

Chapter 10. X-Ray Fluorescence Reference Materials from an Aerosol Generation System

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10.1 INTRODUCTION

A new aerosol generation and mixing-chamber system was developed and designed to deposit samples of known composition on filters, using an IMPROVE sampler. The aerosol generation/mixing system has been used to create reference materials to evaluate the response of the X-ray fluorescence (XRF) system over a wide range of mass concentrations and to assess the calibration of the XRF instrument. Additionally, the new aerosol system has been used to add pure substances to ambient samples to evaluate spectral interferences.

The need for the aerosol generation system emerged from questions regarding the calibration of the XRF system. Ideally, calibration standards mimic ambient samples in mass loadings, deposit pattern, substrate material, and chemical composition. The commercially available standards are prepared on Mylar® or Nuclepore® substrates, not on Teflon® as used in routine IMPROVE sampling. In our system the samples are prepared on Teflon, and they also exhibit the same deposition patterns as field samples since the aerosol chamber is attached to an actual IMPROVE sampler. Commercial standards are typically only available at one or two mass loadings, which are higher than those encountered in the IMPROVE network. The standards are purchased from a single vendor, and there are no alternative sources to provide an independent assessment. Furthermore, XRF calibrations are performed at a reduced instrument current compared to field samples to accommodate the high loadings on the standards. Filter-based reference materials at lower concentrations (representative of IMPROVE field samples) can be prepared using the aerosol generation/mixing system and at a variety of concentrations across the representative range, thereby allowing for multipoint calibration in the range of the samples, which improves the precision of the calibration.

The new system also allows the preparation of samples to evaluate spectral interferences at relevant concentrations. Spectral peaks of sulfur and silicon, for example, lie close to one another in the XRF spectrum, and a large amount of sulfur relative to silicon has been shown to cause interferences to the silicon peak in the IMPROVE network data. By adding ammonium sulfate to ambient filters, it is possible to investigate such interferences under controlled conditions.

10.2 AEROSOL GENERATION SYSTEM

A diagram of the aerosol generation system is shown in Figure 10.1 and a photograph is shown in Figure 10.2. Aerosol deposits are generated from solution with a constant-output atomizer, using compressed air. Aerosols are dried with a diffusion dryer before entering the dilution chamber. Low relative humidity and particle-free dilution air is introduced into the chamber to further dry the aerosol and allow sufficient flow rate for the sampler. The aerosol stream and dilution air are well mixed in the chamber before being pulled through an IMPROVE PM_{2.5} sampler operating at the typical flow rate for IMPROVE samplers. Relative humidity in the chamber is measured continuously to ensure that the particles are completely dry. The

amount of the aerosol deposit is a function of solute, solution concentration, and sampling time. The actual mass deposited on each filter is determined gravimetrically, as described below.

