

The Development of an X-ray Spectral Database for Forensic Science

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The Scanning Electron Microscope (SEM) with associated Energy Dispersive Spectrometer (EDS) is commonly used to characterize the structure and elemental composition of a wide variety of materials of forensic significance. When these materials are extremely limited in size, SEM/EDS is often the only suitable method for characterization available in forensic science laboratories.

Because of the inability to access SEM/EDS data from large numbers of materials, the Federal Bureau of Investigation (FBI) laboratory believes that this discipline has not realized its full potential. The usefulness of SEM/EDS has been limited by the inability to archive spectra within a utility having a true database architecture. The FBI Laboratory has designed such an X-ray database, consisting of storage, query, and display utilities unique to X-ray spectroscopy.

Traditional use of SEM/EDS in Forensic Science

Traditional forensic analysis with SEM/EDS can generally be considered to be qualitative, quantitative, structural, or comparative.

Qualitative methods are used simply to determine the presence of certain elements regardless of absolute concentration.

The objective of *quantitative analysis* is to determine elemental composition as accurately as possible. Sophisticated data analysis converts x-ray intensity from each element into element concentration. Precision and accuracy of this technique is affected by sample homogeneity, sample size, sample preparation, sample/instrument geometry, instrument stability, counting statistics, and sample matrix. Generally, a sample must be homogeneous to a micrometer level, flat, polished, and analyzed with a high take-off angle. The electron beam must be focused on a small area of the sample.

Various *structural imaging methods* are used to create a "picture" of structure, either topographical or compositional.

When any of the above methods are applied to the analysis of several samples, the exam is considered *comparative*. When comparisons are required, the analyst must analyze each under identical conditions.

Many commercial suppliers provide excellent application utilities to perform these traditional analyses. Often they are "bundled" into a sophisticated analytical suite. Additionally, many specific application utilities are available, such as those for Gunshot Primer Residue (GSR) analysis.

Limitations of commercial software applied to Forensic applications

In addition to the traditional uses of SEM/EDS indicated above, forensic science has some specialized requirements:

- ▶ The need to compare the spectrum of a questioned material to that of reference standards. Frequently it is necessary to attempt to "identify" a material. Many samples requiring compositional com-

parison are not suitable for traditional quantitative analysis by SEM/EDS, by nature of their size, matrix composition, or homogeneity. Therefore a method other than quantitative comparisons is necessary. Such a method can be achieved by the simple matching of spectra. Even when elemental composition is unlikely to uniquely identify a material, the composition can serve to associate the material with a particular class of material.

- ▶ The ability to retrieve spectra by nature of a text-based search. Often it is useful to select materials using criteria other than spectral similarity. Such criteria may be color, material class (such as "lipstick"), or manufacturer.

- ▶ The need for multiple spectral display. Often it is useful to display the spectra from numerous samples simultaneously, in order to critically compare composition. It is therefore useful to display them in a fashion that permits critical comparison.

- ▶ The association of a sample image with the stored spectrum

- ▶ The need for evaluation of the significance of association. If a questioned and a known material are determined to be similar in elemental composition, it would then be important to know how significant that association is. This could be achieved by a determination of the variation of composition within that material class.

To achieve this level of information management, a true database architecture is required. The analytical advantages of a database are numerous, and although database management of spectral data has evolved with most other spectroscopic methods (Fourier Transform Infrared Spectroscopy, Mass Spectroscopy), such a capability within x-ray spectroscopy has not.

Historical efforts

McCrone and Delly first attempted to organize materials to include spectra and images in "The Particle Atlas"¹. Although limited for x-ray spectral data, it has been a valuable reference for the SEM analyst.

