Forensics Application of Micro-XRF

Florida Department of Law Enforcement Utilizes Micro-XRF in Trace Evidence Analysis

Scott Ryland (seated) with EDAX Field Service Technician, Craig Theberge.

Recently, we had an opportunity to speak with Scott Ryland, a senior microanalyst with the Florida Department of Law Enforcement (FDLE). The FDLE laboratory owns both an Eagle 2 micro-XRF unit and EDAX SEM-EDS equipment for trace evidence analysis. The typical goal in this type of analysis is to prove that a sample from a known origin is consistent or, preferably, identical to a sample of unknown origin.

For example, comparing glass fragments from a crime scene to glass fragments from a suspect vehicle. In addition, one would like to have non-destructive analytical techniques to allow for repeated analysis on the same minute sample either by law enforcement officials or analysts for the defense of the suspect.

Ryland states, "Paint chips are ideally suited for analysis of the inorganic elements via SEM-EDS." Paint samples typically come in the form of flakes, smears or multi-layered chips with layers ranging in thickness from 10 to 40 micrometers. Paint is an organic film with inorganic solids (i.e. pigments, fillers and extenders). SEM-EDS allows for a reasonably non-destructive analysis on a spot size < 10 micrometers with a large dynamic range, low depth of penetration, and a controlled excited volume size. Using a backscatter electron image, a relatively homogeneous representative portion of each paint layer can be identified for analysis. The low depth of penetration and limited excited volume of the exciting electron-beam ensures that the fluorescent X-rays are derived only from the layer defined in the SEM image.

Forensic glass analysis is best served by micro-XRF for many applications as this analysis relies on the observation of trace inorganic dopants and contaminants in the glass", says Ryland. Modern glass manufacturing methods are capable of maintaining composition of the major components (i.e. oxides of Na, Al, Si and Ca) within 0.1 wt%. With this level of compositional control, the range of refractive index for various types of glasses becomes more restricted making a refractive index measurement, a traditional method of glass differentiation, more limited in value. As typical crime scene glass fragments are on the order of 1mm or more in size, micro-XRF allows for a non-destructive analysis with a large dynamic range and good sensitivity. The analysis can be automated to run many samples unattended. Typical elemental differentiators are as follows:

- Fe-oxide: raw material contaminant, levels on the order of 50-400 PPM in container glasses and 500-2000 ppm in window glasses
- Sr- and Zr-oxides: raw material and manufacturing contaminants, e.g. from ZrO_2 refractory brick used in the glass furnace, typically present in the 20-200 ppm range
- Mg-oxide: raw material for improving the glass structure's resistance to chemical attack, levels of 1-4 wt% in various glasses. At the FDLE, Mg-oxide measurements used to be done on SEM-EDS until this step was made unnecessary by analysis with the Eagle micro-XRF unit
- K-oxide: raw material for lowering the melting point and viscosity of the glass, levels of 0.2-0.5 wt% in various glasses
- As- Se- Ce-oxides: dopants used as color neutralizers
- Ti-oxide: dopant for manufacturing quality control
- Pb-oxide: dopant for improved color and reflectivity

Micro-XRF can also determine "float" glass via a Sn signal originating from the surface of the glass sheet which was in contact with the molten Sn bath during the manufacturing process. Furthermore, since micro-XRF is a completely non-destructive, non-contact measurement, samples are preserved for repeat analysis without risk of contamination of the samples or the spectrometer. This makes micro-XRF ideal to handle a wide variety of materials for forensic analysis. The FDLE also uses the Eagle micro-XRF unit to evaluate inorganic additives in plastics, duct tape adhesives and rubbers. Scott Ryland concludes, "Having both X-ray spectroscopic methods allows the FDLE Microanalysis Section to effectively handle our caseload of paint and glass trace evidence as well as a wide variety of other materials which come through the lab. The SEM-EDS and micro-XRF serve as complementary techniques and our laboratory works far more efficiently having both tools."

Scott Ryland has been with the FDLE for 26 years. He was named Scientist of the Year in 1999 by the FDLE after the major role he played in solving the murder of a 9-year old girl in Florida. This case was featured on Court TV's Forensic Files in an episode entitled "A Bag of Evidence". Scott routinely provides training for forensic analysts within the FDLE and for various professional organizations throughout the United States. He has served as chairman of the Paint Subgroup of the Scientific Working Group for Material Analysis for the past nine years, which is the national committee for standardization of forensic testing procedures in Microanalysis.