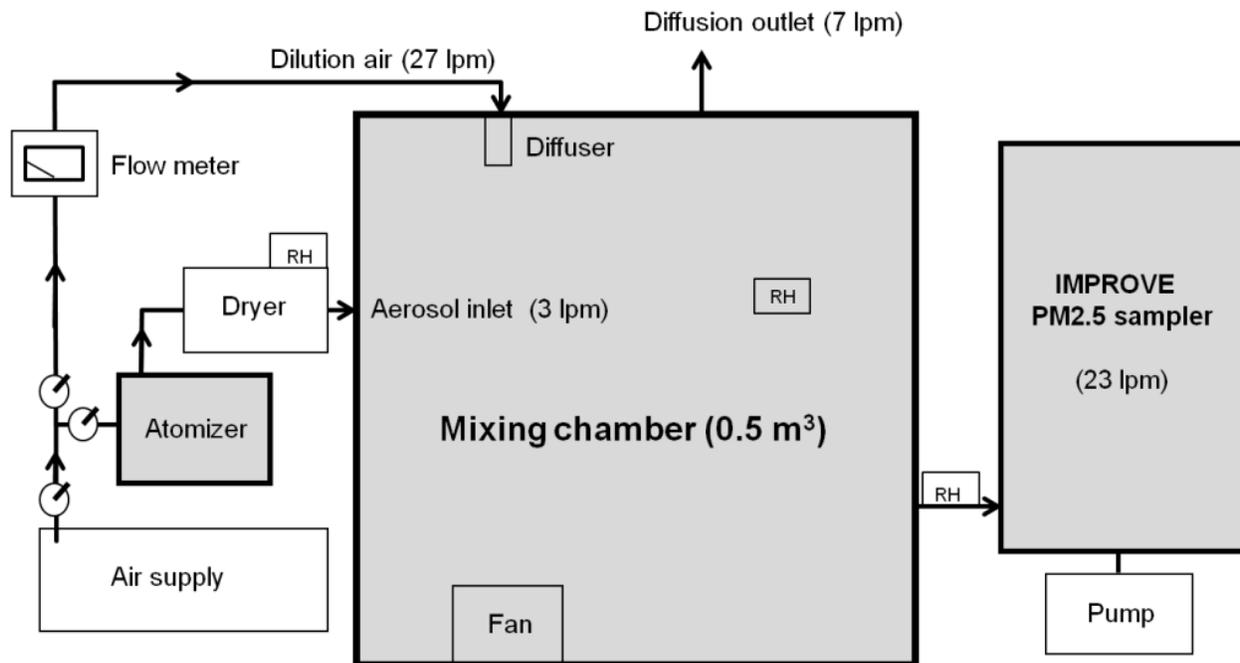


Figure 10.1. Schematic of the particle generation, mixing, and sampling system used to make reference materials. A solution is atomized and the resulting particles are dried and mixed with clean, dry air in the mixing chamber. The suspended particles are drawn through an IMPROVE PM_{2.5} sampler and collected on 25 mm Teflon® filters. Relative humidity (RH) is measured in three locations to ensure that particles are anhydrous.

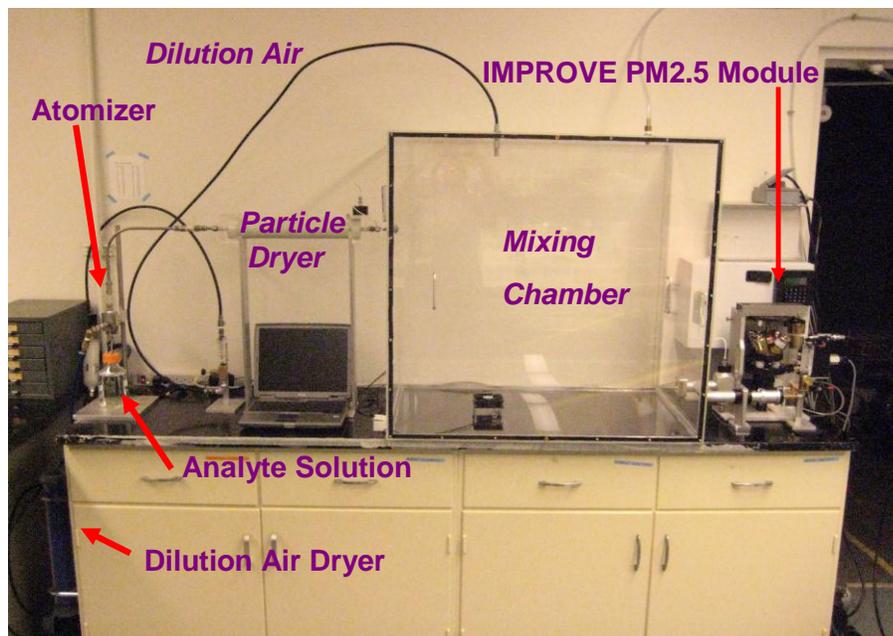


Figure 10.2. Photograph of the aerosol generation system.

10.3 TESTING AND VERIFICATION

Most of the development work thus far has focused on generating sulfate-containing particles. Ammonium sulfate is one of the major components of most ambient aerosols. In addition, sulfate mass loadings on IMPROVE samples are high, allowing for better accuracy in gravimetric measurements. Potassium sulfate was used in some other filter preparations to assess the reliability of the method using a different compound. Solutions were made with 99.999% pure ammonium sulfate or 99.95% pure potassium sulfate in HPLC (high-pressure liquid chromatography) grade, deionized water. Reference materials were made in the mass range representative of field samples and also at higher masses to evaluate XRF instrument performance.

Two types of blanks were generated with each run. Laboratory blanks corresponded to filters that were taken out of the box and analyzed by XRF without ever being installed in the sampler. Chamber blanks were installed in the sampler and collected by running the aerosol generation system with strictly deionized water solutions in the atomizer immediately after a full cleaning of the generation and sampling system. XRF analyses of species in chamber blanks were equivalent to laboratory blanks and showed that elemental contamination was not produced in the generation and sampling systems during filter handling.

As a further test for contamination, transmission FTIR (Fourier transform infrared) spectroscopy was used to scan the prepared reference materials for particle-bound water and organic-compound contamination that, if present, would add unwanted mass. The results showed no detectable amounts of these contaminants.

