X-RAY
SPECTROMETRY

Received: 6 September 2012 Accepted: 15 February 2013

(wileyonlinelibrary.com) DOI 10.1002/xrs.2456

Preparation of sulfur reference materials that reproduce atmospheric particulate matter sample characteristics for XRF calibration

H. Indresand, W. H. White, K. Trzepla and A. M. Dillner*

Energy-dispersive X-ray fluorescence (XRF) is an important tool used in routine elemental analysis of atmospheric particulate matter (PM) samples collected on polytetrafluoroethylene (PTFE) membrane filters. The method requires calibration against thin-film standards of known elemental masses commonly obtained from commercial suppliers. These standards serve as a convenient and widely accepted interlaboratory reference but can differ significantly from samples in their chemical composition, substrate, and geometry. These differences can introduce uncertainties regarding the absolute accuracy of the calibration for atmospheric samples.

Continuous elemental records of the US Interagency Monitoring of Protected Visual Environments (IMPROVE) PM monitoring network extend back to 1988. Evaluation of long-term concentration trends and comparison with other networks demand a calibration that is accurate and precise compared with the uncertainty of the XRF measurement itself. We describe a method to prepare sulfur reference materials that are optimized for calibration of XRF instruments used to analyze IMPROVE PM samples. The reference materials are prepared by using the atmospheric form of the element, by reproducing the sample geometry, and by using the same substrate as in samples. Our results show that stable, pure, anhydrous, and stoichiometric deposits are collected onto the filter substrates, and furthermore, that the reference material masses are accurate and have acceptable uncertainty in the measurement range. The XRF response of the sulfur reference materials is similar to other commercial standards and is linear in the measurement range, and the slope of the multipoint calibration curve has very low uncertainty. These reference materials are valid for the calibration of XRF systems, and they bring improved transparency and credibility to the IMPROVE calibration. Copyright © 2013 John Wiley & Sons, Ltd.

Introduction

Energy-dispersive X-ray fluorescence (XRF) is an important method for routine elemental analysis of atmospheric fine particulate matter (PM) by large monitoring networks.[1] In the US, about 40 000 PM samples from sites across the country are analyzed by XRF every year for the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and the Speciation Trends Network (STN).[2,3] The resulting elemental concentration data are examined for associations with indices of public health,[4] checked for chemical signatures of specific sources' air pollutant emissions[5] and compliance with legal standards for ambient air quality,[6] and tracked over time to verify the atmospheric effects of reducing emissions.[7] IMPROVE samples have been analyzed by XRF for elemental mass in PM collected on polytetrafluoroethylene (PTFE) membrane filters since 1992.[8] The continuous elemental monitoring records of IMPROVE extend back to 1988, and a major objective of the network is the documentation of long-term concentration trends. When evaluating historic trends in element data and when comparisons are carried out between IMPROVE data and other networks, i.e. other XRF analyses, confidence in a measurement is achieved by a good calibration (accurate) and a low uncertainty in the calibration constant (precise) compared with the uncertainties of the XRF measurements themselves.

Commercial standards, made by vacuum-depositing metals or salt onto Mylar or polycarbonate (Nucleopore) films, have been the primary choice for calibrating instruments used for PM analysis since the method was developed three to four decades ago.[1,9] The most commonly used film standards today (Micromatter, Vancouver, BC, Canada) are typically produced with a 50 μg/cm^2 areal density of a deposit containing element(s) and are certified with an uncertainty of $\pm$5%. Attributes of the commercial standards such as stability and uniformity and their wide acceptance were advantageous, as XRF experiments on thin samples were developed and expanding and eliminated the time-consuming step of preparing sample-matched reference materials.[10] NIST Standard Reference Material 2783 (National Institute of Standards and Technology, Gaithersburg, MD, USA) is the only commercial PM reference material available on a filter substrate. This standard, which was prepared by filtration of a homogenous liquid suspension of urban dust from Vienna, Austria, onto Nuclepore polycarbonate membrane (0.4 μm pore size) filters, is a PM matrix containing several elements but is only available at one mass per element.[11] The certificate of analysis provides uncertainties for the certified elements varying from 2% to 19% with an average and median of 10%. Reference rather than certified values are given for important elements such as S and Si with uncertainties of 25% and 3%, respectively.[11]

Particulate matter samples, although assumed to be collected uniformly across the filter, commonly exhibit heterogeneous characteristics on a smaller scale due to the large distribution of particle sizes in the atmosphere and/or due to a backing screen.

---

* Correspondence to: Ann M. Dillner, IMPROVE Program, Crocker Nuclear Laboratory, University of California Davis, One Shields Avenue, Davis, CA, 95616, USA. E-mail: amdillner@ucdavis.edu

IMPROVE Program, Crocker Nuclear Laboratory, University of California, Davis, CA, 95616, USA

These heterogeneous attributes of PM samples are not captured by the uniform vacuum deposits of commercial standards. Furthermore, commercial Micromatter standards can exhibit element mixes unrepresentative of atmospheric particles, e.g. a sulfur layer on top of copper[9] for the calibration of samples in which nearly all sulfur is found in ammonium salts of sulfate.[12,13] In the IMPROVE network samples are collected on a stretched 2.5-cm circular PTFE membrane filter (collection area 3.53 cm^2), as opposed to commercial standards that are prepared on films. Figure 1 is a photograph of an IMPROVE filter sample. Particles are deposited as the particle-laden air is drawn through the filter using a vacuum pump. For support against the air flow, the filter is backed by a metal screen whose design and pattern is reflected in the particle deposit.[14] The pixilated pattern in IMPROVE samples is due to small conical holes (0.0007 cm^2) in the metal screen.