In 1994, a prototype database for x-ray spectra was begun at the FBI to evaluate the utility of an x-ray database and to determine the features that ultimately would be required. The integrated net peak intensities of one peak from each element de-

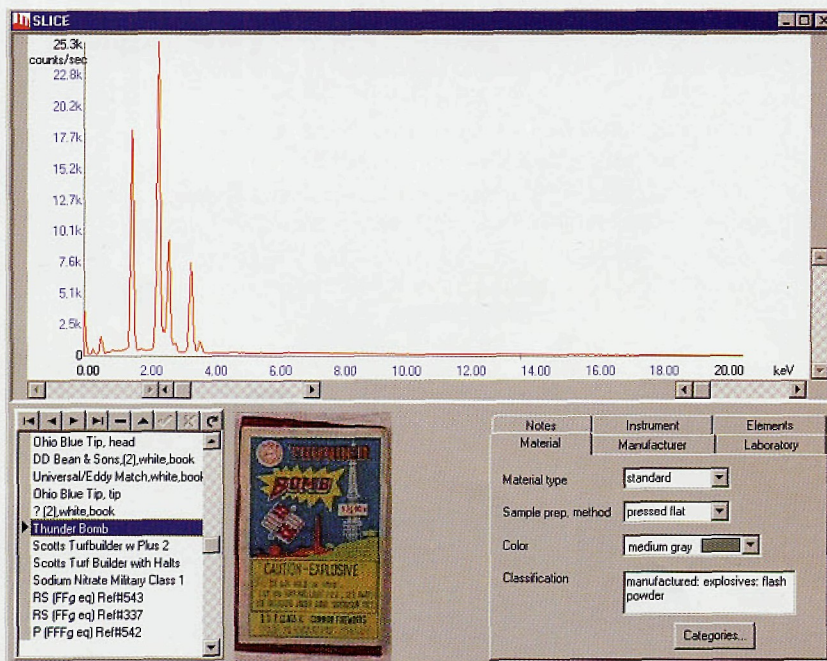
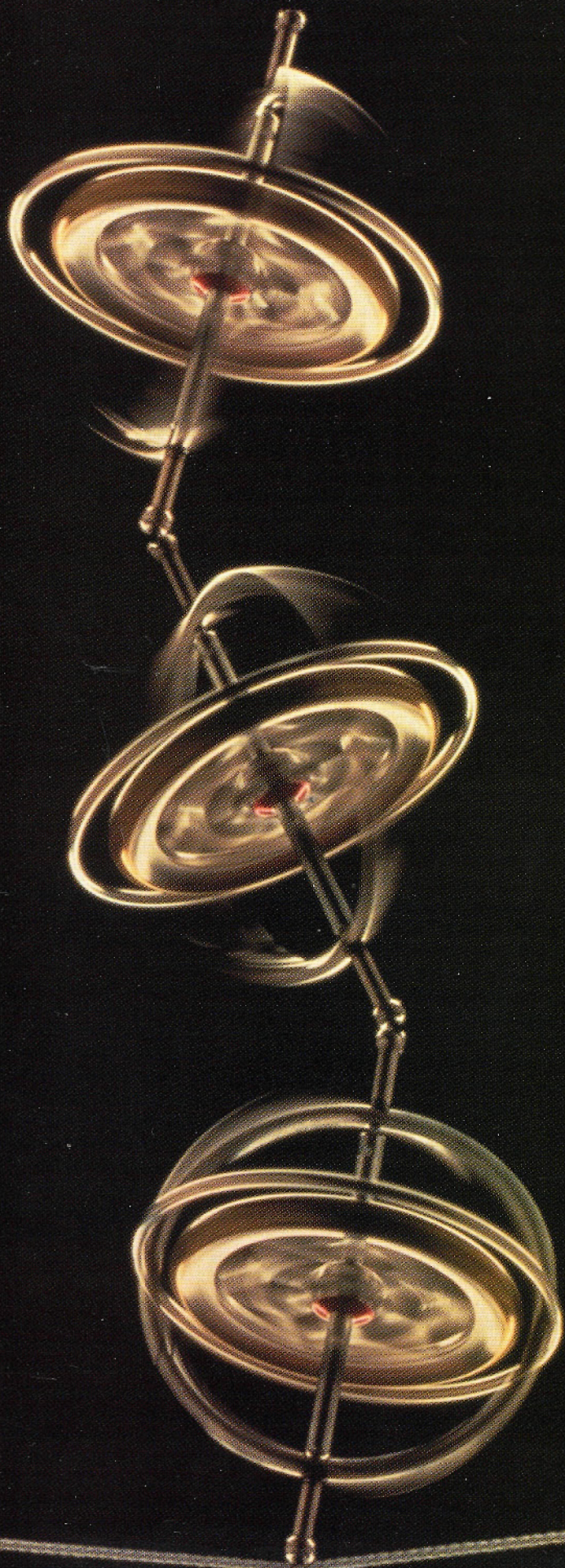


Figure 1: Spectrum input and display page.

