E24 The Development of a Flexible Algorithm for Substance Identification Using Mass Spectrometry

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Learning Overview: After attending this presentation, attendees will better understand the value of ion correlations in mass spectrometric analyses through the demonstration of a dynamic algorithm that provides higher discriminatory power and increased confidence in mass spectrometric compound identification.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by providing a mathematical model for compound identification from mass spectrometric data that is more accurate and more precise than current static/discrete methods. The application of a more selective algorithm will decrease the incidence of false positives and further assist with the identification of unknown compounds.

It is hypothesized that a mathematical model that employs the covariance between ion abundances will provide a more discriminatory algorithm with improved compound identification rates relative to a model that does not take into account the covariance between ion abundances.

Current mass spectrometric methods of substance identification use a static algorithm to determine the identity of a substance. Existing algorithms compare the relative abundance of each peak within a given spectrum to those of discrete reference spectra in a library. However, the variance in ion abundances for this type of comparison is generally around ±20%, which can result in false positives for substance identification. An algorithm that can adapt to varying relative ion abundances using a continuously variable model will provide a more selective and more accurate identification algorithm than the current discrete methods.

Replicate measurements of various chemical standards show that ion abundances within replicate mass spectra of the same compound are not independently variable, but correlated or anti-correlate with coefficients of correlation as strong as an $R^2 \geq 0.8$. Two databases were developed to assess the accuracy and selectivity of this dynamic model. The first database consists of five illicit drugs, and the second database was comprising eight n-alkanes. The ion abundances were normalized to the base peak and the 15–16 most abundant ions were selected to be the dependent variables within the general linear models. The general linear models were constructed within SPSS statistical software using 90% of the spectra in each database. The remaining 10% of the spectra were used to assess the accuracy of the model. The model essentially predicts ion abundances at each *m/z* value, and these predicted abundances are then compared to the measured spectra using Pearson product-Moment Correlations (PPMCs). The significance of different PPMCs were compared through z-tests on Fisher transformations of the PPMCs.

The dynamic/continuous model was able to distinguish between the five illicit drugs with ease. The model provided significantly better ion abundance predictions for true positives than for true negatives, which it a requirement of a successful model. Consecutive n-alkanes (e.g., C16 vs. C17) were difficult to discriminate using comparisons of the PPMS, so additional statistical analyses were performed to provide meaningful assessments for spectral identifications.

Dynamic Algorithm, Mass Spectrometry, Ion Correlations