

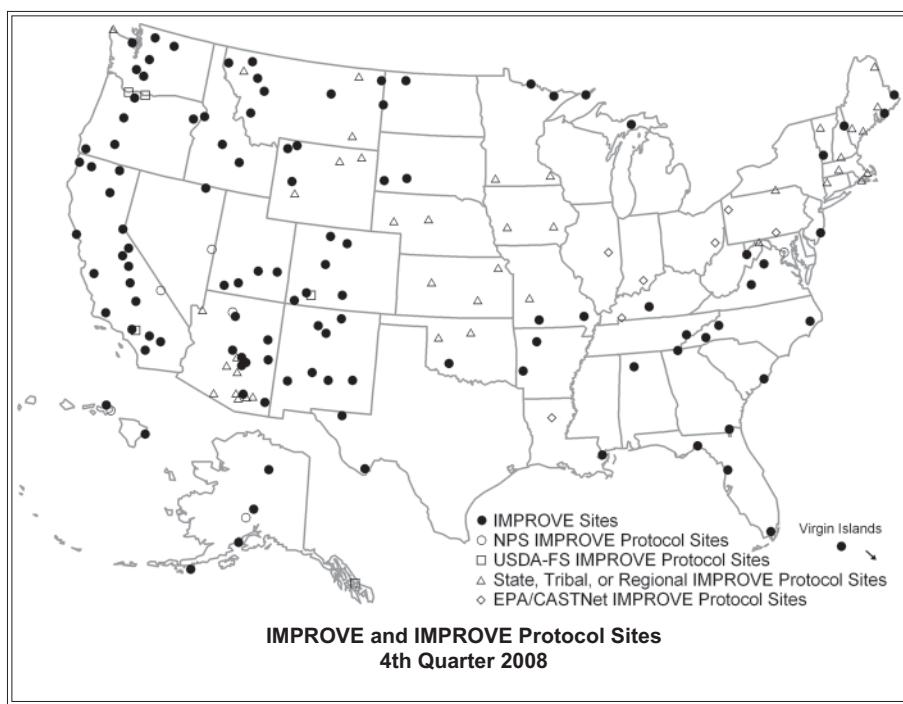
Monitoring update

Network operation status

The IMPROVE (Interagency Monitoring of Protected Visual Environments) Program consists of 110 aerosol visibility monitoring sites selected to provide regionally representative coverage and data for 155 Class I federally protected areas. Additional instrumentation that operates according to IMPROVE protocols in support of the program includes:

- 59 aerosol samplers
- 34 nephelometers
- 4 transmissometers
- 4 digital camera systems
- 58 Webcam systems
- 5 interpretive displays

IMPROVE Program participants are listed on page 8. Federal land management agencies, states, tribes, regional air partnerships, and other agencies operate supporting instrumentation at monitoring sites as presented in the map below. Preliminary data collection statistics for the 4th Quarter 2008 (October, November, and December) are:



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➤ Aerosol (channel A only)	95% collection
➤ Aerosol (all modules)	94% completeness
➤ Optical (nephelometer)	96% collection
➤ Optical (transmissometer)	88% collection
➤ Scene (photographic)	87% collection (does not include Webcams)

A new aerosol monitoring site was established at Gates of the Arctic National Park and Preserve, AK, in October, sponsored by the National Park Service. See page 2 for details.

Data availability status

Data are available on the IMPROVE Web site at <http://vista.cira.colostate.edu/improve/Data/data.htm> and on the VIEWS Web site at <http://vista.cira.colostate.edu/views>. Aerosol data are available through December 2007. Nephelometer and transmissometer data are available through September 2008 and December 2007 respectively.

Photographic slide spectrums are available on the IMPROVE Web site under *Data*. Real-time Webcam displays are available on agency-supported Web sites:

- National Park Service
[http://www.nature.nps.gov/air/
WebCams/index.htm](http://www.nature.nps.gov/air/WebCams/index.htm)
- USDA-Forest Service
<http://www.fsvisimages.com>
- CAMNET (Northeast Camera Network)
<http://www.hazecam.net>
- Midwest Haze Camera Network
<http://www.mwhazecam.net>
- Wyoming Visibility Network
<http://www.wyvisnet.com>
- Phoenix, AZ, Visibility Network
<http://www.phoenixvis.net>

The EPA AIRNow Web site <http://airnow.gov> includes many of these as well as additional visibility-related Webcams. Click on View Other Visibility Webcams.