Because of the limitations of NIST and commercial standards, several researchers have successfully prepared reference materials for determining metals in PM samples by XRF or other methods. A common method is to generate particles from salt or metals solutions or from suspending materials and then deposit dried particles or materials onto filters.[15–22] Mass is measured gravimetrically for individual reference materials or by another chemical analysis [atomic absorption, ion chromatography (IC), and inductively coupled plasma mass spectrometry], especially if a large substrate or a standard with multiple elements is prepared. Another preparation method involves directly and uniformly spiking or doping filter substrates or ambient samples with solutions or plastic mixtures before drying.[23–30] XRF calibrations have also been performed with ambient PM samples that are well characterized by another method.[31]

The objectives of this paper are to describe a method developed to prepare sulfur reference materials that are optimized for calibrating the XRF used for analysis of IMPROVE PM samples, to show that the reference material sulfur mass is accurate and has acceptable uncertainty in the measurement range, and to show that the reference materials are appropriate for use in the calibration of XRF systems. We make sulfur reference materials by adding ammonium sulfate or potassium sulfate particles onto the same PTFE membrane filters used in the network and mimic the deposit pattern by using the field sampling instrument to collect the particles. Many elements are measured in IMPROVE PM samples; however, for this work, we selected sulfur because of its importance in the atmosphere.[7,13] The reference materials are made in a mass range representative of field samples and also at higher masses to evaluate instrument performance. Our preparation method is developed to ensure that pure, anhydrous, and stoichiometric deposits are made onto the filter substrates and to prevent loss or gain of mass by handling. A thorough analysis is performed to evaluate the accuracy and uncertainty in the reference material masses. The uncertainty of the calibration constant derived from a linear regression using the reference materials is evaluated after the linear range of the sulfur measurement is assessed. The XRF system responses of the sulfur reference materials are also compared with the responses of commercial sulfur standards.

Figure 1. Photograph of an ambient fine particulate matter sample collected on a 25-mm polytetrafluoroethylene membrane filter (stretched across a polyolefin ring) in the IMPROVE network. This sample has the typical sample geometry (area, edges, and pixilated pattern) found in deposited particulate matter on filters used for X-ray fluorescence analysis. A support screen located downstream of the filter in the sample holder produces the pixilated pattern on the filter.

In PM sample analysis that aids in federal law making as performed by a large and long-term network such as IMPROVE, it is advisable to establish and demonstrate traceability for prepared reference materials. Traceability can be accomplished by first incorporating good laboratory habits into all steps of the reference material preparation method and the measurement procedure, e.g. purity of reagents, cleanliness of equipment, evaluation of contamination or measurement process flaws, appropriate statistical/mathematical techniques, and calibration of equipment used as discussed by the International Organization for Standardization (ISO, Geneva, Switzerland) in ISO Guide 35.[32] Secondly, traceability is achieved by showing that the deposit masses of the prepared reference materials achieved from the calibration of the balance are accurate and, thirdly, by characterizing the uncertainty in the measured mass as it could be affected by other processes besides the balance characteristics.[32] This paper provides transparency into the calibration of XRF instruments used to analyze IMPROVE samples and documents the traceability of the new standards used in the sulfur calibration.

Materials and methods

Preparation of reference materials

Figure 2 is a diagram of the system used to prepare the sulfur reference materials. Sulfur-containing particles are generated from solutions of ammonium sulfate (99.999% purity) or potassium sulfate (99.95% purity) (Sigma-Aldrich, St. Louis, MO, USA) and pure water (submicron-filtered high-performance liquid chromatography grade, Thermo Fisher Scientific Inc., Waltham, MA, USA) by a TSI 3076 constant-output atomizer (TSI Incorporated, Shoreview, MN, USA). The wet particles flow through a diffusion dryer to remove water. The particles are mixed with additional particle-free dry air (0.45 l/s) in a 500-l rectangular chamber made of Plexiglas (Acrylic) to provide additional drying and sufficient volume for the IMPROVE sampler that operates at 0.38 l/s (22.80 liter per minute). A TSI filtered air supply (model 3074B) provides the dry and particle-free compressed air for the atomizer (2.40×10^5 Pa) and the chamber. The particles are collected on filters using an IMPROVE sampler with a Gast ROC-R vacuum pump (Gast, Benton Harbor, MI, USA). The IMPROVE PM$_{2.5}$ (PM with an aerodynamic diameter below 2.5 μm) sampler uses a cyclone that

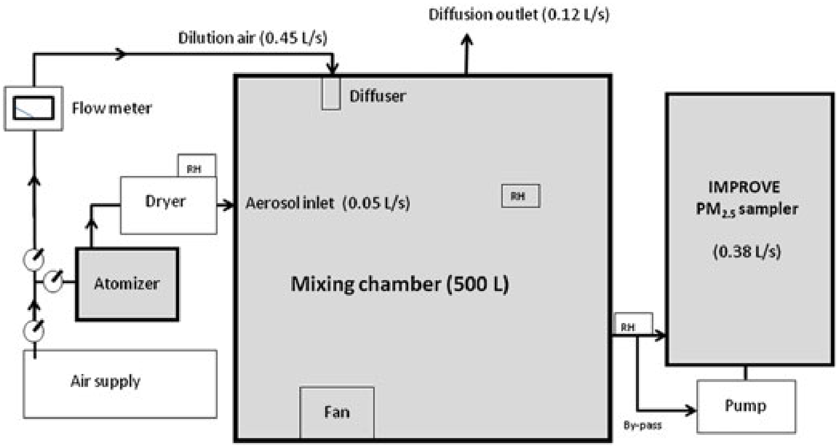

Figure 2. Schematic of the particle generation, mixing, and sampling system used to make sulfur reference materials. Ammonium sulfate or potassium sulfate solutions are atomized, and the resulting particles are dried and mixed with particle-free, dry air in a 500-l mixing chamber. The suspended particles are drawn through an IMPROVE particulate matter ($PM_{2.5}$) sampler and collected on 25-mm polytetrafluoroethylene membrane filters. Relative humidity is measured in three locations to ensure that particles are anhydrous.

provides a 50% particle size cut at an aerodynamic diameter of 2.5 μm when sampling at its nominal flow rate.[2] The deposit mass of each reference material is a function of solution concentration and sampling time.

Particles flow into the mixing chamber from the left side panel, the make-up air enters through the top panel through a diffuser, and the sampler in-take is placed on the right panel (Fig. 2). The chamber is always over-pressurized, and excess air diffuses out through an orifice at the top. A fan positioned on the bottom facing up toward the make-up air inlet ensures a clockwise circular flow with turbulence, which is observed during tests with illuminated white Powder Puffer silica particles (Regin, Oxford, CT, USA). IMPROVE filter cassettes that have a metal support screen as described in the Introduction section are used for filter collection. The sampler inlet diameter used in the IMPROVE sampler is maintained in the laboratory setup to preserve the airflow pattern within the sampler. Thus, the deposit pattern of ambient particles onto PTFE membrane filters is maintained when preparing reference materials (Fig. 1). A by-pass line is employed to ensure constant outflow, and thus, steady-state conditions in the system when the sampling manifold is not operated during initial system equilibration and during filter change. After an initial ramp-up time, the particle concentration remains constant in the chamber that allows the mass of reference material to be predicted on the basis of a simple system calibration between sampling time and filter mass for each specific solution concentration.

