



Questioned Documents Section – 2011

J2 Multivariate Statistical Procedures for the Analysis of Questioned Documents

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The goal of this presentation is to demonstrate the application of multivariate statistical procedures for the association and discrimination of different paper types based on elemental profiles that were generated using inductively coupled plasma mass spectrometry.

This research will impact the forensic science community by: (1) demonstrating an enhanced methodology for the analysis of paper samples; and, (2) addressing the need for statistical evaluation of comparisons involving forensic evidence.

Forensic examinations of questioned documents can involve numerous types of analysis, for example, handwriting, ink, and paper analysis. Historically, the comparison of paper has been based on physical properties such as dimensions, color, and weight. More recently, research has focused on differentiating papers based on the elements present as a result of the manufacturing and handling processes, as well as impurities in the starting materials. However, much of this research used older, less sensitive instrumental techniques, in which elements are analyzed one at a time. Such procedures are time-consuming and therefore not attractive for practical applications in forensic laboratories.

Inductively coupled plasma mass spectrometry (ICP-MS) is a highly sensitive, multi-element technique that is widely used for elemental profiling purposes. In the context of questioned documents, the technique can be used to generate an elemental “fingerprint” or “profile” of paper samples, which can then be compared, using multivariate statistical procedures, to determine similarities and differences based on the identity and levels of elements present.

In this work, a variety of paper samples were analyzed by ICP-MS to generate elemental profiles and statistical procedures were then applied to associate or discriminate the samples based on the elemental profiles. Reams of different types of paper (e.g., recycled paper, copier paper, and multi-purpose paper) produced by different manufacturers were collected from local office supply stores. Three sheets were selected from each ream and five samples were analyzed per sheet, allowing an assessment of element variability both within and between each ream. Each paper sample was microwave-digested in nitric acid and hydrogen peroxide and the resulting digests were analyzed by ICP-MS.

The first step in the analysis was to identify a suite of potentially useful elements for the discrimination of paper samples. A subset of digests was analyzed in the full scan mode to generate elemental profiles. Any elements that: (1) were present at significant levels in the procedural blanks; (2) varied significantly in concentration within a sheet; or, (3) were present at levels below the instrument’s limit of quantitation were eliminated from the elemental suite. The remaining paper digests were then analyzed by ICP-MS using the selected ion monitoring mode for the remaining elements of interest. Elemental concentrations in each sample were quantified and expressed as $\mu\text{g element/g paper}$.

The resulting elemental profiles were then assessed using various statistical procedures. Variation in elemental concentration within and among reams of each type of paper was assessed using two-way analysis of variance (ANOVA), testing the null hypotheses that: (1) there was no difference in mean element concentration among the sheets (i.e., within ream); and (2) there was no difference in mean element concentration among the reams. Principal component analysis (PCA) was then used to associate or discriminate the paper samples, based on elemental profiles. Reams of the same type of paper were closely associated, while reams of different types of paper could be differentiated. Additionally, elements contributing most to the variance in the data set were identified, with the result that paper samples could be associated or differentiated using fewer elements than in the original suite.

Questioned Documents, Trace Elements, Inductively Coupled Plasma Mass Spectrometry