Monitoring update continued on page 3....

Visibility news

Gates of the Arctic National Park and Preserve joins IMPROVE network

A new IMPROVE Protocol site was established in late October 2008 to represent air quality at Gates of the Arctic National Park in north central Alaska. The site is located at Bettles, Alaska, north of the Arctic Circle. The code designation for this new site is GAAR1, and the first samples were collected on November 4, 2008.



The sampler is housed in a shelter to provide protection from the harsh Alaskan winters. The shelter has two small rooms. One room contains the sampler modules and is kept near ambient temperature to maintain sample integrity. The other room is insulated, houses the controller, and can be heated to provide comfort for the operator. The site is operated by Rachel and Max Hanft, local Bettles residents.

The Gates of the Arctic sampler was installed by Jose Mojica of UC-Davis. The installation at this site presented challenges not encountered during most IMPROVE installations. Temperatures hovered around -17°F on the days of installation, causing the glycerin-filled gauges to freeze and the electrical cables to turn brittle. Jose (who was tempered by Southern California winters) made the most of his situation and kept an optimal core temperature by wearing three days' worth of clothing under his snow gear, and by maintaining two personal heaters directed at him while working indoors. The thick clothing and little nuances, such as having to thaw most of the equipment with a personal hair dryer, made an installation that would normally have taken five hours turn into a two-and-a-half day adventure. Despite the small setbacks, the help provided by Andrea Blakesley of the National Park Service made the installation a success.

For more information contact Chuck McDade at the University of California-Davis. Telephone: 530/752-7119. Fax: 530/752-4107. E-mail: mcdade@crocker.ucdavis.edu.

Correction notice

The 3rd Quarter 2008 issue of this newsletter, delivered in December 2008, displays an error on page 4. All PM levels in the NAAQS table should read $\mu\text{g}/\text{m}^3$. The microgram symbol did not print in the hardcopy version of the newsletter, but appeared as it should in the electronic version. Readers receiving the hardcopy version please note this error. The corrected table appears below.

Table 1. History of the PM National Ambient Air Quality Standard.

Final Rule	Indicator	Ave. Time	Level	Form
1971	TSP - Total Suspended Particles	24-hour	260 $\mu\text{g}/\text{m}^3$ (primary)	Not to be exceeded more than once per year
			150 $\mu\text{g}/\text{m}^3$ (secondary)	
1987	PM ₁₀	24-hour	75 $\mu\text{g}/\text{m}^3$ (primary)	Annual average
			50 $\mu\text{g}/\text{m}^3$	Annual average
1997	PM _{2.5}	24-hour	150 $\mu\text{g}/\text{m}^3$ *	Not to be exceeded more than once per year
			65 $\mu\text{g}/\text{m}^3$	98 th percentile
2006	PM ₁₀	24-hour	15 $\mu\text{g}/\text{m}^3$	Annual arithmetic mean, average over 3 years
			150 $\mu\text{g}/\text{m}^3$	Initially promulgated 99 th percentile form; when 1997 standards were vacated, form of 1987 standards remained in place (not to be exceeded more than once per year on average over a 3-year period)
			50 $\mu\text{g}/\text{m}^3$	Annual arithmetic mean, average over 3 years
2006	PM _{2.5}	24-hour	35 $\mu\text{g}/\text{m}^3$	98 th percentile, average over 3 years
			15 $\mu\text{g}/\text{m}^3$	Annual arithmetic mean, average over 3 years
	PM ₁₀	24-hour	150 $\mu\text{g}/\text{m}^3$	Not to be exceeded more than once per year on average over a 3-year period

* When not specified, primary and secondary standards are identical.

PUBLISHED BY:

Air Resource Specialists, Inc.