Relative humidity (RH) and temperature are measured at the outlet of the particle diffusion dryer, inside the mixing chamber, and directly upstream of the IMPROVE sampler. During reference material production, the diffusion dryer RH is always below 30% and the mixing-chamber RH is always below 20% to ensure that the particles are dried to well below the efflorescence RH, the point where a solid phase is reached from a liquid or hydrated phase, which has been observed to be between 30% and 40% for ammonium sulfate.[33]

Rigorous laboratory procedures are practiced to minimize contamination of the reference materials, including using high-purity compounds and water, drying particles to below their efflorescence RH, disassembling and cleaning the chamber with water and ethanol prior to using a different solution strength or compound, handling filters with clean tweezers, and using particle-free dry air in the atomizer and chamber.

Reference materials are made by collecting the suspended particles on PTFE membrane filters (Teflo, 25 mm, 3.0-μm pore size, Pall Life Sciences, Ann Arbor, MI, USA), which are the same type used in the IMPROVE network for mass and elemental monitoring. Ammonium sulfate solutions of several strengths, 0.0002 mol/l (2.6×10^{-5} kg/l), 0.0189 mol/l (0.0025 kg/l), and 0.0616 mol/l (0.0081 kg/l), and one potassium sulfate solution of 0.0189 mol/l (0.0033 kg/l) with sampling times from 30 s to 30 min are used to produce masses per filter of 0.5- to 143-μg sulfur in potassium sulfate reference materials and 0.7- to 800-μg sulfur in ammonium sulfate reference materials.

To evaluate potential contamination of the reference materials, two types of blanks are generated in the study, namely laboratory blanks and chamber blanks. Chamber blanks are samples that are collected by using only pure water in the atomizer (no solute) and running the chamber and sampler in the same manner as for reference materials. A new set of chamber blanks are collected after the system has been cleaned, just prior to collecting another group of filters with a different solution concentration or compound. The volume of air sampled on each chamber blank filter is equivalent to one and two volumes of the mixing chamber or 25 and 50 min of sampling. Chamber blanks indicate if there is contamination from the water, air, and chamber or filter handling. Laboratory blanks are filters that are not installed into the sampler but are treated in the same manner as the prepared reference materials in all other respects. Laboratory blanks show the variability in response of the XRF system to clean PTFE membrane filters.

Additional reference materials are made from a solution of several inorganic and organic solutes. The aqueous solution is made by mixing salts of the following compounds; ammonium sulfate, potassium sulfate, potassium chloride, potassium hydrogen phthalate, calcium sulfate dehydrate, and sodium chloride in pure water so that the concentration of each compound is 0.002 mol/l. These multicomponent reference materials served as a model for typical reference material deposits being made in our laboratory and are used in our tests of reference material stability and for estimating mass uncertainty. The total masses of the mixture deposits are 29, 95, 99, and 429 μg to roughly span the mass range in prepared ammonium sulfate reference materials.

Mass determination of reference materials

Gravimetric analysis is used to determine the mass of S on each reference material.[32] Gravimetric analysis is also used to determine if there is particle mass on the blanks. A Cahn C-31 Microbalance (Cahn Instruments, Ventron Corp. Cerritos, CA, USA), sensitive to ±1 μg, is used to measure the mass of the PTFE membrane filter prior to adding particles (pre-weight) and after adding particles (post-weight) to obtain the particle deposit mass by difference. Polonium strip ionization units are used to reduce the electrostatic effects prior to and during weighing. The balance is housed in an air-conditioned filter handling room where the set temperature and humidity in the room is 22 ± 3 °C and 35 ± 5%, respectively. Calibration of the balance is achieved with a 200.000-mg Mettler-Toledo calibration weight (Mettler-Toledo, LLC, Columbus, OH, USA). The accuracy of the 200.000-mg weight is certified with a tolerance of 0.44% at the 95th percentile confidence level, and the certification is traceable to NIST standards (traceability number MT5061). PTFE membrane filters normally weigh between 40 and 50 mg. Element masses (all masses are given in microgram) are stoichiometrically derived from the total mass of the compound on the filter. For example, the mass of sulfur in an ammonium sulfate reference material is the total mass of the deposit multiplied by the atomic weight of sulfur (32.07) and divided by the molecular weight of ammonium sulfate (132.14). The uncertainty of the weighed mass deposit on the prepared reference materials is addressed in the Results section.

Ion chromatography analysis

The concentrations of ions from IC analysis of each ammonium and potassium sulfate reference material are used to confirm the mole ratios of ions and the gravimetric determination of sulfur. The IC analysis is the last step in the filter analyses, as the filters are destroyed during the extraction procedure. An ion chromatograph (Dionex Model DX-600 or ICS-2000, Thermo Fisher Scientific Inc., Waltham, MA, USA) at the Environmental Chemistry Department, Research Triangle Institute, Research Triangle Park, North Carolina, is used to obtain the mass of negative and positive ions Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, and K^+. Each filter is placed in a polypropylene tube with 15-ml deionized water after being wetted with 25-μl of nanopure ethanol. Extraction tubes are sonicated for 60 min before being refrigerated overnight prior to analysis. For some of the reference materials, dilutions are made from the extracts to match the calibration range of the instrument. The minimum detection limits (MDLs) for the ions measured from PTFE membrane filter deposits listed earlier are 0.03, 0.02, 0.06, 0.06, 0.04, and 0.02 μg, respectively. The uncertainty is composed of a concentration-proportional part (typically 5%) accounting for calibration and measurement errors and a constant part (typically MDL/3) accounting for noise.

Fourier transform-infrared spectroscopy

Transmission Fourier transform-infrared spectroscopy (FT-IR) is used to evaluate the prepared reference materials for particle-bound water and organic-compound contamination, that if present, would add unwanted mass. Each filter is inserted into a constructed sample purge chamber in a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a mercury cadmium telluride/A (narrow band) detector. The Thermo Scientific OMNIC software is operated to obtain spectra, and the Thermo Scientific TQ Analyst software is used to process spectra. The instrument and sample chamber are purged with H_2O and CO_2 free air provided by a PureGas (Broomfield, CO, USA) purge gas generator. The sample compartment is purged for 2 min prior to collecting an FT-IR scan. Background and sample spectra between 4000 and 600 cm^{-1} are obtained from the average of 32 scans and with a spectral resolution of 4 cm^{-1}.