Continued on page 10



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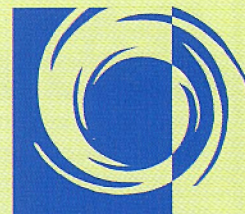
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The Development of an X-ray Spectral Database for Forensic Science

Continued from page 8

ected were summed, and the individual peaks detected were ratioed to the sum. This value, representing percentage of x-ray counts, was entered into the database ("R-base"). Also entered was a description of the standard, a unique number identifier, standard preparation method, color, date, and the peak/background ratio of the tallest peak detected. Several hundred spectra representing various materials categories were ultimately collected. Specific materials categories included: duct tape adhesives, cosmetics, alloys, paints and more.

"Identifications" were accomplished by database queries using percentage x-ray counts of each element in a questioned material. Text searches revealed compositional relationships of descriptively similar materials. Compositional searches could be made using relative peak heights if the sample was particularly small or contaminated. The database structure was satisfactory but cumbersome to use because; data entry was manual, spectra could not be downloaded into reports, and spectra could not be interactively overlapped. The design satisfied the original analytical and comparative needs, however, and served to demonstrate the utility of the "database concept" for forensic science applications.

In order to develop a contemporary full-featured utility, spectroscopy and database contractor services were obtained through standard procedures for Federal procurements.²

Present design

This database was designed as a Windows based application, intended to function with a contemporary EDS system resident on a PC. Spectra are converted to the EMSA format which has emerged as an industry standard. Two functional spectral display windows are used - an analysis window and a search window. Imported spectra are processed, analyzed, and stored from the analysis window. The search window displays the spectral "hits" resulting from a search.

Storage of standard spectra and associated information.

Upon importing, the spectrum is displayed in the upper portion of the spectrum analysis page (Figure 1). Typical qualitative utilities are available for analysis of the spectrum. In the lower left field a list of imported spectra is displayed. In the bottom center an image of the sample can be displayed. The lower right field includes information regarding sample analysis and information regarding the specimen, grouped under tabs. This information includes sample preparation, manufacturing details, composition, analysis parameters, laboratory details, color, material class and additional notes. Material classes are organized in a hierarchical tree. Prompts and drop-down menus aid data entry.

Data retrieval

Display of a single record includes all information stored with that entry, including spectrum, text, composition, and image (Figure 1).

Database queries can be made by selecting any individual or multiple criteria, including keyword, material classification, best fit, or composition (Figure 2).

Keyword: Text searches may be made from any words in the text fields associated with the spectrum, including the notes page.

Material classification: All entries within the materials category are selected.

Best fit: A search may include the entire spectrum, or a selected portion of it (for example to exclude lines of low atomic number elements). Spectra within the materials category searched are sorted according to fit (Figure 3).

Composition: A relational peak search permits searches based on the presence and ratio of specific peaks, or the presence of a specific element. Queries use a few logical operators, such as greater than, less than.

Fundamental assumptions:

In order for a database to function effectively, materials of similar composition and structure must produce a similar spectrum. Therefore default analysis conditions are applied to the analysis of all materials to be included in the database, specifically: 25 kv, a mid-value pulse processor time constant, 100s live time with a beam current selected to yield a dead time of 30%. The samples are prepared in such a manner as to yield as flat an analysis surface as possible. A constant SEM-sample-detector geometry is maintained. Magnification is selected in order to provide an analysis area sufficient to produce a spectrum indicative of the average composition or the sample. Although these conditions are not necessarily optimal for each sample, they will consistently return a spectrum that reflects average composition. As a result, any spectral differences are the result of actual compositional differences between samples.

Additional applications

In addition to the most obvious uses of this database stated above, it may also be possible to apply it to assessments of frequency of occurrence, and compound "identification".

