

Generation and Applications of Teflon Filter **Reference Materials for IMPROVE XRF Elemental Analysis**

AAAR 28th Annual Conference Minneapolis, MN 3G.19 26-30 October 2009

Hege Indresand, Krystyna Trzepla-Nabaglo, Brian P. Perley, Warren H. White, Charles E. McDade, Ann M. Dillner IMPROVE Program, Crocker Nuclear Laboratory, University of California, Davis

1. IMPROVE XRF analysis

The IMPROVE network is a long-term monitoring program at over 150 national parks and wilderness areas in the US. Particulate matter (PM) samples are collected every third day and analyzed for chemical species to assess trends in visibility as required by the Regional Haze Rule.

Elemental analysis of Teflon filter deposits is done by Cu-Anode Vacuum and Mo-Anode Energy Dispersive X-ray Fluorescence (XRF) systems. Commercial calibration standards used in XRF are made of materials that are unlike PM and deposited on substrates that are unlike Teflon filters. Furthermore, the mass range of commercial calibration standards is limited and often much higher than sample masses. Our goal was to build an aerosol generation and sampling system to make reference materials (RMs) equivalent to IMPROVE samples that can be used to evaluate and calibrate the XRF system. Additionally, the system would enable us to apply known deposits onto ambient samples to study interferences.

2. Generation of reference materials (RMs)

Particles are generated from a solution with a TSI constant-output atomizer (3076) and dried with a diffusion drver. A TSI air filter supply (3074B) provides dry and particle-free air for the atomizer and for the dilution air. A mixing chamber (0.5 m³) ensures that particles are well-mixed before being drawn through an IMPROVE PM25 sampler. The deposit on each filter is a function of solute, solution concentration, and sampling time.



Gravimetric analysis is used to determine the mass of the RMs. The balance uncertainty is 1.4 µg/cm², but the total uncertainty in the mass is from handling, water, and other material on the filter. Several procedures and methods are being used to minimize and quantify total uncertainty. During production the mixing-chamber RH is monitored to ensure that the particles are dried well below their efflorescence relative humidity. Blanks analyzed by XRF showed minimal elemental contamination (Figure 1). Also, water and organic contamination was not detected when filters were analyzed by transmission FTIR (Figure 2). Furthermore, we will supplement our gravimetric analysis with independent laboratory measurements (XRF, IC) of elements and ions deposited on the RMs.



FIGURE 1 Total elemental mass of laboratory blanks and chamber blanks, which were collected with de-ionized water solutions for 25 or 50 minutes (1x and 2x chamber volume). The chamber and laboratory blanks were comparable and below 0.40 µg/cm², which is 14% of the lowest RM mass and 0.043 % of the highest RM mass.



FIGURE 2 Potassium hydrogen phthalate (KHP) and calcium sulfate dihydrate RMs are examples of samples that contained organics and water respectively. The ammonium sulfate RM (bottom spectrum) do not show water or organic contamination



Teflon filters (25 mm) with ammonium sulfate and potassium sulfate deposits in a mass range of 0.7 – 224 µg/cm² S were used to evaluate the sulfur XRF analysis. The RMs provided an assessment of the XRF response over a large mass range as can be seen in Figure 3 for ammonium sulfate filters. The XRF response of sulfur RMs showed linear and non-linear regions (Figure 4). Comparing Micromatter Inc. sulfur standards responses to the RMs. no systematic bias was identified (Figure 5).





XRF spectra of ambient FIGURE 6 sample with considerable Si and Al mass analyzed by XRF before and after adding ammonium sulfate deposits to each filter (only Al, Si, S energy region shown).

FIGURE 7 The percent difference of Si and Al counts as a function of the S to Fe mass concentration ratio. The plot confirms that high levels of sulfur compared to soil elements can interfere with the counts (peak areas) of aluminum and silicon



FIGURE 8 Preliminary attempt to create C RMs that are closer in mass to IMPROVE samples than Micromatter standards, which are 30 - 100x higher than the mean Cl concentration measured (0.3 µg/cm²).

Funding for this project has been provided by the National Parks Service contract # C2359-06-4026 The authors would also like to acknowledge the staff at Crocker Nuclea Laboratory at the University of California. Davis for all of their assistance