X-ray fluorescence measurements

The XRF measurements are made by one of the energy-dispersive systems housed at Crocker Nuclear Laboratory at the University of California Davis. This system is used for analysis of Na through Fe in $PM_{2.5}$ deposits on PTFE membrane filters collected in the IMPROVE network. The XRF system directly excites PM samples using an X-ray tube with a Cu anode (CA8-L, General Electric, Piscataway, NJ, USA) operated at a 10-mA current and at 20-kV voltage. The incident angle of the X-ray beam to the sample is 35° from normal, and the detection angle is 55° from normal. The diameter of the X-ray beam is on the order of 1 cm. Filter samples are loaded into plastic 35-mm slide mounts and inserted into a sample chamber operated under vacuum (<46.7 Pa) where they remain stationary during analysis. The exposure is fixed at 1000 s for IMPROVE field samples (and prepared S reference materials), and dead time imposed by the detector circuitry is recorded for each filter. The live times over which fluorescence is counted are generally above 90%. A liquid nitrogen-cooled Si(Li) detector (Canberra, Meriden, CT, USA) with a nominal energy resolution of 165 eV at the K_β line of Mn is used to detect characteristic X-rays. A MicroVAX system (Digital Equipment Corporation, 1960s to 1990s) operates the data acquisition program and data processing program RACE developed in-house.[34]

For most of the data analysis in this work, except in evaluating contamination, we use the raw instrument response, not the calibrated mass for S. Instrument response is reported as counts, which are the counts per bin (bin size is 17 eV) corrected for detector dead times in the 1000-s analysis time and normalized to the 10-mA anode current used for IMPROVE samples. For the most heavy ammonium and potassium sulfate reference materials, the detector live times are as low as 652 and 532 s, respectively. The semi-empirical matrix corrections normally applied to IMPROVE network sample data from PM samples are omitted. This matrix correction is not appropriate for pure samples such as ammonium sulfate or potassium sulfate, and in this work, one of the goals is to evaluate the linearity of the S signal in XRF system.

To provide quantification of elements in an ambient IMPROVE PM sample (and prepared S reference materials), a set of standards containing one Micromatter Mylar standard per element are used for XRF calibration. The Mylar standards, which contain one or two elements each, have larger masses of elements than most IMPROVE samples and are analyzed for 300 s with a lower current (2.6 mA) than ambient samples (or prepared S reference materials) to maintain counting live times above the 90% level typical of samples. MDLs for elements measured by XRF analysis are evaluated in Hyslop and White.[35] Uncertainties for IMPROVE element data are reviewed in Hyslop and White[36] and include errors associated with X-ray counting statistics, calibration of XRF instruments, collected air volumes, and sampling. In this work, only the analytical uncertainty based on counting statistics is applicable and varies by element and mass. For sulfur mass determined by XRF, the analytical uncertainty is in the order of 1% at the 50th percentile network-wide recorded mass of sulfur.

To compare commercial standards responses to prepared reference materials responses, ten sulfur standards (Micromatter) with certified masses near 13 μg/cm^2 S are analyzed simultaneously with the reference materials. These standards were purchased in 2006 and 2007 and are stored in ambient conditions in the laboratory. Analysis of the commercial standards is carried out with system settings equivalent to the method used for Micromatter standards described earlier, and the instrument response is reported as counts, which are the counts per bin (bin size is 17 eV) corrected for detector dead times in the 300-s analysis time and normalized to the 2.6-mA anode current used for standards.

Results

Preparation and evaluation of sulfur reference materials

Figure 3 shows the sulfur masses of the 80 sulfur reference materials produced for this work. A total of 32 ammonium sulfate reference materials were produced with sulfur masses ranging from 0.7- to 75-μg sulfur, which encompasses the mass range observed in the IMPROVE network (2009 data). Nine potassium sulfate reference materials were produced with sulfur masses ranging from 4- to 75-μg S, also in the IMPROVE range. An additional 32 ammonium sulfate and seven potassium sulfate reference materials were produced with masses above the IMPROVE range (75- to 800-μg S). These reference materials were accompanied by 20 chamber blanks and 16 laboratory blanks.

To accurately determine sulfur mass on prepared reference materials, the mass of the material on the PTFE membrane filter must be accurately determined, there must be no water or other contamination in the deposited material or on the filter, and the relative amount of sulfur (stoichiometry) of the deposited particles must be known. In addition, for repeated use of the reference materials, the sulfur mass must be stable over time. Each of the known potential sources of error in the mass measurement of sulfur is evaluated to assess the accuracy, stability, and uncertainty of the deposit masses.

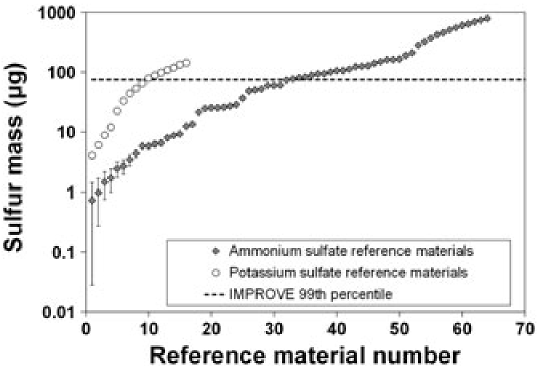

Figure 3. Sulfur mass of the 64 ammonium sulfate and 16 potassium sulfate reference materials. The mass uncertainty (0.7 and 0.5 μg, respectively) is given as vertical error bars. The IMPROVE measurement range for sulfur is shown by the horizontal dashed line as the 99th percentile value.

Purity and dryness of reference materials

To evaluate the potential for contamination due to the aerosol generation and collection system and filter handling practices, the chamber (samples collected in the same manner as the reference materials except that the atomizer contained only water, no ammonium or potassium sulfate) and laboratory blanks (no sample collected) were compared. Gravimetric analysis of the laboratory and chamber blanks showed no particulate mass on the filters within mass measurement uncertainty as discussed in the following sections. Figure 4 shows the average mass and standard deviation for species detected by IC (Cl^-, SO_4^{2-}, NH_4^+, and K^+) and by XRF (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, and Fe) for the 20 chamber blanks compared with the 16 laboratory blanks. First, the plot shows that blank levels for all species are very low (<0.3 μg). A statistical analysis [analysis of variance with a Dunnett's two-way pairwise test by SYSTAT 13.0 (Systat Software, Inc. Chicago, IL, USA)] of the variance for the two types of blanks showed that they are equivalent at the 95% confidence levels for all species. The reported masses for both laboratory and chamber blanks are likely due to the filter composition or incomplete background correction in the XRF measurement. Thus, species determined by IC and XRF in chamber blanks are equivalent to laboratory blanks and showed that elemental contamination is not produced in the generation and sampling system or during filter handling.

