Forensic analysis of an artificial sweetener commonly employed in hoax powder attacks using Morphologically Directed Raman spectroscopy

PARTICLE SIZE

CHEMICAL IDENTIFICATION

PARTICLE SHAPE

Introduction

In the wake of the September 11th terrorist attacks, there was an influx of white powder events throughout the United States. A white powder event is when an unknown white powder is received in the post. More often than not, the attacks do not contain any toxic materials and are carried out for the sole purpose of causing terror and damaging infrastructure. Since these attacks, the FBI and US Postal Service have responded to thousands of white powder events.

This application note details how Morphologically Directed Raman Spectroscopy (MDRS) using the Morphologi G3-ID can be applied to the forensic identification of commercially sourced white powders commonly used in hoax powder attacks.

Artificial sweeteners are one of the most commonly employed commercial sources of white powders. These blends are simple mixtures of a sweetening agent and bulking material. Since, the sweetening agents used are several times sweeter than a comparable amount of table sugar, a bulking agent or filler, such as dextrose, is required. Detection of the sweetening agent allows identification of the brand of sweetener.

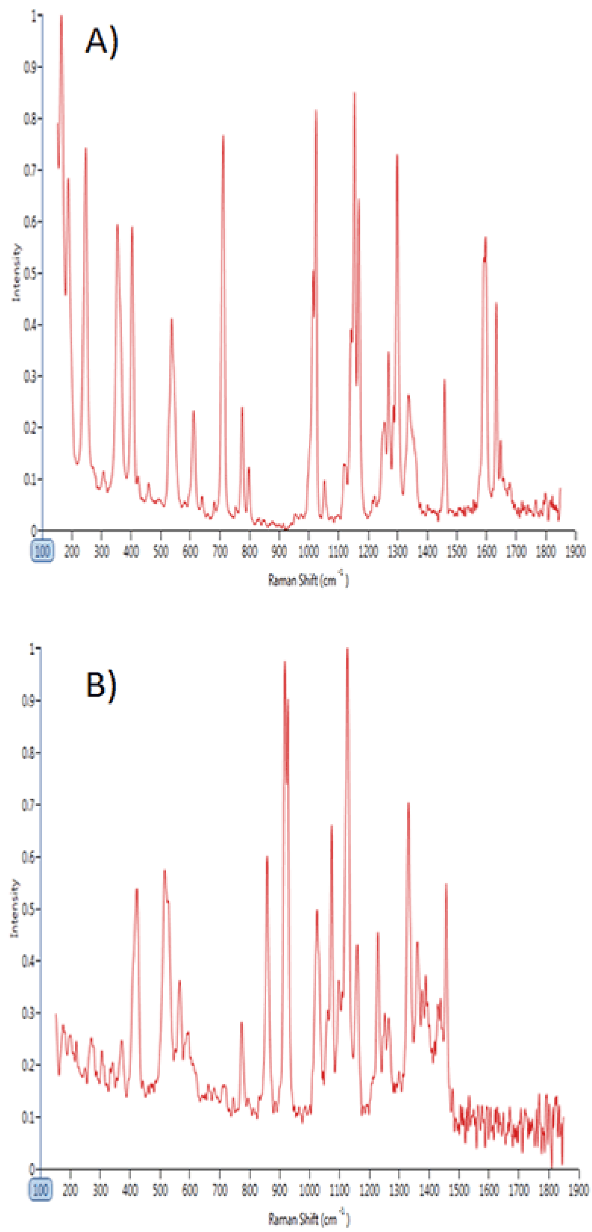
Raman spectroscopy is a useful technique in forensic science for determining molecular chemistry because it is rapid, reliable, does not require contact with the sample, and is non-destructive. The technique can be used to verify that hoax powders are artificial sweeteners. However, when doing a traditional bulk analysis, the high volume of bulking material present has a tendency to drown out the Raman signature of the sweetening agent. Raman microspectroscopy has the advantages of bulk Raman spectroscopy but can also be used to analyze and identify the various chemically distinct components of the white powder.

Information from particle morphology and size is also valuable for differentiating artificial sweeteners that are mixtures of the same components. Automatic image analysis takes the subjective element out of the measurement of particle size and morphology. It also makes the process more rapid than counting and measuring the individual particles within a greater mixture.

