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DETECTION OF STICKY COTTON VIA RELEASE OF VOLATILE COMPOUNDS

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Abstract

Cotton samples exhibiting varying levels of whitefly honeydew contamination were subjected to 180°C temperatures under a stream of air. Honeydew present on the cotton underwent thermochemical degradation with concomitant production of the compound 5-hydroxymethylfuraldehyde (HMF). HMF is volatile at 180°C and was collected from the gas phase on an adsorbent material and measured using gas chromatography. Results indicate that HMF production is correlated with stickiness level as measured by the sticky cotton thermodetector and with sugar levels as measured by both HPLC and by the glucose oxidase enzyme method. This study provides the foundation for the development of a rapid, cost effective, and portable method for the detection of sticky cotton based on the release and subsequent measurement of volatile compounds.

Introduction

It is generally agreed that the primary cause of cotton stickiness is the presence of sugars on the surface of the cotton fibers. These sugars may be of plant origin as a consequence of cotton plant physiology or of insect origin in the form of honeydew excreted by phloem feeding insects such as the cotton aphid (*Aphis gossypii*) or silverleaf whitefly (*Bemesia argentifoli*). Insects are responsible for most cases of cotton stickiness (Sisman and Schenek 1984), and due to the correlation of insect derived sugars with cotton stickiness a variety of methods have been developed to measure the sugar content of cotton. Many of these methods have been included in a comprehensive survey of sugar test methods (Brushwood and Perkins 1993). Of these methods, HPLC is perhaps the most effective for both the identification and quantification of the individual sugars present. The major drawbacks of employing HPLC as a screening method for stickiness on cotton are the fact that it is relatively time consuming, taking up to 30 minutes to analyze a single sample, and the equipment can be cost prohibitive. An enzymatic method (Gamble 2001) has been demonstrated to be capable of reliably determining the extent of insect honeydew contamination by measuring the amount of oligosaccharides present in a cotton extract. This method, however, also suffers from the inability to provide rapid results.

Previous research (Gamble 2002) has demonstrated that trehalulose and melezitose, the primary oligosaccharides comprising whitefly honeydew, are subject to thermochemical degradation at sufficiently high temperatures. One of the products of sugar degradation is 5-hydroxymethylfuraldehyde (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 and other volatile compounds produced as a result of the thermochemical degradation of honeydew sugars present on contaminated cotton can be measured and correlated with the amount of honeydew present. If such a correlation 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 provide a more rapid and cost effective alternative to methods currently employed.

Materials and Methods

Cotton samples exhibiting a range of whitefly honeydew contamination were obtained from the Western Cotton Research Laboratory, USDA-ARS. The samples were ginned at ambient temperature, thus avoiding degradation of the sugars due to thermochemical reactions. The criterion used to identify samples based on stickiness potential was the measurement provided by the sticky cotton thermodetector (SCT). Operation of the SCT was as described previously (Brushwood and Perkins 1993). Results on 17 samples ranged from 1 to 70 sticky counts, indicating potential stickiness ratings ranging from non-sticky to extremely sticky.

Each sample was weighed to the nearest gram and subsequently extracted with 20 parts (w/w) cold, deionized water. The extract was analyzed for glucose content using a Yellow Springs Instrument Co. Model 2700 Bioanalyzer. 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. The initial measurement was subtracted from the final measurement following hydrolysis and the resultant quantity, ΔG, is reported as ppm in the water extract.

An aliquot of 0.5 ml was analyzed for individual sugars using high performance anion exchange chromatography (HPAEC) performed on a Dionex DX-500 using pulsed amperometric detection. Two Dionex Carbopac PA-1 (4 x 250 mm) columns 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 are reported as ppm in the water extract.

Duplicate 1 gram samples of each cotton were heated to 180°C under a stream of air for three hours using a Scientific Instruments Services (Ringoes NJ) Thermal desorption Sample Collection System. The resultant air stream was subsequently passed over a Supelco (St. Louis MO) Solid Phase Microextraction fiber coated with 100 µm polydimethylsiloxane adsorbent. The fiber was then desorbed directly onto a Hewlett-Packard 5890 Gas Chromatograph equipped with an Ultra-2 column. The sample was introduced by splitless injection at 250°C. 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 detection at 250°C. Hydrogen at a flow rate of 0.45 ml/min was used as the carrier gas.