To determine if any contamination is present in the reference materials, all species measured by XRF and IC, except for S, K, NH_4^+, and SO_4^{2-}, where applicable, are compared with laboratory blank levels by an analysis of variance and Dunnett's test. The statistical analysis showed that for the majority of elements and ions detected by IC and XRF in the prepared reference materials, their masses are equivalent to laboratory blanks. In a few cases, a statistical difference is observed, but in each case, these differences are due to recognized systematic biases or interferences in XRF and IC instrument responses. For example, the spectral deconvolution program used to analyze IMPROVE samples interprets the potassium K_β peak present in potassium sulfate reference material spectra as calcium. This reported

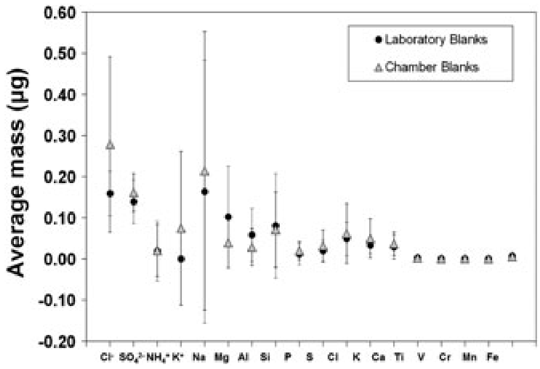

Figure 4. Average masses and standard deviations for all species that are measured by ion chromatography (Cl^-, SO_4^{2-}, NH_4^+, and K^+) and X-ray fluorescence (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, and Fe) in laboratory and chamber blanks. Chamber blanks are made in the system (Fig. 2) by atomizing pure water, and laboratory blanks are analyzed directly after removal from filter box. Concentration levels in both types of blanks are very low (uncertainty for the deposit mass by gravimetric analysis is ±2.8 μg), and the mass on chamber blanks is equivalent to laboratory blanks, indicating that the filters are not contaminated when subjected to the process used to produce reference materials.

calcium is thus not a contaminant but occurs because the calibration table only recognizes Ca and not potassium K_β, because their peak energies are indistinguishable in our peak processing software. Normally this does not affect the Ca measurement because K mass is very low in PM samples collected in the network. Overall, the results from this analysis show that there is no contamination of inorganic ions or elements on prepared sulfur reference materials.

All blanks, ammonium sulfate, and potassium sulfate reference materials are analyzed by FT-IR to determine if there is water or organic compound contamination. The spectra from the blank filters only have peaks attributable to the PTFE membrane, and the reference materials spectra only have peaks attributable to the PTFE membrane filter, the S–O bond in sulfate, and the N–H bond in ammonium. No peaks indicative of water or organic materials are observed.[37] This analysis indicates that reference materials are anhydrous and that there is no measurable organic material contamination.

Figure 5 shows the calculated mole ratio for ammonium sulfate and potassium sulfate reference materials from IC analysis, which for both compounds is 2. The IC analysis for the ammonium sulfate reference materials reported on in this paper gave erroneous ammonium values due to an instrument and calibration problem specific to the analysis of this ion. Thus, the data shown in Fig. 5 is from an additional set of 20 ammonium sulfate reference materials that were prepared and analyzed by IC after the IC method was corrected. The measurement uncertainties calculated for the mole ratios (shown as vertical error bars in Fig. 5) are in the order of 5% for ammonium sulfate filters and 7% for potassium sulfate filters. For all except the lowest mass ammonium sulfate filter and one additional ammonium sulfate filter, the mole ratios are well within the measurement error of the theoretical value of 2. The standard deviations of the percent difference in cation to sulfate molar ratios compared with theory are ±4% for the ammonium sulfate filters and ±1% for the potassium sulfate reference materials. Thus, the observed mole ratios for both compounds indicate that stoichiometry is preserved in the filter deposit.

The final analysis performed to assess the sulfur measurement by gravimetric analysis is to compare the mass of sulfur from the sulfate ion determined by IC to the sulfur mass determined from gravimetric analysis of the total deposit mass. This comparison is an independent validation of our method for making pure, anhydrous, and stoichiometric reference materials and using gravimetric analysis to determine sulfur mass. Figure 6 shows the linear regressions of sulfur measured by IC compared with gravimetric mass. The agreement between gravimetric analysis and IC is within 1.5% for ammonium sulfate reference materials. Potassium sulfate reference materials show a similarly good agreement (within 2.8%) with IC. Thus, IC data show that mole ratios are preserved in the particle deposits prepared on PTFE membrane filters, and the agreement between IC and gravimetric mass for sulfur validates our method.

Stability of reference material mass

To evaluate the stability of the reference materials, the filters were stored in Petri dishes sealed in a plastic bag in our weighing room and were handled about twice a week by several different technical staff from January through October of 2010. The standard deviations of hundreds of measurements of the multicomponent reference materials (filter and deposit) are nearly the same for all four masses, ±2.0, ±2.0, ±1.8. and ±2.0 µg, and there is no trend to indicate the loss or gain of mass on the filters during the ten months of these experiments. We used model reference materials to avoid excessive handling of the sulfur reference materials and to be able to test the stability of a broader type of deposit than just sulfur compounds. The room temperature was on average 21 ± 0 8 °C, and RH ranged from 27–48%. These results show that the multicomponent reference materials are stable and that no handling or environmental factors affect their mass, and we can conclude that effects of physical and environmental factors do not compromise the deposited particles and thus the mass over time.

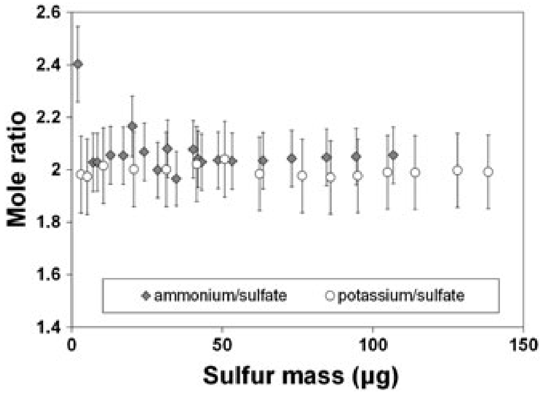

Figure 5. Potassium ion-to-sulfate (K^+/SO_4^{2-}) and ammonium-to-sulfate (NH_4^+/SO_4^{2-}) mole ratios calculated from ion chromatography data as a function of sulfur mass (calculated from SO_4^{2-} mass) for 36 reference materials. Data are shown with error bars, which are calculated from the measurement uncertainties for the two ions. The K^+/SO_4^{2-} mole ratios are from the potassium sulfate reference materials presented in this manuscript. The NH_4^+/SO_4^{2-} mole ratios are from an additional set of ammonium sulfate filters made with the same method. All mole ratios except for in two ammonium sulfate filters indicate that stoichiometry is preserved on the filter deposit.