When Raman microspectroscopy is paired with automatic image analysis of the particles, as in Morphologically Directed Raman Spectroscopy (MDRS), physical and chemical information about the components of the mixture can be obtained. This can be used for discrimination and brand identification between mixtures, thus making it an ideal tool for the investigation of suspicious white powders.

Methods

Two commercially available artificial sweetener blends, Sample A (saccharin / dextrose) and Sample B (sucralose / dextrose) were automatically dispersed onto a quartz plate using the integrated Sample Dispersion Unit (SDU) on the Morphologi G3-ID instrument. A spectral reference library was created using point spectra for each of the components of interest (Figure 1) using standards purchased from Sigma Aldrich.



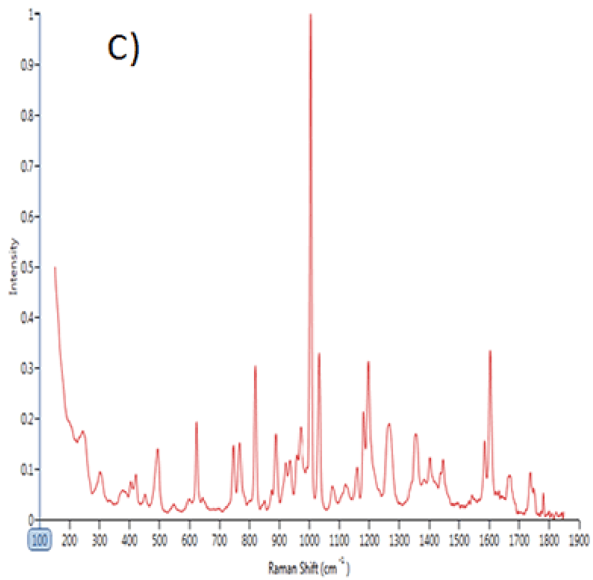


Figure 1: Point spectra of A) saccharin, B) dextrose and C) sucralose

The samples were analyzed with the Morphologi G3-ID. Morphological data was measured using the 10x objective magnification and Raman spectra were then automatically collected from selected particles with the 785 nm semiconductor laser. Particles with a circle equivalent diameter (CED) greater than 7.0 μm were tagged for chemical targeting by the image analysis software. Morphological data was collected for approximately 150,000 particles in Sample A and 100,000 particles in Sample B. Of these, of 3000 particles per sample were targeted for Raman spectroscopy over the spectral range of the instrument (150cm-1 to 1850 cm-1). The total morphological and chemical analysis time was approximately 18 hours.

The individual particle spectra were then compared against the reference spectral library and correlation calculations performed. A correlation value close to 1 indicates a close match to that reference and a value close to zero indicates no match. Using these correlation values, the particles were chemically classified and particle size distributions (PSD) of the individual component populations were generated.

Results

The automated imaging data alone was not enough to definitively identify the components within each sample by size or shape. However, with the assistance of the Raman chemical identification, individual components can be classified as demonstrated by the scatterplots of correlation score to each component shown in Figure 2 and Figure 3. In these plots the correlation values of a particle to one component of the blend are potted on the x-axis vs the correlation value to the other component on the y-axis. For each sample, the scatterplots show the two distinct populations as the correlation value approaches 1 for each component. It can also be seen that there are few aggregated particles in the blend with mid correlation values to each of the components.