5-hydroxymethylfuraldehyde, melezitose, glucose and fructose were purchased from Sigma Chemical Co. (St. Louis MO) and trehalulose was obtained as a 95% syrup from Mitsui Sugar Co. (Japan).

Results and Discussion

The gas chromatogram of pure 5-hydroxymethylfuraldehyde (HMF) adsorbed onto the SPME fiber at room temperature has a primary response at t = 7.0 minutes. A secondary response observed at t = 5.8 minutes is due to the degradation of HMF in the injection chamber. 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 chromatograms for the volatile degradation products of the saccharides melezitose and trehalulose show peaks at t = 7.0 minutes, in both cases identified as HMF. The secondary peak at t = 5.8 minutes is also observed in both cases. Trehalulose also 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 as a measure of trehalulose.

The chromatogram obtained by heating honeydew-contaminated cotton is more complex than is the case for the individual sugars. This is due primarily to the presence of volatile compounds arising from non-sugar components of the cotton fiber. The response peaks at t = 7.0 and 6.4 minutes are nevertheless easily distinguishable. Figure 1 shows a comparison of total insect honeydew oligosaccharide content (as measured by ΔG) with the gas chromatographic peaks at t = 7.0 and 6.4 minutes (as integrated area) for the 17 honeydew contaminated cotton samples. There is a good correlation between the measurements, indicating that measurement of HMF released as a result of thermochemical degradation is potentially an alternative determination of sugar contamination on the cotton fiber. A comparison of total sugar (as measured by HPLC) with the gas chromatographic peaks at t = 7.0 and 6.4 minutes (as integrated area) is shown in Figure 2. The correlation between the measurements is high in this case also, and serves to corroborate the potential utility of the HMF measurement.

Figure 3 shows a comparison of thermodetector counts with the gas chromatographic peaks at t = 7.0 and 6.4. The correlation in this case is very good, and demonstrates that measurement of these volatile products is a viable method for screening sticky cotton. Methodologies for the measurement of volatile compounds, which can be used for real-time monitoring, are currently under investigation. These methodologies include 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 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

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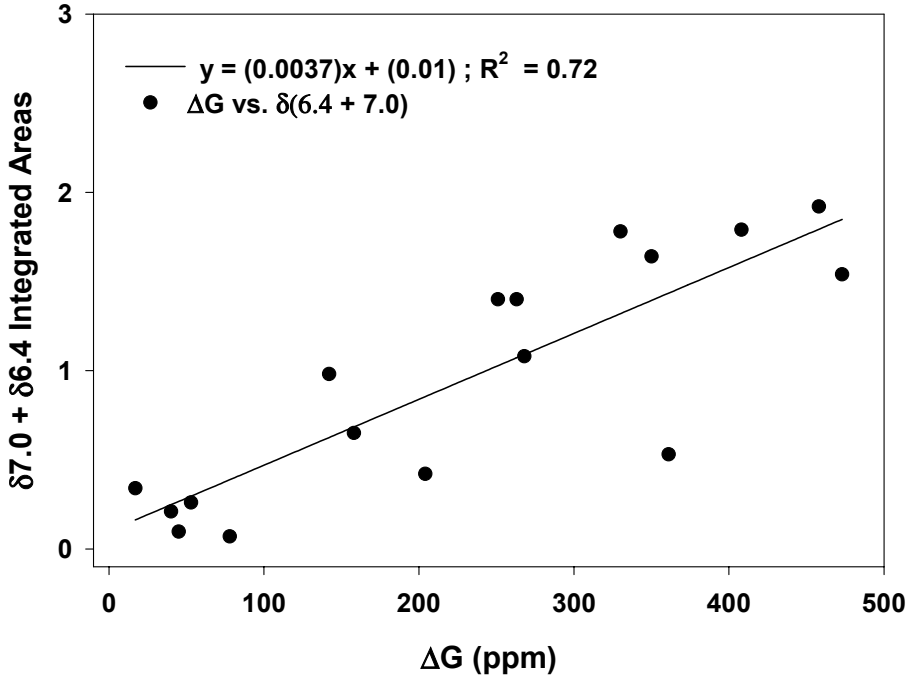

Figure 1. Comparison of total oligosaccharide measured by ΔG and the gas chromatographic peaks at δ6.4 and δ7.0.