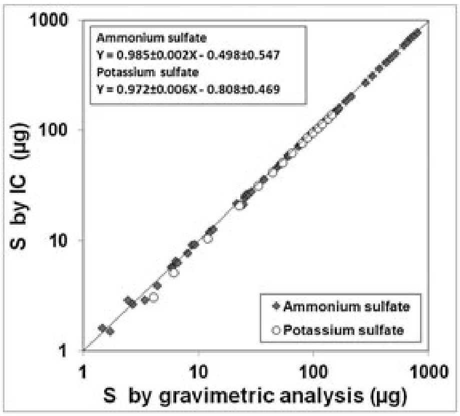

Figure 6. Sulfur mass measurements from ion chromatography (IC) compared with gravimetric mass for ammonium and potassium sulfate reference materials. The linear regressions (with 95% confidence levels for the slope and intercept) for each reference material set are Y = 0.985±0.002X − 0.141±0.155 and Y = 0.972±0.006X − 0.229±0.133, respectively, and show the good agreement between IC and gravimetric sulfur mass. This plot provides additional evidence that stoichiometry is intact on reference materials and that sulfur calculated from weighed total deposit mass is accurate.

Uncertainty of reference material mass

Results from the gravimetric analysis of the multicomponent reference materials are used to calculate the uncertainty of the sulfur mass in sulfur-containing reference materials. As discussed in the previous section, the average standard deviation of repeated weighings of all four model reference materials covering a wide range of deposit masses on PTFE filters is ± 2 µg. Because there is no multiplicative uncertainty or bias observed in the deposits, this standard deviation of gravimetric measurements is the measured balance uncertainty in weighing filters (±2 µg). The uncertainty in the deposit mass only of each reference material is the propagated uncertainty from weighing the filter before and after deposition and is equal to √8 µg or approximately 2.8 µg, using the balance uncertainty for both gravimetric measurements. The relative uncertainty of the mass measurement, given that the absolute uncertainty in the deposit mass is ±2.8 µg, is $y(\%) = (2.8x^{-1})*100\%$.

The relative uncertainty of the sulfur mass on the reference materials is a function of the relative amount of sulfur on the filter and is thus different for ammonium sulfate and potassium sulfate reference materials for the same sulfur mass. Table 1 shows the uncertainty in the sulfur mass for reference materials at various percentiles of the 2009 IMPROVE network sulfur masses. Overall, the uncertainty in the sulfur mass of all reference materials is low except for filters with sulfur mass deposits of only a few micrograms of sulfur. In the IMPROVE 50th to 99th percentile measurement range for sulfur (15- to 75-µg S), the uncertainty of the sulfur mass in ammonium sulfate reference materials is less than 5%.

Table 1. Uncertainty in the sulfur mass for reference materials at various percentiles of the 2009 IMPROVE sulfur mass range

IMPROVE network distribution (%)	IMPROVE sulfur mass 2009 (µg)	Sulfur uncertainty based on RM type	
		Ammonium sulfate (%)	Potassium sulfate (%)
1	0.7	94	71
5	1.8	39	29
25	5.3	13	10
50	9.6	7	6
75	18.7	4	3
95	44.2	2	1
99	74.5	1	1

IMPROVE, Interagency Monitoring of Protected Visual Environments; RM, reference material.

Using sulfur reference materials in X-ray fluorescence calibration

Linearity of the X-ray fluorescence measurement of sulfur in reference materials

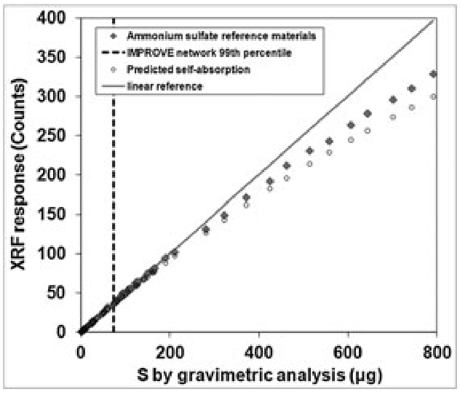

Figure 7. The X-ray fluorescence instrument response in counts for sulfur as a function of sulfur mass in microgram covering the whole mass range (0.7- to 800-µg sulfur) of prepared ammonium sulfate reference materials. Counts are corrected for detector dead time and normalized to the anode current. The XRF system behaves linearly in the IMPROVE measurement range (shown by the vertical dashed line) for ammonium sulfate reference materials. The nonlinearity for masses larger than the IMPROVE network range of sulfur is explained by model predictions of self-absorption of sulfur through the ammonium sulfate matrix (shown in the figure as 'predicted self-absorption').

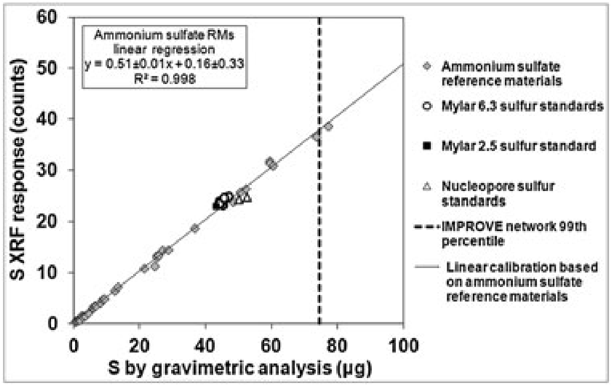

Figure 8. A sulfur calibration based on the ammonium sulfate reference materials (RMs) in the IMPROVE sulfur measurement range. Instrument response is given in counts that are corrected for detector dead times and XRF anode current used. The calibration line (Y = 0.51±0.01X + 0.16±0.33) with uncertainties that are equal to three times the standard deviation shows that low uncertainty in the slope is obtained (±2% at the 99% confidence level). The instrument responses of commercial Mylar (2.5 and 6.3 µm) and nucleopore sulfur (CuS_x) standards are shown. The mass of commercial standards is calculated using the reported areal density (µg/cm^2) and the collection area of an IMPROVE filter (3.53 cm^2). There is reasonable agreement between the commercial standard responses and the calibration based on prepared RMs.