1901 Sharp Point Drive,
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Fort Collins, CO 80525

The IMPROVE Newsletter is published four times a year (February, May, August, and November) under National Park Service Contract C2350064025. To submit an article, to receive the IMPROVE Newsletter, or for address corrections, contact:

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IMPROVE Newsletters are also available on the IMPROVE Web site at http://vista.cira.colostate.edu/improve/Publications/news_letters.htm.



Publications and presentations

The following is a sampling of articles and presentations related to IMPROVE monitoring, published in 2008:

Archuleta, C. A., Adlhoc, J., and Copeland, S. A. 2008. IMPROVE data substitution methods for regional haze planning. Presented at the Air & Waste Management Association Visibility Specialty Conference, Moab, UT, April.

Ashbaugh, L.L., and Hyslop, N. P. 2008. New Methods for Quality Control, Data Validation, and Flagging of IMPROVE Data. Presented at the Air & Waste Management Association Visibility Specialty Conference, Moab, UT, April.

Hyslop, N. P., McDade, C.E., and White, W. H. 2008. Uncertainty in the IMPROVE Measurements. Presented at the Air & Waste Management Association Annual Conference, Portland, OR, June.

Hyslop, N. P., and White, W. H. 2008. Interagency Monitoring of Protected Visual Environments (IMPROVE) Detection Limits. Presented at the Air & Waste Management Association Visibility Specialty Conference, Moab, UT, April.

Hyslop, N. P., and White, W. H. 2008. Observed Precision in the IMPROVE Particle Monitoring Network. Presented at the Air & Waste Management Association Visibility Specialty Conference, Moab, UT, April.

McDade, C.E., White, W.H., and Dillner, A. M. 2008. Comparisons of Sulfur and Sulfate Measured in IMPROVE. Presented at the Air & Waste Management Association Visibility Specialty Conference, Moab, UT, April.

White, W. H. 2008. A Cabinet of Curiosities: IMPROVE's On-line Data Advisories. Presented at the Air & Waste Management Association Visibility Specialty Conference, Moab, UT, April.

Hyslop, N.P., and White, W.H. (2008) An evaluation of Interagency Monitoring of Protected Visual Environments (IMPROVE) collocated precision and uncertainty estimates. *Atmospheric Environment*, 42, 2691-2705.

White, W.H. (2008) Chemical markers for sea salt in IMPROVE aerosol data. *Atmospheric Environment*, 42, 261-274.

Visibility news continued on page 6....

Monitoring update *continued from page 1*

Operators of distinction

New York State participates in the IMPROVE Protocol aerosol monitoring network, by operating an urban site in the South Bronx NEY01) and New York's operator, Richardson Colas, services the sampler.

Rich works for the New York State Department of Environmental Conservation (DEC) - Division of Air Resources. He was hired as Lab Equipment Designer in 1998 to help operate, maintain, and provide quality assurance for the state's extensive air monitoring network. He has operated the IMPROVE Protocol site in the South Bronx in New York City since 2005. "Our South Bronx site is one of the most extensive of the 80 ambient air monitoring sites in New York State operated by the DEC," said Rich. "In addition to the particulate monitoring, we also have a full suite of gaseous analyzers at the site to evaluate other EPA criteria air pollutants for state compliance with the National Ambient Air Quality Standards." The station is one of two National Air Toxics Trends sites in New York State, and is used by various state agencies and universities to perform health-related air quality studies.

Rich earned a B.S. degree in Electrical and Computer Engineering from the New York Institute of Technology. Before joining DEC, he had no prior experience in air quality monitoring, but the DEC provided excellent training. His

engineering background also helped him catch on quickly and today he is responsible for instrument operation in numerous air monitoring networks and studies.

When not working, Rich loves to spend time and dine out with his wife, Joan, and one-year-old daughter, Siimone Celeste. One of their favorite foods is Thai. Rich also has a hobby of racing radio-controlled cars, and is involved with local organizations to better himself and others.

Rich is a native New Yorker and loves it. "I have a passion for this state," said Rich, "Helping our state environmentally through my work responsibilities allows me to exercise that passion."



The New York IMPROVE Protocol monitoring site, in South Bronx, is one of several monitoring sites maintained by Rich Colas.

Monitoring update continued on page 7....

