Differentiating Cane White Sugar from Beet White Sugar Using Ion Chromatography Profiles

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ABSTRACT

Recently in Europe, there have been reports of illegal trading in Serbia and Montenegro, whereby the origin of white, refined sugar could not be certified. Other countries in Europe and other parts of the world have also most likely suffered from illegal intermixing of beet white sugar (BWS) with cheaper to produce cane white sugar (CWS). A method is, therefore, urgently needed that is (a) capable of distinguishing between CWS and BWS, and (b) can measure the percentage of CWS in a CWS/BWS mixture (final goal). Raffinose and theanderose have been advocated as differential markers. However, raffinose is present in both BWS and CWS (although to a much lesser extent in CWS). Pure theanderose is not available, and small IC-IPAD (ion chromatography with integrated pulsed amperometric detection) peaks have been found in BWS samples where theanderose eluted in CWS samples. Low raffinose in conjunction with numerous cane marker peaks across IC-IPAD 45min profiles of 7°Brix blind BWS/CWS samples were successfully used to detect 20% CWS adulteration. Increasing the °Brix levels to 10 allowed detection of 10% CWS adulteration. Chromatography libraries of CWS, BWS and BWS/CWS samples for direct comparisons will aid adulterant detection. Further studies using chemometric modeling are to be undertaken to enhance adulterant detection. At the least, the use of IC profiles can be used as a screening method before verification and quantitation with more sophisticated techniques, such as DSC and NMR.

Objective

This study was undertaken to see if long (45min) IC-IPAD profiles, following a NaOH/NaOAc gradient method, could be used to differentiate BWS/CWS mixtures.

Materials and Methods

IC-IPAD profiles

See Eggleston and Grisham (2003) for full method. A Dionex BioLC instrument and CarboPac column were used. Eluent conditions were:100mM NaOH isocratic (0.0-1.1min; inject 1.0min), a gradient of 0 to 300mM NaOAc in 100mM NaOH (1.1-40.0min), and return to 100mM NaOH (40.1-45.0min) ro re-equilibriate the column. Final sample °Brix's were measured on a refractometer and °Brix's of samples in a run were standardised, by adding de-ionized water, before analyses, and the

samples were not filtered.

BWS, CWS, and BWS/CWS samples

Most samples were obtained from the SPRI sugar library or from Zuckerforschung Tulln Gersellschaft. Individual sugars in the BWS/CWS mixtures were weighed into a plastic test-tube as a percentage, and then shaken vigorously.

Results and Discussion

Firstly, IC profiles for CWS samples from all over the world were compared. Most cane peaks were present in CWS samples from all the different geographical sources, and some are known to form during processing (Eggleston et al, 1997). Therefore, at this present time, IC profiles cannot be used to differentiate the geographical source of the CWS.

Secondly, the IC profiles of six BWS samples (European origin) were compared to two CWS samples. When chromatographs were directly overlaid, there were the obvious low raffinose peaks characteristic of CWSs compared to BWSs. A blow up of a portion of the chromatograph (23.5-42.0min) showed that there were numerous other peaks that were characteristic of CWS, which were not background noise (Eggleston et al, 2004). With clearly different regions of BWS and CWS samples, we were encouraged enough to, thirdly, test the use of IC profiles to differentiate three blind samples (7°Brix) that were made from the SPRI sugar library, with one containing a mix of BWS/CWS. The use of overlaid and blown-up portions of the chromatograms allowed for a 100% correct diagnosis of the three blind samples. This successful identification of the first three blind samples, spurred us on to, fourthly, test five more blind samples also made from the SPRI library and 7°Brix, ensuring that some BWS/CWS mixes were included. The use of overlaid and blown-up portions of the chromatograms allowed for an 80% correct diagnosis of the samples. Only a 90% BWS/10% CWS mix was not be diagnosed correctly, and this was most likely because of slight shifting to higher retention times (Eggleston et al, 2004). This highlights the need for stable retention times which can be achieved with column heaters, and standardization of chromatogram patterns using an internal standard.

Fifthly, a further study of seven blind samples (7°Brix) sent to Dr. Eggleston's labororatory in the U.S. from Dr. Pollach in Austria was undertaken. An 86% correct diagnosis of the seven blind samples was achieved, with an 80%BWS/20%CWS mixture diagnosed incorrectly (Eggleston et al, 2004). We thought an increase in the °Brix level from 7 to 10 could improve this. This was proved right when we subsequently analyzed five more blind samples from the SPRI library (with BWS/CWS mixtures included) injecting a 10°Brix sample onto the IC column. Diagnosis was 100% correct and 10% CWS adulteration was detected.

Conclusions

Most cane peaks on IC-IPAD chromatograms are present in CWS samples from around the world. IC cannot be used to differentiate the geographical sources of the CWS. Low raffinose in conjunction with numerous cane marker peaks across IC-IPAD profiles of 7°Brix blind BWS/CWS samples were successfully used to detect 20% CWS adulteration. Increasing the °Brix levels to 10

allowed detection of 10% CWS adulteration. Detection is also improved when the peak retention times are stable. Constant temperature columns and autosamplers will certainly help to stabilize retention times, but interpretation of the chromatograms will also be greatly assisted with the use of an internal standard. Training of the chromatographer will be needed for careful interpretation of the IC profiles. Chromatography libraries of CWS, BWS and BWS/CWS samples need to be built to aid adulterant detection. Further studies using chemometric modeling are proposed to enhance adulteration detection, by detecting adulterant IC markers that cannot be found visually. At the least, the use of IC-IPAD profiles can be used as a screening method that can detect a range of different compounds in one chromatogram. Suspect samples could then be further verified and quantification with more sophisticated techniques, such as stable isotope determinations, nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC).

Literature Cited

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