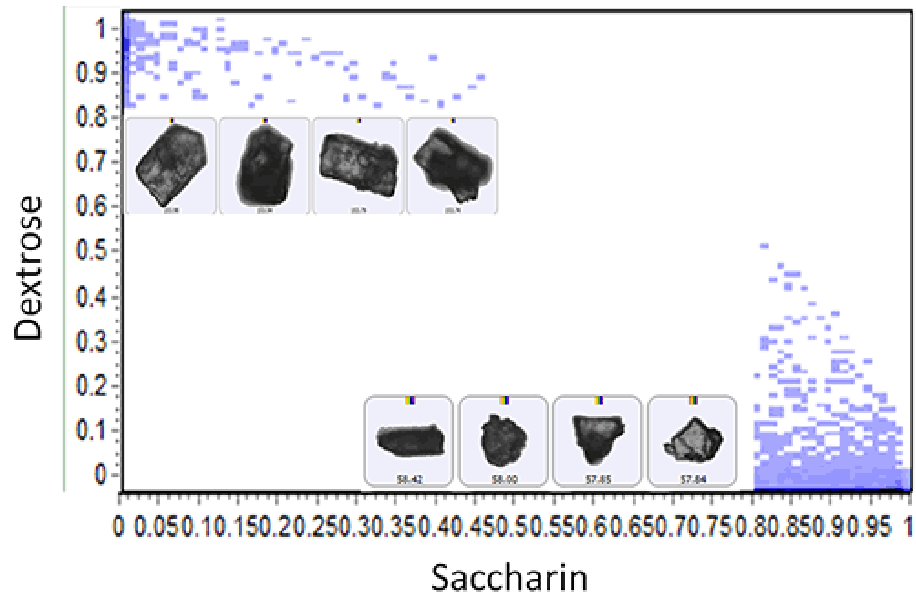


Figure 2: Scatter plot of the particle correlation values to saccharin versus dextrose for Sample A accompanied by example particle images.

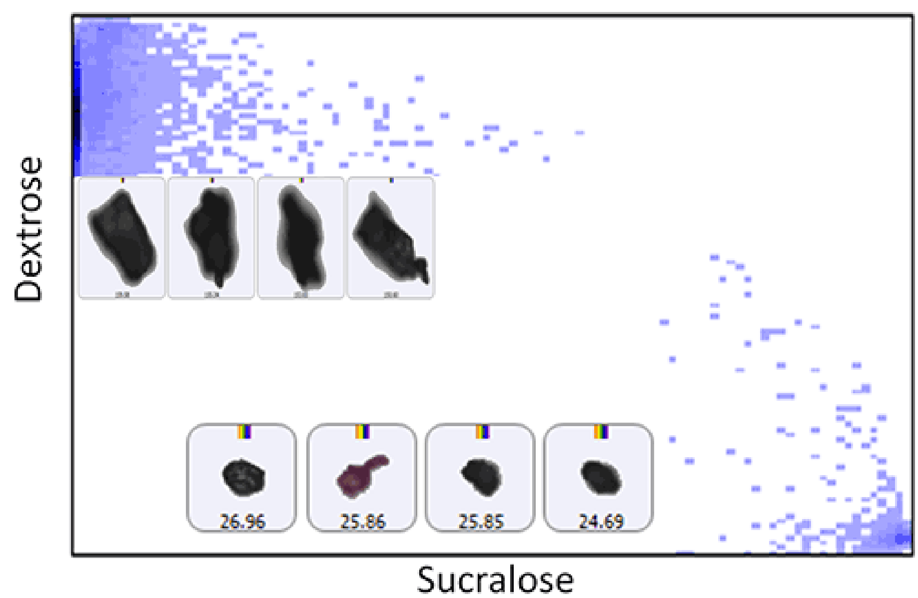


Figure 3: Scatter plot of the particle correlation value of sucralose versus dextrose for Sample B accompanied by example particle images.

Particle size distributions were generated and compared for each of the chemical classes identified. In both samples, the PSD of the dextrose component is similar to that of the overall blend as shown in Figure 4 and Figure 5, while the active sweetener components have a markedly different PSD from their overall respective blends. Without the automated particle specificity afforded by MDRS, smaller particles present in a lower volume would be masked by the larger volume of dextrose in a traditional bulk Raman analysis. Therefore the individual sweetening component PSD of an artificial sweetener blend is a class characteristic, which could be employed in determining the particular brand of artificial sweetener that was utilized in a hoax powder attack.

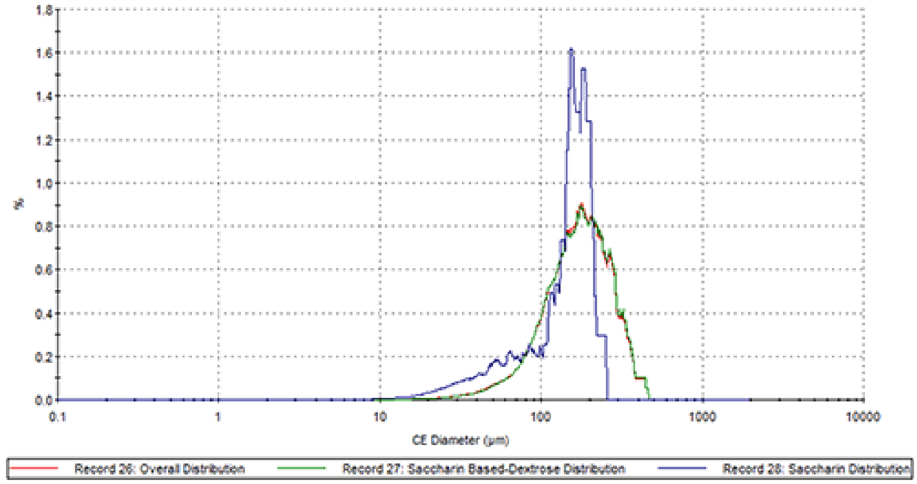


Figure 4: The comparison of the saccharin PSD (blue), the dextrose PSD (green) and the overall PSD (red) in Sample A

