Improving XRF Analysis of Atmospheric Particulate Matter Samples: Calibration by Ideal Reference Materials and Investigating Interferences

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Calibration of XRF systems is improved by using standards that reproduce relevant characteristics of the sample. The commercial standards available today, produced by sputtering onto Mylar or Nuclepore films, differ in potentially significant respects from particulate matter (PM) collected on Teflon filters. We generated reference materials (RMs) that more closely mimic ambient samples to assess the adequacy of commercial XRF standards for calibrating a custom-built energy dispersive XRF system. The system utilizes direct excitation in vacuum with a Cu-Anode tube and a SiLi-detector to measure elements Na through Fe in PM samples for the IMPROVE network (Interagency Monitoring of Protected Visual Environments, http://vista.cira.colostate.edu/improve/).

An aerosol generation and sampling system was created to make RMs with two sulfur-containing compounds, ammonium sulfate (AS) and potassium sulfate (KS). Particles were collected on 25 mm Teflon filters using an IMPROVE sampler. Gravimetric analysis was used to determine the mass of sulfur, which was independently confirmed by ion chromatography (IC). The mass range, which extended from 0.7 to 224 $\mu g/cm^2$ S was used to explore both linear and non-linear response regions in the sulfur X-ray counts. The agreement of AS and KS RMs indicated that the sulfur response was independent of the two compounds used. The observed departure from linearity of sulfur X-rays at higher RM masses was satisfactorily accounted for by a theoretical self-absorption model. Using several RMs in the sulfur mass range measured across the network, namely the linear response region, gave an uncertainty in the RM "calibration" constant of 1.4% at a 99^{th}%tile confidence level for both compounds. In comparison, the Micromatter Inc. standards between 12 – 14 $\mu g/cm^2$ S, certified with a 5% uncertainty, varied by ±5% from the RM response line. This work shows that RMs can be used to assess the accuracy and linearity of XRF systems, and furthermore, improve the calibration precision.

Additional consideration was given to the influence of sulfur on the spectral interpretation of aluminium and silicon in PM samples. IMPROVE PM data provide empirical evidence that aluminum and silicon masses are incorrectly reported when sulfur mass is elevated in samples. We studied this apparent interference under controlled conditions. Parallel ambient $PM_{2.5}$ samples were collected using IMPROVE samplers in a rural area where silicon and aluminum is elevated but sulfur is not a main PM constituent. Pure ammonium sulfate was then deposited onto the filters with the same method used to generate RMs to produce a range of S/Si observed in the network PM data. The samples were analyzed by XRF before and after addition of sulfur using both the IMPROVE instrument, and a commercial instrument, with a CaF_2 secondary target and Ge detector. Preliminary results for samples with relatively high Si masses showed that high S/Si ratios produced an over estimate of silicon in our instrument and an under estimate of silicon mass consistent with attenuation losses in the commercial instrument.