Feature article

Aerosol generation system developed as new tool for air quality researchers

(by C. McDade, Hege Indresand, and Ann Dillner, University of California - Davis)

Introduction

IMPROVE scientists at UC-Davis are developing a new aerosol generation system, designed to deposit samples of known composition on filters. These specially prepared samples will provide an independent tool to assess the calibration of the x-ray fluorescence (XRF) laboratory analysis method, and will allow investigation of cross-element interferences in the XRF spectra. The filters made by the aerosol generation system can also give information about detection limits (minimum of the range) and saturation effects (maximum of the range) of the XRF instrument.

This work is being conducted by Dr. Hege Indresand, a postdoctoral scholar at UC-Davis, along with her advisor, Dr. Ann M. Dillner. Crocker Nuclear Laboratory's machine shop has provided the needed custom equipment, manufactured to exact specifications.

Rationale

The need for the aerosol generation system emerged from questions about the calibration of the XRF system. Currently, calibration standards are purchased from a single vendor, and there are no alternative sources to provide an independent assessment. Furthermore, the elemental concentrations on the purchased standards are generally higher than those encountered in the IMPROVE network. XRF calibrations are performed at reduced instrument current to accommodate the high loadings on the standards, and then the actual field samples are analyzed at a higher current. Filter samples at lower concentrations (more representative of IMPROVE field samples) can be prepared using the aerosol generation system, so that XRF calibration checks can be performed under the same conditions as field sample analysis.

The commercially available standards are prepared on Mylar® or Nuclepore® substrates, not on Teflon® as used in routine IMPROVE sampling. Calibration samples prepared on Teflon® filters by the new aerosol generation system will better simulate the conditions of IMPROVE sample collection.

Not only are the samples prepared on Teflon®, they will also exhibit the same deposition patterns as field samples since the aerosol chamber is attached to an actual IMPROVE sampler. Although the initial development work has focused on the preparation of Teflon® filter samples, the aerosol generation system should also be applicable to the preparation of samples on quartz and nylon filters.

The new system will also allow the study of interference in the XRF analysis. Sulfur and silicon, for example, lie close to one another in the XRF spectrum, and large amounts of sulfur relative to silicon can cause interferences to the silicon peak. By varying the relative amounts of compounds in the atomized solution, it will be possible to investigate such interferences under controlled conditions. In addition to preparing laboratory filters with the selected elements, it will also be possible to add controlled amounts of elements to field samples to investigate the effects of higher concentrations and related interferences.

System design

The aerosol generation system, housed at Crocker Nuclear Laboratory at UC-Davis, consists of three major parts: 1) an atomizer to create a fine aerosol from a liquid solution, 2) a mixing chamber to provide a uniform airmass from which to sample, and 3) an IMPROVE sampler module (cyclone, filter assembly, and pump) to allow samples to be collected under the same conditions as IMPROVE filter samples. A diagram of the aerosol generation system is shown in Figure 1 and a photograph is shown in Figure 2.