Evaluating the variation of composition within a group of similar materials can permit assessment of the strength of an association. If a similarity is unique to the group, then the associative value is significant. Conversely, if the similarity is common, then the value for association is limited. That is, an association between materials that are compositionally common is less significant than one that occurs infrequently. The immediate developmental goal is to include each compositionally distinct member

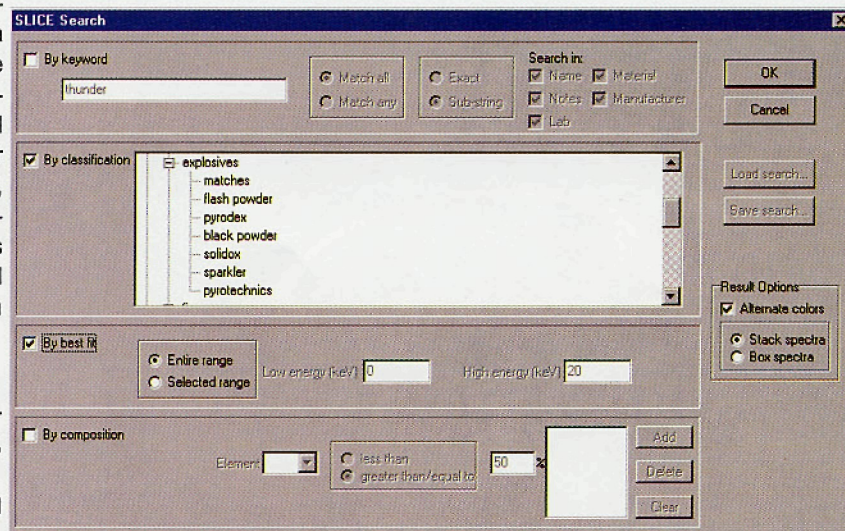


Figure 2: Query page.

Continued on page 12

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The Development of an X-ray Spectral Database for Forensic Science

Continued from page 10

within a materials category. If, however, materials are routinely included that have been randomly acquired, we perhaps could entertain the ability to determine frequency of occurrence as well. The significance of compositional variations can be determined only subsequent to the collection of vast numbers of individual items.

Attempts at "compound identification" appear promising. Elemental analysis can never provide definitive compound identification, as XRD can. SEM/EDS of a compound can only yield an elemental profile. If, however, that profile is matched against the profiles of other compounds, a list of possible identifications could be produced. The success of this method would depend on the variability of peak ratios within a series of compounds consisting of the same elements.

Current development

The FBI has established an international working group consisting of representatives from the RCMP in Canada, BKA in Germany, NICC in Belgium, and various forensic and investigative agencies in the US. The goal of this group is to develop a centrally maintained x-ray database management system, available remotely to participating agencies.

Development of this database consists of two phases. The first was to establish a "stand-alone" database capability resident on a user SEM. Much of this development is largely complete, resulting in the utility known as "SLICE" (Spectral Library Identification and Classification Explorer). This prototype data-

base utility is presently used at the FBI for general forensic applications.

The second phase consists of the development of a centralized database to permit member laboratories to access and contribute data. This development will include infrastructure, standardization, "rules of use", and management. Although SLICE currently is nearly spectrometer independent, development will eliminate the significance of spectral variables resulting from differences in beam voltage, sample geometry, spectral resolution, and detector response. As an example of the current performance, spectra obtained from a thin film in a TEM at 200 KV, 150 eV resolution, and a Be window, were paired successfully to spectra acquired from a bulk specimen in an SEM at 15 KV, 135 eV resolution, with a Moxtek window.

Conclusion

As a result of this effort, we have implemented a spectral database that includes the utilities necessary to perform all of the specialized functions listed in the section "limitations of commercial software" above, and has proven to be an effective utility for SEM in Forensic Science.

The ability to query the spectra of vast numbers of standard materials has enhanced the ability of this organization to use SEM/EDS in a comprehensive manner. Each of the mentioned utilities has been used in casework to provide the advantage of easy to use spectral reference, and to provide investigative direction from previously unmanageable associations.

As with any database resource the full advantage will become more significant as the number of records increases. In order to expediently populate the database with materials data, laboratories with existing materials collections will be asked whether they might contribute to our effort. It is anticipated that the importance of this utility for identifications and comparisons in Forensic Science will continue to grow. ■

1. The Particle Atlas, Edition Two, McCrone W.C., Delly J.G., Ann Arbor Science Publishers, Inc, 1973
2. xk, Inc, www.xk.com.

