Differentiation of Seized Marijuana Samples using Automated Headspace Solid-Phase Microextraction Coupled to Gas Chromatography-Mass Spectrometry/Flame Ionization Detector and Principal Component Analysis

Jessica Winborn[1], BS; James Sweet[2], PhD; Jorn Chi-Chung Yu[1], PhD, D-ABC*

[1]*Department of Forensic Science, Sam Houston State University, Huntsville, TX 77340*

[2]*U.S. Customs and Border Protection, Laboratories and Scientific Services Directorate, Houston Laboratory (Southwest Regional Science Center)*

U.S. Customs and Border Protection

ABSTRACT

In this study, an automated headspace solid-phase microextraction coupled to a gas chromatograph with dual detectors (a mass spectrometer and a flame ionization detector) (HS-SPME-GC-MS/FID) method has been applied to seized marijuana samples with principal component analysis (PCA) to analyze their cannabinoid profile in order to assess common origin between seizures.

Results from this study show that the analysis of cannabinoid profiles using HS-SPME-GC/MS and PCA has great potential for differentiating marijuana samples. Future research will include the analysis of other non-cannabinoids present in the chemical profile of marijuana samples to improve the discriminatory power of this method.

INTRODUCTION

Marijuana is a schedule I drug under the federal Controlled Substances Act but state legislation varies (1). Recent changes in legislation have raised new concerns for law enforcement. One of these concerns is whether legally grown marijuana is being diverted out of states where its use is legal. The ability to track the flow of marijuana to and within different jurisdictions will be an important tool for law enforcement officials.

Solid-phase microextraction (SPME) is an extraction technique where the sorbent material coats a thin fiber (2). In headspace SPME (HS-SPME) the fiber is exposed to the air above the sample and volatile analytes partition onto the fiber. After extraction the fiber can be introduced to an analytical instrument where the analytes desorb off of the fiber for analysis.

Principal component analysis (PCA) is a multivariate statistical technique that is useful for extracting latent information from large data sets. PCA is commonly used to identify patterns in data to emphasize the similarities and differences present. It reduces large data sets to sets of orthogonal variables called 'principal components' that capture the data's variance (3). The results of PCA can be used to distinguish different sources between samples.

MATERIALS AND METHODS

HS-SPME

- 10 mg of ground marijuana incubated at 150°C for 5 minutes
  - Three sources with four samplings from each in triplicate
- Polydimethylsiloxane (PDMS) fiber exposed to sample headspace for 5 minutes
- Fiber desorbed in GC inlet for 30 seconds at 220°C
- Fiber was conditioned at 250°C for 20 minutes

GC-MS/FID

- 35% phenyl fused silica column
- Carrier gas flow: 1.2 mL/min
- Initial oven temperature: 170°C held for 1 minute
- 1st ramp: 15°C/min to 250°C
- 2nd ramp: 5°C/min to 270°C
- 1.4 minute hold at 270°C
- Detectors: MS scanned 40-450 amu; FID at 250°C

PCA

- Total ion chromatogram (TIC) data was normalized (each data point divided by the sum of all points)
- The entire TIC was considered - Areas of high variation within sample source and areas of low variation between sources were removed
- PCA was performed using the statistical program R with the ChemoSpec package

RESULTS

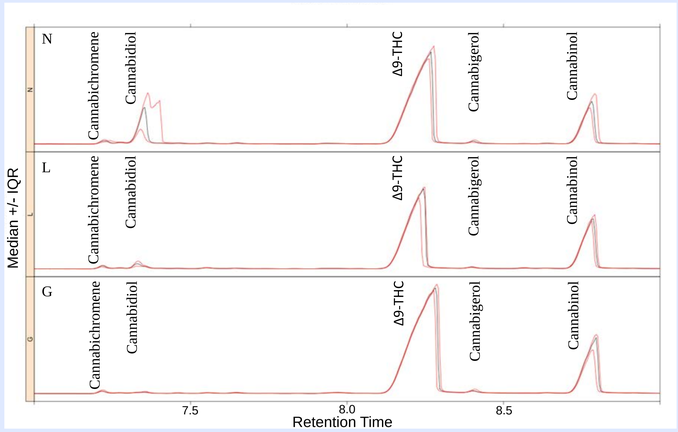

Figure 1: Variation plots of chromatogram data from retention times 7 to 9 minutes for three sources of marijuana.

Variation plots were used to visually examine the chromatograms. The black line represents the median and the red lines represent the upper and lower interquartile ranges. Areas of high variation within the same sources and areas of low variation between all three sources were excluded from PCA.

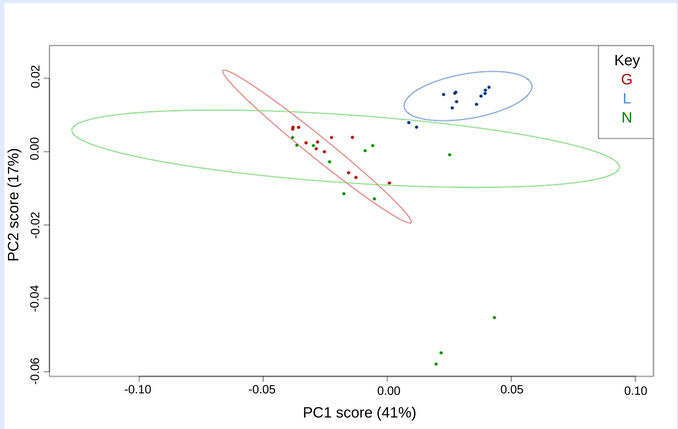

Figure 2: Score plot for principal component 1 (PC1) and principal component 2 (PC2) for three sources of marijuana with 95% confidence intervals.

The score plot was used to visualize the similarities and differences between the sample sources. PC1 encompassed 41% of the data variance and PC2 encompassed 17% of the data variance.

DISCUSSION & CONCLUSIONS

The samples from source L cluster in a grouping that is distinct from the other two sources. The clusters of source G and N overlap with each other. Source L can be analytically differentiated from sources G and N.

It can be concluded that HS-SPME combined with PCA shows potential for determining common origin between marijuana seizures.

Mass spectrometer provided better confidence in peak identification; FID provided better chromatogram for quantitation.

Limitations:
While the sources of marijuana came from separate seizures, the initial origin of each is unknown. Source G and N may have come from the same or different origins.

Future Work:

- Improving the method to capture more variation between sources
- Using marijuana from known origins

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