The fundamental measurement technique of gravimetric analysis was used to determine the mass of sulfur on each ammonium sulfate (or potassium sulfate) filter. The measured mass of ammonium sulfate or potassium sulfate was converted to mass of sulfur, assuming a pure compound was collected (no water or impurities). After the filters were weighed, they were analyzed by XRF, and many were then analyzed by ion chromatography (IC) to provide an independent measure of sulfate concentration. The IC measurement showed that sulfur mass based on ammonium sulfate mass was accurate. IC is a destructive technique (it requires extraction of the filter in solution), so it cannot be performed a priori to determine the concentration before XRF analysis.

Testing using IC has established the reliability of gravimetric mass as a quantitative technique for these sulfur reference materials. Figure 10.3 shows the linear regression of sulfur measured by IC compared to gravimetric analysis as a function of deposit mass. The agreement between gravimetric analysis and IC is within about 2% for ammonium sulfate and within about 3% for potassium sulfate.

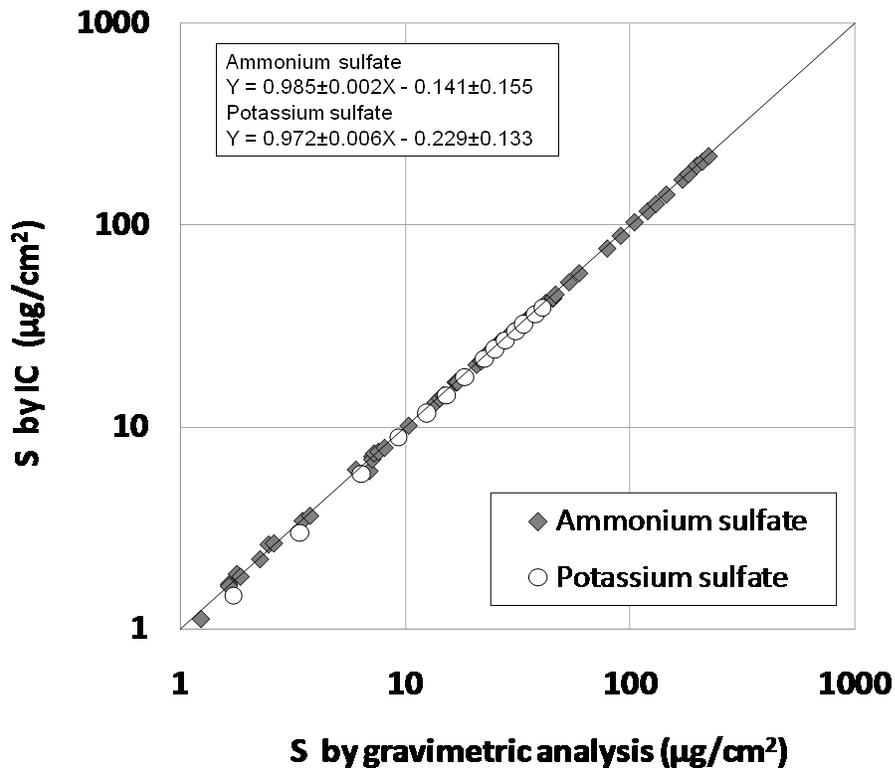


Figure 10.3. Sulfur (S) mass measurements from ion chromatography (IC) compared to gravimetric analysis for ammonium sulfate and potassium sulfate reference materials. The linear regressions (with 95th percentile confidence levels for the slope and intercept) for each reference material are given on the figure and show the good agreement between sulfur from IC and gravimetric analysis.

The sulfur reference materials have been used to evaluate the sulfur response in the UC Davis XRF system and to assess the feasibility of using the new reference materials in routine system calibrations. An additional commercial XRF instrument (PANalytical Epsilon 5) at the Desert Research Institute (DRI) was used in an interlaboratory comparison of the sulfur response of prepared reference materials, two commercial standards, and 28 ambient samples from the IMPROVE network. When each laboratory calibrated its XRF instrument using its own set of commercial standards, the reported sulfur concentrations on the 28 ambient samples differed by over 10% between the two laboratories. When both instruments were calibrated against the new UC-Davis-prepared reference materials, however, sulfur concentration agreement improved to within 1%. Hence, the two laboratories produce the same result when they both calibrate with reference materials that mimic all features of the element and the sample.

Further work has begun to produce deposits on Teflon filters of other elements analyzed in the XRF system. Sodium chloride has been successfully atomized and deposited on filters. Other elements with major importance for the Regional Haze Rule will also be considered for future work. The chamber will also be used to evaluate uncertainty, measurement detection

limits, and spectral interferences. Although the initial development work has focused on the preparation of Teflon filter samples, the aerosol generation system is also applicable to the preparation of samples on quartz and nylon filters. Currently underway is a project that deposits ammonium sulfate on quartz filters to evaluate the impact of particles on pyrolysis of organic carbon.