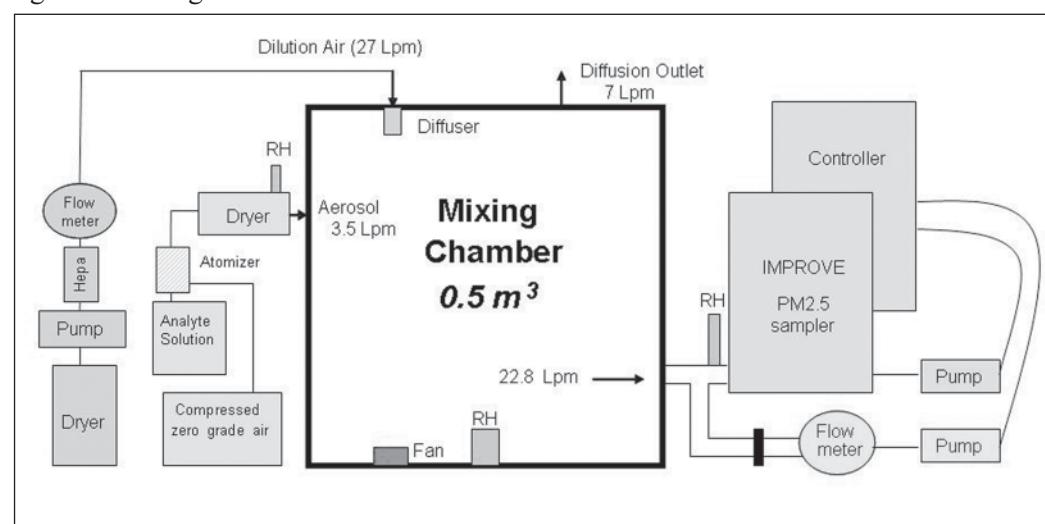


Figure 1. Operational diagram of the aerosol generation system at UC-Davis.

Aerosol deposits are generated from a solution with a constant-output-atomizer using compressed zero-grade air with a flow rate of 3.5 lpm. Aerosols are dried with a diffusion-dryer before entering the 0.5 m³ dilution chamber. Low relative humidity and particle-free dilution air is introduced into the chamber at a flow rate of 27.0 lpm. The aerosol stream and dilution air are well mixed in the chamber before being pulled through an IMPROVE PM_{2.5} sampler operating with a flow rate of 22.8 lpm, which is the typical flow rate for IMPROVE samplers. Relative humidity in the chamber is measured continuously to ensure it remains below 20%. The IMPROVE PM_{2.5} sampler allows four consecutive samples to be collected with sampling times varying between 10 seconds and 24 hours. The amount of the aerosol deposit is a function of solute, solution concentration, and sampling time.

Results

Most of the development work thus far has focused on generating ammonium sulfate. Ammonium sulfate is one of the major components of most ambient aerosols, and it presents only one element (sulfur) that is detectable by XRF, so it is not subject to cross-element spectral interference. More recently, potassium chloride samples have been prepared. Potassium chloride was chosen because it easily aerosolized and both elements are detected well by the UC-Davis XRF system. Solutions were made with 99.999%

pure compounds in HPLC-grade de-ionized water. Solution strengths on the order of 0.0001 to 0.1 M (Molarity) were utilized to generate aerosols. For these concentrations, sampling times were between 30 seconds and 21 minutes. Blank filters were also created using pure HPLC-grade deionized water with sampling times of 25 and 50 minutes.

The mass on each blank and analyte filter was determined by gravimetric mass analysis. The measured mass of ammonium sulfate and potassium chloride was converted to mass of S, K, and Cl assuming that the pure (no water or impurities) compound was collected. After the filters were weighed, they were analyzed by the IMPROVE Cu vacuum XRF system (Cu-XRF). Some of the ammonium sulfate filters have been analyzed by ion chromatography (IC) as a secondary reference for mass. Ultimately, it is hoped that gravimetric mass will provide an accurate value for the mass of material deposited on the filter. IC is a destructive technique (it requires digestion of the filter in solution), so it cannot be performed *a priori* to determine the concentration before XRF analysis. Ongoing testing and development work is focusing on establishing the reliability of gravimetric mass as a quantitative technique for accurately determining the sample mass of the filters produced by the aerosol generating system.

Aerosol generation continued on page 6....

