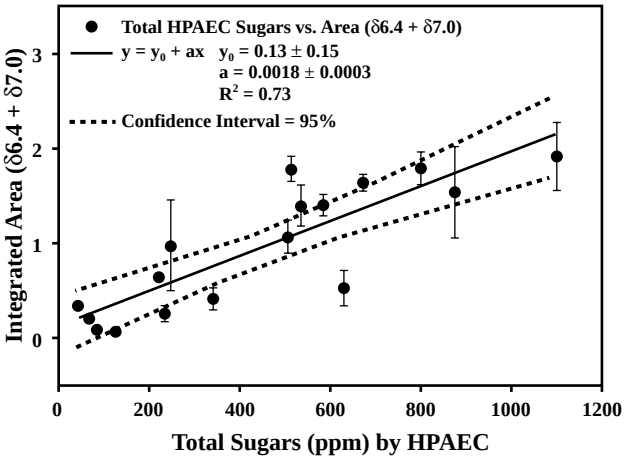

Figure 7. Comparison of total sugar content on cotton lint as measured by high performance anion exchange chromatography (HPAEC) with the combined integrated areas of the t = 6.4 and t = 7.0 peaks in the gas chromatograms of 17 whitefly honeydew-contaminated cottons. Bars indicate standard error.

The work presented here shows that the measurement of total volatiles resulting from the thermochemical degradation of sugars can be used as an alternative screening method for sticky cotton. From the results presented for 17 whitefly honeydew-contaminated cottons, in fact, the measurement appears to be superior to the two direct measurements of total surface sugars. The utility of the measurement is hindered by the fact that complete thermochemical degradation of all surface sugars can take up to 3 hours to accomplish at 180°C. Continuing research is being performed with the goal of achieving a measurement of honeydew contamination within seconds of heating the cotton sample. To accomplish this, it must be demonstrated that a relationship exists between total volatile production and the rate of volatile production. Assuming that this relation exists, then the initial rate of volatile production upon heating will be a function of the initial concentration of surface sugars, as well as temperature. Methodologies for the measurement of volatile compounds used for real-time monitoring are currently under investigation, including Photoionization Detection and Ion Mobility Spectroscopy, both of which have demonstrated utility as rapid, cost-effective and reliable methods for monitoring volatile emissions from explosives, narcotics, etc. The Ion Mobility Spectrometer is currently being investigated for utilization in the separate but related problem of rapidly identifying plastic waste in cotton (Eiceman et al. 2002), with promising results. The ultimate goal is the development of a system which can be used in the field, at the gin, or in the textile mill to detect sticky cotton rapidly and reliably.

REFERENCES

Brushwood, D., Perkins, H. 1993. Cotton sugar and stickiness test methods. Canadian Textile J. 110(6):54-62.

Brushwood, D. 1998. Carbohydrates on silverleaf whitefly contaminated cottons. Textile Chemist and Colorist 30(2):33-35.

Eiceman, G.A., Bergloff, J.F., Funk, P.A. 2002. Comparison of emission profiles for volatile organic compounds from cotton and polypropylene-based tarp [On-line]. J. Cot. Sci. 6:40-51. Available at http://www.jcotsci.org/2002/issue01/pdf/art05.pdf.

Gamble, G.R. 2001. Evaluation of an enzyme based method for the detection of stickiness potential [On-line]. J. Cot. Sci. 5:169-174. Available at http://www.jcotsci.org/2002/issue04/pdf/jcs02i4-4.pdf.

Gamble, G. 2002. The thermochemical degradation of melezitose and trehalulose as related to cotton stickiness. Textile Res. J. 72(2): 174-177.

Sisman, S., Schenek, A. 1984. Bremen honeydew test- new method for testing the sticking tendency of cotton. Melliand Textilberichte (English Ed.) 13(10): 593-595.