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## MULTIVARIATE STATISTICAL ANALYSIS OF PARTICLE X-RAY SPECTRA

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Multivariate statistical analysis (MSA) is a powerful tool for the analysis of series of spectra. 1,2 This paper explores an application of MSA to a series of energy dispersive X-ray (EDX) spectra acquired in the scanning electron microscope (SEM) from a series of particles. The raw data were series of spectra previously acquired to test analytical procedures for trace element detection.3 This paper explores the possibility of performing the trace element detection with MSA components that have been extracted from the raw data without any a priori assumptions about the information content of the particle spectra. Particles were prepared from two analytical glasses, dispersed onto carbon substrates and coated with carbon. The compositions of the two glasses are substantially similar, except that one glass (K-3106) contains 0.7 wt.% Fe, whereas the other glass (K-3069) does not contain Fe at a detectable level. Spectra were acquired with a 20 kV accelerating voltage from 35 different particles of each glass, with particle diameters that ranged from 1 - 10 µm, and with acquisition times of 15, 60 and 200 s. A test data file of 75 spectra was composed for each acquisition time by arranging the 70 acquired spectra in no particular order in a composite file, and inserting 5 duplicate spectra as a test of reproducibility. MSA was performed using software developed at Oak Ridge National Laboratory.<sup>2</sup>

The MSA results for this application are shown in the figures for the spectral series with acquisition times of 60 s (Fig. 1) and 15 s (Fig. 2). In both figures, plot (a) shows a normalized plot of the eigenvalues of the variance-covariance matrix of the 75 spectra, which gives the fraction of information conveyed by successive moments of the data; plot (b) shows spectral components for each data set that were composed as an Fe identifier, as detailed below; and plot (c) shows a histogram of the intensity values for this component for the raw data set of 75 spectra. The majority of the eigenvalues in (a) form a line on the semi-log plot, which is consistent with variations among spectra due only to Poisson statistics. The last five eigenvalues in each data set, which are actually orders of magnitude lower than the others, denote the five duplicate spectra, which convey no independent information. The first few eigenvalues provide statistically significant variations of the series of spectra that are distinct from the baseline noise level. The transition eigenvalues (~4-10) correspond to variations in the series of spectra that are not due to Poisson statistics alone, but which are not readily separated from the noise level. The circled eigenvalue in each plot is that which most contributes to the Fe-indicator component in (b). This component is well above the noise level in Fig. 1 but not in Fig. 2. The Fe-indicator components shown in plot (b) of the two figures were formed using a procedure that can be generally applied to extract a histogram of intensity values for any characteristic feature of a large series of spectra. The Fe  $K_{\alpha}$  intensities for MSA spectral components 0 through 3 were measured and used as weighting factors to compose the Fe indicator spectra. This procedure essentially concentrates all of the Fe intensity into one of the four spectral components. The much higher noise level of Fig. 2b relative to Fig. 1b is consistent with the plots in (a). The first-derivative type feature in the Si-K, Pb-M and Pb-L X-ray peaks, especially evident in Fig. 1b, is likely present because of a slight difference in EDX detector calibration when the spectra were acquired from each glass. Such a feature may arise from a shift of as little as ~1 eV. However, there is still a net positive correlation of Fe with Pb and C intensities, and a negative correlation with Si and O. Such a correlation is unexpected, given that the two glasses are identical in composition apart from the trace Fe concentration, and may suggest a systematic error in the procedure that was used to extract the Fe indicator spectrum. Even given this potential systematic error, the histogram in Fig. 1c shows good discrimination in the 60 s spectra between the Fe concentrations of the two glasses. In contrast, the histogram for the 15 s acquisitions in Fig. 2c shows several problems that arise from the poor separation of the Fe-bearing components from the noise level: the two distributions are no longer unambiguously resolved, the lower mode of the distribution is shifted strongly from zero intensity, and there are outliers from the distribution. The discrimination of the essential component from the noise level in the plots in (a) appears to be the determining factor for the efficacy of trace element detection.<sup>4</sup>

- 1. P. Trebbia and N. Bonnet, *Ultramicroscopy* 34(1990)165.
- 2. I.M. Anderson and J. Bentley, Proc. Microscopy & Microanalysis 1997, 931.
- 3. J.A. Small, Proc. Microscopy & Microanalysis 1997, 901.
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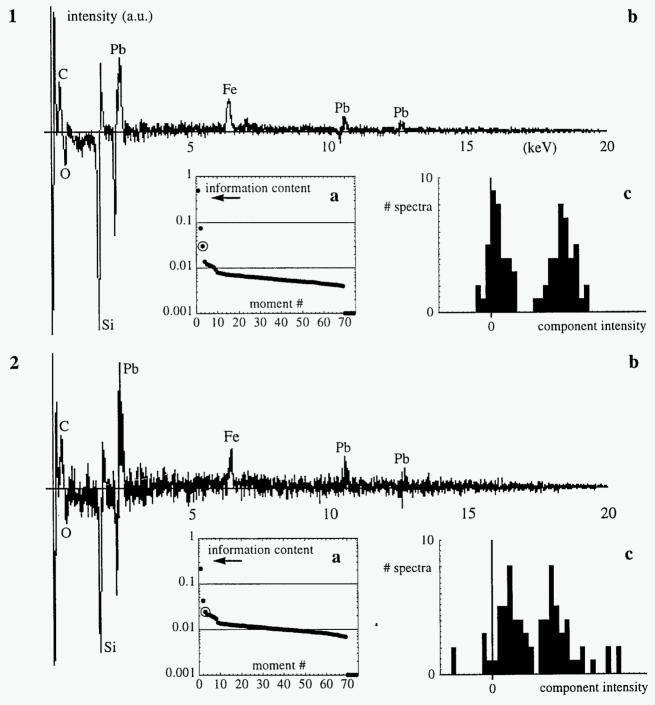


Fig. 1 MSA results for 60 s spectral series: (a) information content of principle moments; (b) spectral component composed as an Fe identifier; (c) histogram of intensity values for component in (b).

Fig. 2 Analogous plots to Fig. 1 for 15 s spectral series. See text for details.

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