Quantitative characterization of particulate matter is demanded for many environmental and geological applications. If the particles of interest are present at low abundance in the bulk samples, only individual particle analysis can deliver information on the dispersion of heavy elements in the sample. In order to derive relevant information on the sources or weathering of these particles, accurate chemical information is necessary including major, minor and trace elements. The major composition of individual micro-particles including low atomic number elements can be quantitatively determined using electron-probe X-ray microanalysis (EPMA). This technique can deliver also speciation information on high-Z elements, if they are present at major concentration level. For the analysis of trace components of heavy metals or actinides only micro X-ray fluorescence (µ-XRF) has sufficient sensitivity to detect amounts below $10^{-10}$ g. The two X-ray emission techniques, µ-XRF and EPMA deliver complementary information. Both for EPMA and µ-XRF, the matrix and attenuation effects caused by the differences in the size and shape of the particle can be taken into account accurately using Monte Carlo (MC) simulations. Quantification is achieved by iterative adaptation of the simulated elemental concentrations until the deviations between the simulated and experimental peak areas fall within the statistical uncertainties of the recorded fluorescent lines. A significant advantage of the MC simulation based quantification scheme compared to other methods is that the simulated spectrum can be compared directly to the experimental data in its entirety, taking into account not only the fluorescence line intensities, but also the scattered/bremsstrahlung background of the X-ray spectra. A relative standard deviation of 5-20 % can be reached using the MC quantification scheme using either of the two methods.

If the measurement of the same particle type is possible using both EPMA and µ-XRF, the major composition derived from EPMA can be used as matrix composition for µ-XRF trace analysis. The combination of the two methods is demonstrated on different excitation conditions and particle types. Fly ash, soil and sediment particles containing actinides as well as water suspended particles enriched with heavy metals due to river pollution were studied. The latter particles were found to be heterogeneous, containing an aluminosilicate core covered by a layer enriched in manganese and heavy elements (Zn, Pb, Cd).