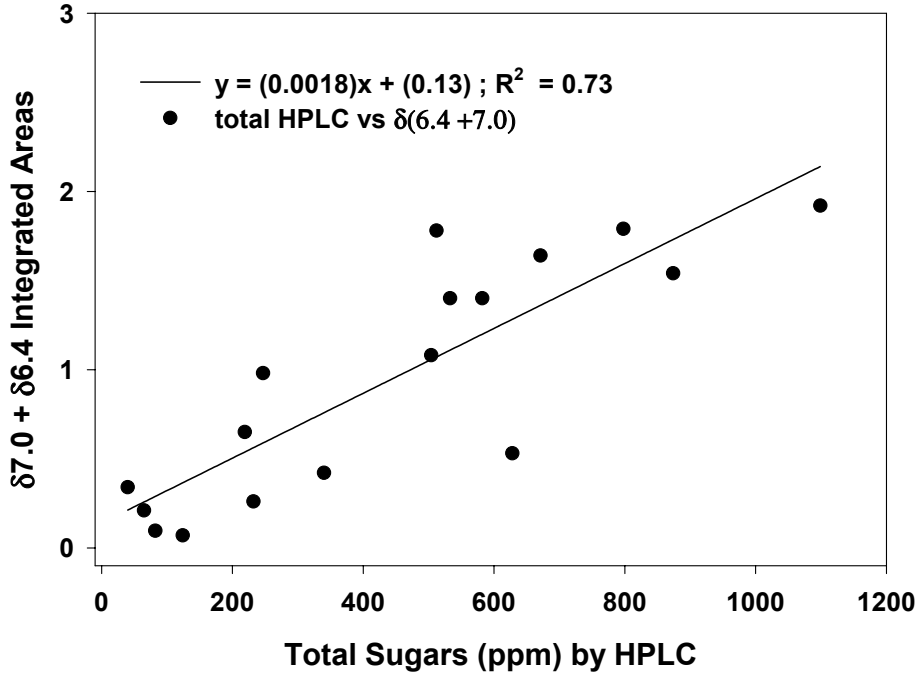

Figure 2. Comparison of total sugar by HPLC and the gas chromatographic peaks at δ6.4 and δ7.0.

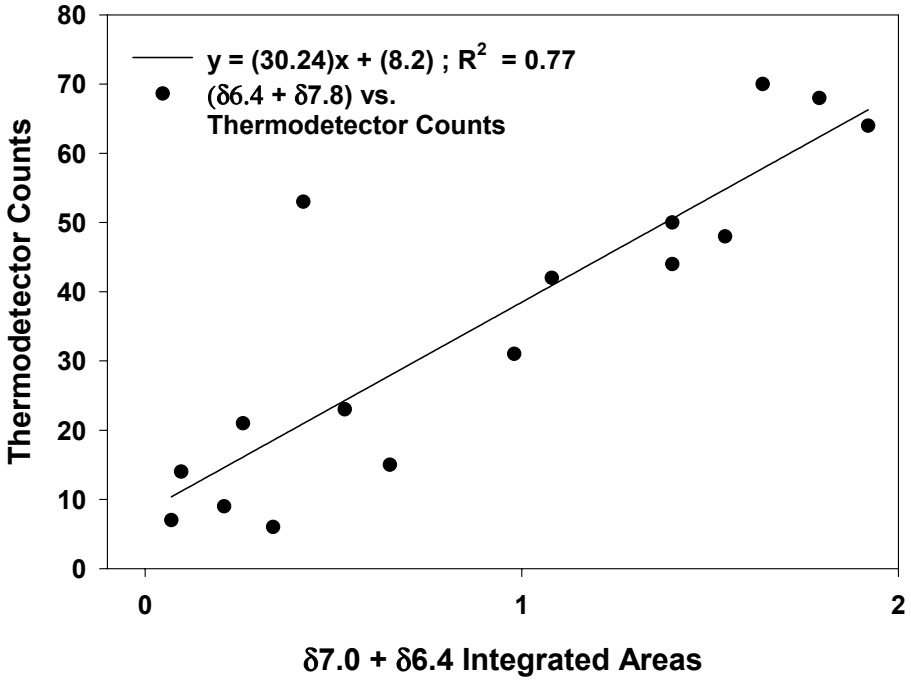

Figure 3. Comparison of gas chromatographic peak areas at δ6.4 and δ7.0 with thermodetector counts.