J4 Differentiation of Document Paper Based on Elemental Profiles Using Inductively Coupled Plasma-Mass Spectrometry, Inductively Coupled Plasma-Optical Emission Spectroscopy, and Multivariate Statistical Procedures

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After attending this presentation, attendees will understand how trace elements can be used to differentiate different types of document paper, such as copy paper and recycled paper. Inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) are used to generate element profiles for different paper types from the same manufacturer. A combination of statistical procedures, including analysis of variance (ANOVA) and principal components analysis (PCA), are then used to differentiate the paper by type based on the trace elements present.

This presentation will impact the forensic science community by generating element profiles for different paper types. These profiles potentially offer greater discriminatory information than the physical and chemical methods currently used in paper analysis. Demonstration of the statistical procedures will provide an objective method that can be implemented in forensic laboratories for the analysis of questioned documents.

Paper analysis typically relies on comparing physical characteristics of the paper such as color, thickness, and brightness. However, due to improvements in the production process, these physical characteristics do not necessarily allow differentiation of paper. As a result, alternative methods for analyzing and comparing paper samples are necessary.

Trace elements present in paper originate from impurities in the raw materials, as well as from processes used during paper production. These elements may provide greater discrimination of paper by both type and production plant. However, due to the low levels of these elements, sensitive instrumental techniques are necessary for the analysis.

Preliminary research conducted demonstrated the potential of differentiating two different paper types based on element profiles generated using ICP-MS. However, the instrumentation is very expensive and analysis using this technique involves high running costs. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) may be a viable alternative to ICP-MS for this purpose. In this research, element profiles for a larger number of different paper types will be obtained using both ICP-MS and ICP-OES and multivariate statistical procedures will be used to assess discrimination of paper according to type based on the elements present. Results will be used to assess the potential of ICP-OES compared to ICP-MS for this purpose.

In this research, two reams each of five different types of paper produced by the same manufacturer were purchased. Paper samples were microwave-digested using nitric acid and hydrogen peroxide prior to instrumental analysis. A subset of samples, representative of all paper types, was initially analyzed using ICP-MS in full scan mode to identify potentially characteristic elements for each paper type. Such elements were those that: (1) were present at levels above the instrument limit of detection; (2) were not present at significant levels in the procedural blank; and, (3) did not vary significantly in concentration within a ream of paper. The full sample set was then analyzed by ICP-MS using the selected ion monitoring mode and quantifying the elements of interest. Samples were then analyzed by ICP-OES, quantifying the same elements.

The resulting element concentrations were normalized according to the initial mass of paper digested, and separated into two data sets: the first contained element concentrations determined by ICP-MS and the second contained element concentrations determined by ICP-OES. Analysis of variance (ANOVA) was performed on each data set separately to assess variation of each element within a ream, between reams of the same paper type, and between reams of different paper types.

Each data set was then subjected to principal components analysis (PCA), which is a multivariate statistical procedure used to identify sources of variance within a data set. The PCA scores plot is a scatter plot in which chemically similar samples are grouped, with distinction from samples that are chemically different. The PCA loadings plots can be used to identify the variables contributing most to the variance in the data set. In this research, the scores plots were used to assess association of reams of the same paper type, with discrimination of different types, based on the element profiles. The loadings plots were used to identify those elements that were responsible for the association and discrimination observed. Both scores plots were also assessed to determine if one technique, ICP-MS or ICP-OES, offered improved discrimination of the paper types based on elemental profiles.

Questioned Documents, Trace Elements, Spectroscopic Techniques