The XRF system response in counts as a function of sulfur mass on ammonium sulfate reference materials is shown for all prepared reference materials (Fig. 7) and for those reference materials intended for sulfur calibration (Fig. 8), which is equivalent to the observed sulfur range in the IMPROVE network. The XRF system responds linearly in this region, namely from 0.7- to 77-µg sulfur, which encompasses the IMPROVE network 1st through 99th percentile measured sulfur (0.7- to 75-µg S) in 2009. Potassium sulfate reference materials (not shown) show the same response and trends as ammonium sulfate reference materials, confirming that for these reference materials, the response of sulfur is independent of the compound in the deposit.

The sulfur reference materials with masses up to one order of magnitude larger than the 99th percentile IMPROVE value are made to test the linearity of the XRF system at high masses. Figure 7 shows that nonlinearity occurs in the instrument response at high sulfur masses (above 200-µg S). At the largest S mass (800 µg), the error in the raw sulfur response compared with a linear response is 24%. The departure from the linear of the sulfur response curve is modeled by calculating the attenuation of the incident Cu X-rays and the fluorescing S X-rays through the deposit from the known properties of ammonium sulfate[38] (data are obtained from the website www.nist.gov/pml/data/xraycoef/index.cfm/). The counts resulting from the attenuated S X-rays (predicted self-absorption in Fig. 7) as a function of mass are calculated by applying the percent S attenuation to the estimated counts based on the linear region of lower S masses. The agreement between observed and calculated attenuation shows that self-absorption is the main cause of the nonlinear response.

An X-ray fluorescence calibration using reference materials

Thirty three ammonium sulfate reference materials covering the IMPROVE range are used to calculate a multipoint linear calibration for sulfur. Figure 8 shows the linear regression between the XRF instrument response for sulfur in counts and the sulfur mass (μg) determined by gravimetric analysis. The linear response in the XRF instrument in this range validates the use of a linear regression. The calibration (regression) line with uncertainties equal to three standard deviations or the 99% confidence level is given in the figure. Low uncertainty in the calibration curve slope, namely 2% at the 99% confidence level, is obtained even though the uncertainty in the individual reference materials in most of the mass region of the calibration curve is greater than 2% (Table 1).

In addition to the sulfur calibration based on ammonium sulfate reference materials, Fig. 8 shows the XRF system response of several commercial Mylar (2.5 and 6.3 μm thick) and two nucleopore sulfur (CuS_x) standards. To show the response of the commercial standards in the mass per filter units used for our reference materials, the reported areal densities of the commercial standards are multiplied by the collection area ($3.53\ cm^2$) of an IMPROVE filter. The commercial Mylar standards are within ±6% of the reference material calibration line. One nucleopore sulfur standard is 9% lower. This comparison shows that a calibration using prepared sulfur reference materials will not significantly shift the reported sulfur by XRF analysis calibrated with commercial standards.

In summary, the sulfur reference materials show that the XRF instrument behaves linearly in the measurement range and that the observed nonlinearity in heavier sulfur deposits is due to the self-absorption of S X-rays. Utilizing the reference materials in a calibration, as illustrated in Fig. 8, provides low uncertainty in the sulfur calibration and also indicates that the sulfur response will not be significantly different from calibrations used by IMPROVE in the past.

Conclusion

We have developed a method for producing sulfur reference materials for the calibration of XRF instruments used to analyze atmospheric PM samples collected in the IMPROVE network. The reference materials replicate the matrix and geometry of the PM samples and the substrate supporting the samples because they are created by collecting ammonium sulfate and potassium sulfate particles on PTFE membrane filters in the same manner as ambient samples are collected. The uncertainty in the calibration associated with matrix differences is minimized by mimicking the physical and chemical forms of ambient PM samples. By reproducing the deposit geometry, we also minimize the uncertainty associated with nonuniformities in PM deposits that differ from the uniform and sharp-edged deposits in commercial standards. Furthermore, when a standard has a different deposit area than the sample, which is typically the case for commercial standards, the deposit area of the IMPROVE sample must be known to obtain mass per filter. By using reference materials that replicate the deposit area of the sample in our calibration, we eliminate the uncertainty associated with collection area measurements.

The sulfur masses on reference materials (ranging from 0.5- to 800-μg S) are scrutinized for accuracy, and a thorough analysis is performed to determine uncertainty. All known sources of error are evaluated and found to be small. We show that filter contamination is negligible, that deposits are anhydrous, that compound mole ratios are preserved through the preparation procedure, and that no loss or gain in mass by environmental factors or by filter handling occurs. Because the gravimetric uncertainty is shown to be independent of the mass deposit, the relative uncertainty in the sulfur mass is only a function of the balance uncertainty for the two gravimetric measurements needed to calculate deposited mass (±2.8 μg) and the amount of sulfur in the compound used. For ammonium sulfate reference materials with masses larger than 15-μg S, the relative uncertainty of the sulfur mass is less than 5%. The relative uncertainty in the sulfur mass in all the reference materials is low, except for filters with only a few microgram of sulfur. Based on our method and our analyses we ascertain that the sulfur mass is accurate.

Using the prepared ammonium sulfate reference materials, we calculate a multipoint calibration in the IMPROVE measurement range for sulfur. The XRF system has a linear response, which indicates that a linear calibration is a valid approach. At higher reference material masses (above 200-μg sulfur), nonlinearity is observed and is explained by the self-absorption of sulfur X-rays. We obtain low uncertainty in the simulated multipoint linear calibration, namely 2% at the 99% confidence level. A comparison with commercial standards shows that the calibration with prepared sulfur reference materials will not significantly shift the sulfur measurement compared with historic calibrations.

The sulfur reference materials described here are optimized for the calibration of XRF analyses used for samples collected in the IMPROVE PM monitoring network. The set of prepared reference materials spans the range of sulfur mass encountered in the network samples and provides the basis for a precise multipoint linear regression approach to calibrating an XRF system. Our reference materials bring improved transparency and credibility to our sulfur calibration because they minimize the need to account for differences in geometry, matrix, and substrates between ambient samples and standards. This paper documents the traceability of our reference materials for the IMPROVE program. We are now using the template developed for sulfur to create reference materials for other elements.

