

STUDY OF MICROHETEROGENEITY USING μ XRF, INAA, AND CHEMOMETRIC METHODS

John L. Molloy, John R. Sieber and Rolf Zeisler
National Institute of Standards and Technology, Gaithersburg, MD

Micro X-ray Fluorescence (μ XRF) has been used to nondestructively investigate elemental heterogeneity by constructing two-dimensional maps of elemental concentrations in reference materials. Chemometric methods of analysis, such as principal component analysis (PCA), show promise in describing complex data patterns obtain using μ XRF to study various samples. PCA can identify if “nugget” effects exist within a material, a case where an element is enriched in small, isolated areas of the sample. Each element must be treated according to its level of heterogeneity within the sample as determined by comparison of mapping data to a PCA model. The model is built based on the variation of analyte signal at a single location within the sample. Examples of this analysis methodology are shown for several different reference materials to demonstrate how PCA treatment can be used to identify which elements exhibit nugget effects within the ng and μ g mass range. Additionally, a method of calculating the minimum recommended mass for solid samples is suggested. PCA methods are iteratively used on X-ray maps from which adjacent data points have been averaged, simulating an increasing X-ray spot size. This is repeated until the mass sampled in a map is indistinguishable from data taken at a single location.

While the above analysis is straightforward and relatively fast, it is difficult to confirm the results obtained using other available techniques. Instrumental Neutron Activation Analysis (INAA) is a potentially useful technique for this purpose. It is able to measure small samples of material in the range of 1 mg to 100 mg, thus bridging the gap between current, bulk analysis methods and μ XRF as well as other solid sampling microanalysis methods such as graphite furnace and laser ablation techniques. INAA gives complimentary information to μ XRF because the more penetrating radiation is able to thoroughly probe thicker samples containing many heavy elements. However, analyses investigating microheterogeneity using μ XRF typically do not agree with results obtained using INAA because of the former's limited penetration depth within the sample. It is possible to compare the microheterogeneity observed in a sample using μ XRF by placing a high Z element behind a sample. The resulting signal obtained from that high Z element shows attenuation at locations which correlate with nuggets present within a sample. This can reveal if nuggets observed in traditional μ XRF maps have been revealed completely or if only a small portion of a larger nugget has been exposed to routine analysis. In this way, a picture of the entire sample can be obtained and combined with mapping data taken simultaneously to give a complete analysis of the microheterogeneity present within the sample.