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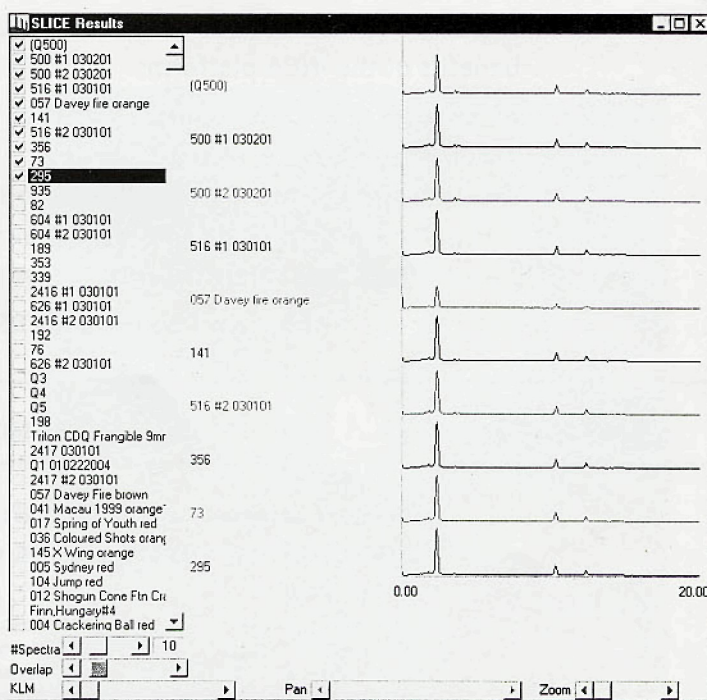
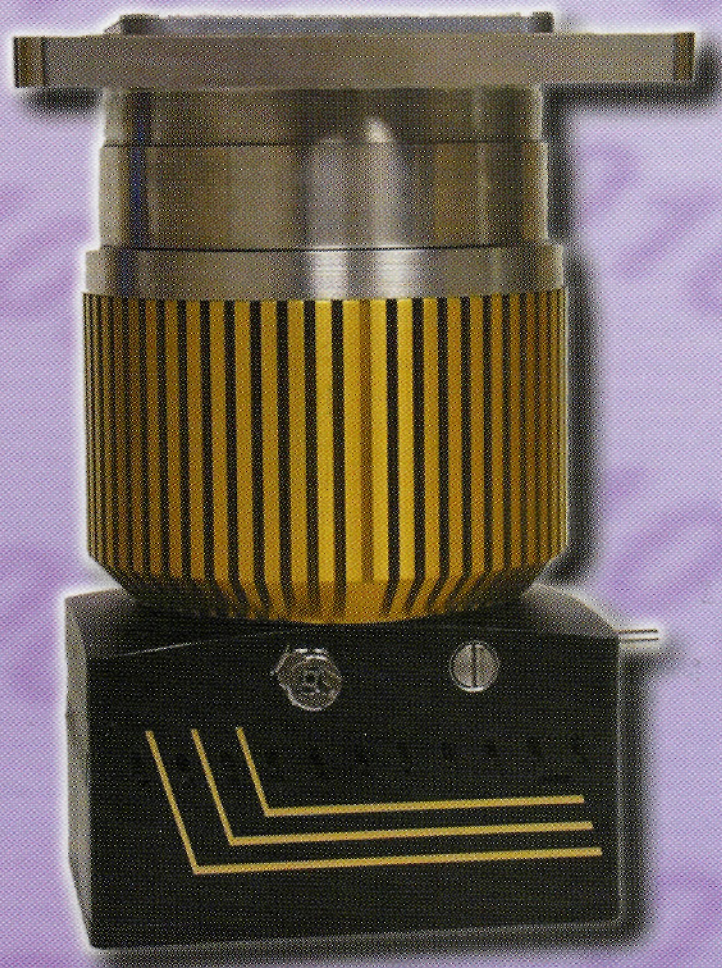


Figure 3: Search results page.

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