Acknowledgements

Research support is given by the National Park Service (Interagency Monitoring of Protected Visual Environments) under contract P11ATW0802 to the University of California at Davis, USA. The authors gratefully acknowledge the support of Crocker Nuclear Laboratory including Brian P. Perley, Charles E. McDade, Brian Devine, Frank Latora, Timothy Essert, Burton Mehciz, and Mei I. Tang. We thank our collaborators Eva D. Hardison and David Hardison at RTI, NC, USA, for the IC analysis.

References

[1] B. Kellog, W. T. Winberry Jr., *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*, Center for Environmental Research Information, US Environmental Protection Agency, Cincinnati, OH, USA, **1999**.
[2] J. L. Hand, *IMPROVE Report V: Spatial and Seasonal Paterns and Temporal Variability of Haze and its constituents in the United States*, Cooperative Institute for Research in the Atmosphere, Colorado State University, Fort Collins, Colorado, USA, **2011**.
[3] Annual Data Summary Report for the Chemical Speciation of PM2.5 Filter Samples Project (Jan 1–Dec 31, 2009, Prepared for the US Environmental Protection Agency), Research Triangle Institute International, Research Triangle Park, North Carolina, USA, **2010**.
[4] F. Laden, L. M. Neas, D. W. Dockery, J. Schwartz, *Environ. Health Perspect.* **2000**, *108*, 941.
[5] S. K. Friedlander, *Environ. Sci. Technol.* **1973**, *7*, 235.
[6] US Environmental Protection Agency, Title 40: Protection of the Environment, Part 50, Appendix Q.
[7] W. C. Malm, B. A. Schichtel, R. B. Ames, K. A. Gebhart, *J. Geophys. Res.* **2002**, *107*, 4627.
[8] W. C. Malm, J. F. Sisler, D. Huffman, R. A. Eldred, T. A. Cahill, *J. Geophys. Res. Atmos.* **1994**, *99*, 1347.
[9] A. R. Stiles, T. G. Dzubay, R. M. Baum, R. L. Walter, R. D. Willis, L. J. Moore, E. L. Garner, J. W. Gramlich, L. A. Machlan, *Twenty-Fourth Annual Conference on Applications of X-Ray Analysis*, University of Denver, Denver, CO, USA, **1975**.
[10] U. Watjen, H. Cave, *Nucl. Instrum. Methods Phys. Res., Sect. B* **1996**, *109*, 395.
[11] S. A. Wise, R. L. Watters, Certificate of Analysis Standard Reference Material 2783, National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA, **2002**.
[12] W. C. Malm, B. A. Schichtel, M. L. Pitchford, L. L. Ashbaugh, R. A. Eldred, *J. Geophys. Res. Atmos.* **2004**, *109*.
[13] W. H. White, L. L. Ashbaugh, N. P. Hyslop, C. E. McDade, *Atmos. Environ.* **2005**, *39*, 6857.
[14] C. E. McDade, A. M. Dillner, H. Indresand, *J. Air Waste Manage. Assoc.* **2009**, *59*, 1045.
[15] R. D. Foster, *X-Ray Spectrom.* **2000**, *29*, 467.
[16] C. Vanhoof, V. Corthouts, N. De Brucker, *Adv. X-Ray Anal.* **2000**, 43.
[17] Z. Spolnik, K. Belikov, K. Van Meel, E. Adriaenssens, F. De Roeck, R. Van Grieken, *Appl. Spectrosc.* **2005**, *59*, 1465.
[18] Ambient air monitoring: analysis of As, Cd, Cr, Cu, Mn, Ni, Pb, Sb, and Zn as particulates on air filters, Panalytical B.V., Almelo, The Netherlands, **2009**.
[19] O. Haupt, C. Schaefer, S. Strauss, W. Dannecker, *Fresenius J. Anal. Chem.* **1996**, *355*, 375.
[20] R. B. Kellogg, N. F. Roache, B. Dellinger, *Anal. Chem.* **1981**, *53*, 546.
[21] C. F. Wang, S. L. Jeng, C. C. Lin, P. C. Chiang, *Anal. Chim. Acta* **1998**, *368*, 11.
[22] R. J. C. Brown, K. E. Jarvis, B. A. Disch, S. L. Goddard, *Int. J. Environ. Anal. Chem.* **2011**, 1.
[23] J. Billiet, R. Dams, *Mikrochim. Acta* **1981**, *2*, 37.
[24] T. G. Dzubay, *J. Trace Microprobe Tech.* **1987–88**, *5*, 327.
[25] M. Iwatsuki, T. Kyotani, S. Koshimizu, *Anal. Sci.* **1997**, *13*, 807.
[26] C. Mans, S. Hanning, C. Simons, A. Wegner, A. Janssen, M. Kreyenschmidt, *Spectrochim. Acta Part B-At. Spectrosc.* **2007**, *62*, 116.
[27] C. Neelmeijer, J. Huller, M. Mader, B. Borchers, R. A. Jarjis, *Nucl. Instrum. Methods Phys. Res., Sect. B* **1998**, *140*, 191.
[28] J. P. Quisefit, P. Dechateaubourg, S. Garivait, E. Steiner, *X-Ray Spectrom.* **1994**, *23*, 59.
[29] W. K. Stankiewicz, Z. A. Mzyk, B. M. Roter, *Mikrochim. Acta* **1996**, *123*, 137.
[30] V. Szilagyi, Z. Hartyani, *Microchem. J.* **2005**, *79*, 37.
[31] S. Yatkin, M. Gerboles, A. Borowiak, *Atmos. Environ.* **2012**, *54*, 568.
[32] ISO Guide 35: Reference materials – general and statistical principles for certification, International Organization for Standardization, Geneva, Switzerland, **2006**.
[33] T. B. Onasch, R. L. Siefert, S. D. Brooks, A. J. Prenni, B. Murray, M. A. Wilson, M. A. Tolbert, *J. Geophys. Res.-Atmos.* **1999**, *104*, 21317.
[34] J. F. Harrison, R. A. Eldred, *Adv. X-ray Anal.* **1974**, *17*.
[35] N. P. Hyslop, W. H. White, *Environ. Sci. Technol.* **2008**, *42*, 5235.
[36] N. P. Hyslop, W. H. White, *Atmos. Environ.* **2008**, *42*, 2691.
[37] B. C. Smith, *Infrared Spectral interpretation: A Systematic Approach*, CRC Press, **1998**.
[38] O. Haupt, B. Klaue, C. Schaefer, W. Dannecker, *X-Ray Spectrom.* **1995**, *24*, 267.