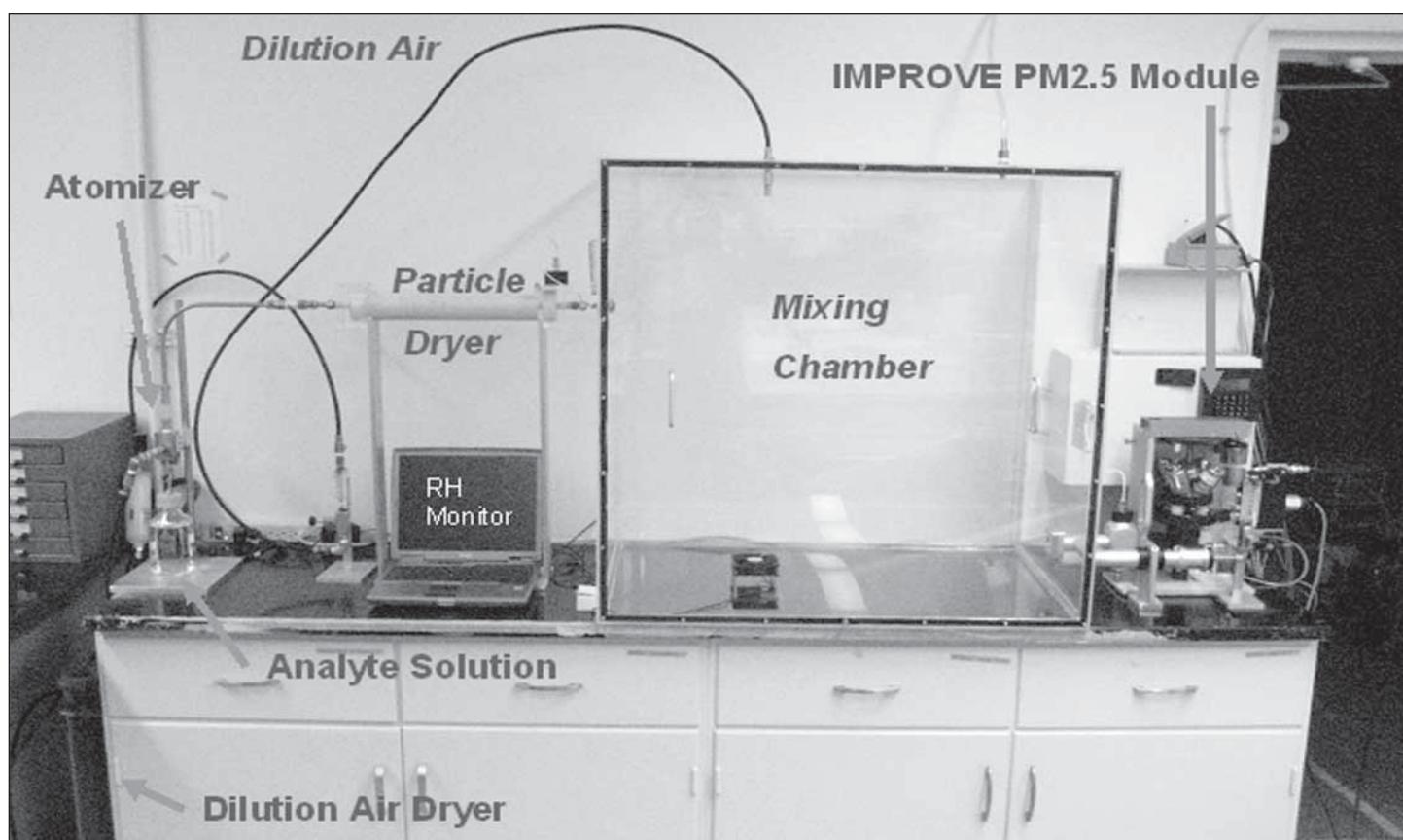


Figure 2. Photograph of the aerosol generation system at UC-Davis.

Aerosol generation continued from page 5....

Figure 3 illustrates preliminary results of some of the first system tests, showing a cross-comparison of sulfur mass per filter determined by IC and by gravimetric mass. It is apparent that the IC and gravimetric mass measurements agree well, suggesting that weighing the deposited mass provides a reliable assessment of its elemental concentration. The filter loadings shown here are typical of those observed in the IMPROVE network. An ambient sulfur concentration of 3 $\mu\text{g m}^{-3}$, for example, equates to about 100 $\mu\text{g}/\text{filter}$.