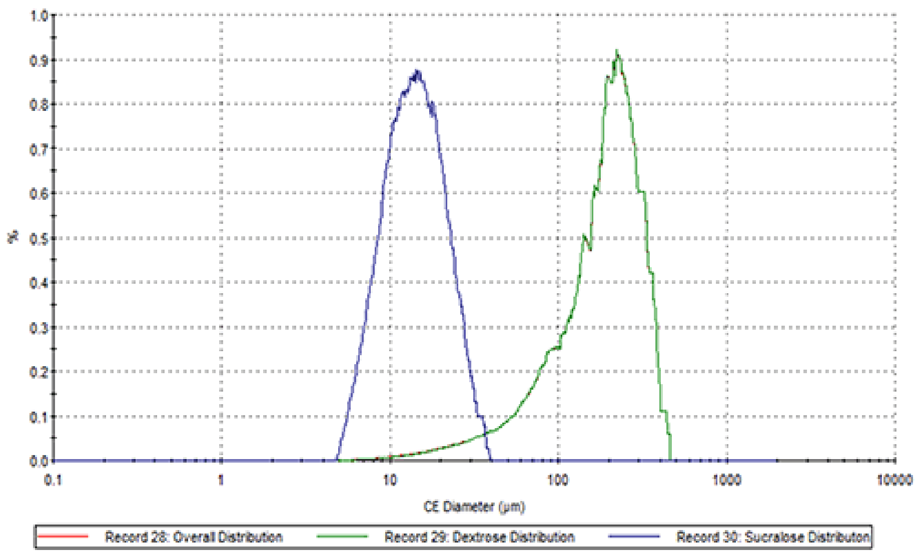


Figure 5: The comparison of the sucralose PSD (blue), the dextrose PSD (green) and the overall PSD (red) in Sample B

Figure 6 shows the relative proportions of the sweetening agent and the dextrose bulking material for both samples. The ability to identify the low volume contribution components from the bulk material and determine morphological parameters about them can be useful for source attribution and contaminant analysis. In addition to determining what kind of sweetener was employed in a hoax powder attack, such information may also give some insight into a possible location from where the attack could have originated, via identification of trace materials that the sample could have picked up in transit.

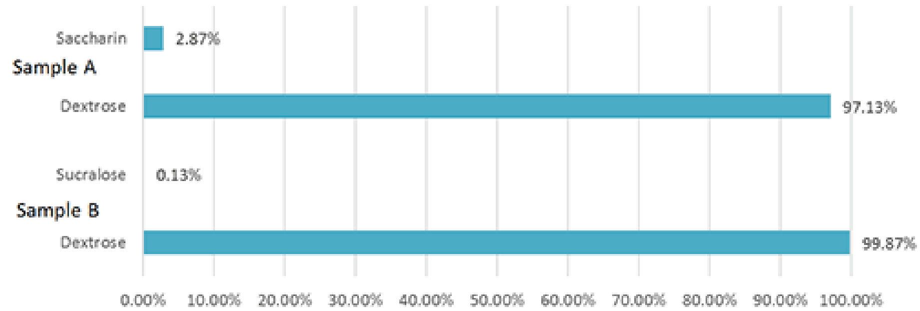


Figure 6: Contribution of each component within the two samples by volume Percentage.

Conclusion

Morphologically Directed Raman Spectroscopy provides valuable information for characterizing suspicious powders used in fake bioterrorism attacks. Component specific characterization was achieved via coupling automated image analysis with the molecular identification power of Raman microspectroscopy. The Morphologi G3-ID was used to chemically identify and classify a large number of individual component particles of an artificial sweetener. This can be instrumental in the forensic analysis of hoax powder attacks, aiding source determination or exclusion.

The technique of MDRS can also be applied in a variety of other forensic contexts, such as aiding the detection of contaminants in drug mixtures and identification of counterfeit substances, as well as in a range of other industries.

Acknowledgements

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