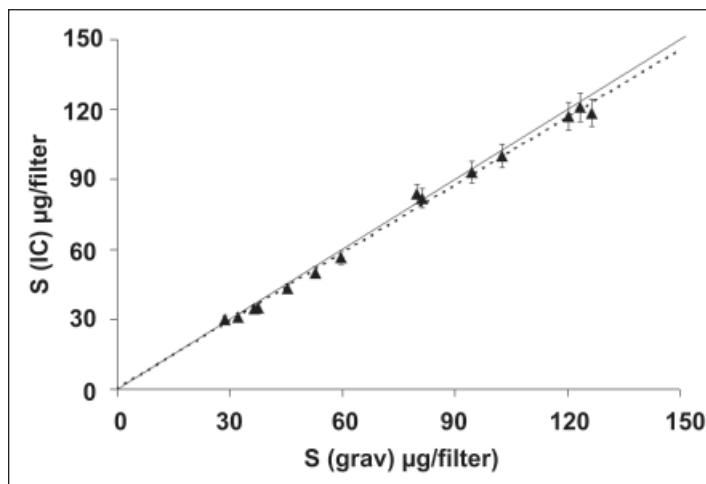


Figure 3. Comparisons of sulfur mass per filter as determined by IC and gravimetric mass analysis on Teflon® filter samples made with pure ammonium sulfate.

To ensure the highest quality data and to make gravimetric measurement of the filters a reliable method for determining the mass of elements of interest, it is important to fully characterize the chamber and filters to ensure that there is no contamination on the filters (no water or other material) and that the compounds in the solution are stoichiometrically transferred to the filter. Filter handling procedures are being carefully developed and tested to ensure that deposit amounts are known with a high degree of precision and accuracy. Humidity control is especially important to ensure that gravimetric determinations accurately reflect elemental concentrations and are not biased by adsorbed water. Relative humidity is measured in real time inside the chamber and is maintained well below the efflorescence point of the analyte during sampling (the point at which the particle is effectively dry).

Additional work to ensure that there is no water on the filters is ongoing. The chamber blanks were analyzed gravimetrically and by Cu-XRF. The average gravimetric mass of twelve blanks was $0 \pm 1 \mu\text{g}$. All filters were within the balance uncertainty of $2 \mu\text{g}$. In addition, no major contaminants were found by Cu-XRF in any of the blanks. Laboratory blanks (not exposed filters) and chamber blanks were equivalent. The molar ratio of potassium and chlorine

on each filter should be equal to one if the analyte is being transferred to the filter completely. From the preliminary Cu-XRF data from KCl samples, the average molar ratio is 1.00 with a standard deviation of 0.02, which indicates that the analytes in the prepared solutions are correctly and successfully transferred to our filters from the system.

Future work

To more fully characterize the aerosol in the chamber, a TSI scanning mobility particle sizer (SMPS) has been used to measure the particle size and concentration in the chamber during filter generation. This additional tool is used to estimate the mass on the filter prior to analysis. Multiple analysis by gravimetric and XRF analyses of single samples produced in the chamber is also being considered to provide bases for better determination of analytical uncertainties.

In the future, broader ranges of concentrations of elements will be deposited onto filters to study detection limits and saturation effects. Other multi-species deposits will be created as well, to help understand and evaluate some possible inter-elemental effects that may be contributing to measurement bias. Development and testing of the aerosol generation system will continue throughout the upcoming year. Filters prepared with this system are expected to provide a valuable independent assessment of the accuracy of the IMPROVE elemental concentration data.

For more information contact Chuck McDade at the University of California-Davis. Telephone: 530/752-7119. Fax: 530/752-4107. E-mail: mcdade@crocker.ucdavis.edu.

Visibility news continued from page 3**Data advisory released****Data losses during episodes of heavy smoke**

- Affects: Module A - Fine mass, elements, f_{abs}
- Period: All

The Teflon® membrane filters used in modules A and D of the IMPROVE sampler can clog and rupture at the high organic carbon (OC) concentrations associated with some regional fire events. Mass, elemental, and light absorption data can thus be under-represented (biased) during episodes of dense smoke. The degree to which bias may affect a particular data analysis can usually be assessed from the ion and carbon data, as the nylon and quartz filters used in modules B and C rarely clog.

A complete discussion of this and all other data advisories can be found on the IMPROVE Web site at http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm.

For more information or to submit an advisory, contact Bret Schichtel at CIRA. Telephone: 970/491-8581. Fax: 970/491-8598. E-mail: schichtel@cira.colostate.edu.

IMPROVE

The IMPROVE Newsletter

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IMPROVE STEERING COMMITTEE

IMPROVE Steering Committee members represent their respective agencies and meet periodically to establish and evaluate program goals and actions. IMPROVE-related questions within agencies should be directed to the agency's Steering Committee representative.

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without upsetting the balance of
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