TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS
Dr. Marc Pitchford / IMPROVE Steering Committee Chair
FROM: Eric Boswell / NAREL
COPY: Dr. Charles McDade / UC-Davis
AUTHOR: Jewell Smiley / NAREL
DATE: August 4, 2007
SUBJECT: UC-Davis Laboratory Audit

Introduction

On May 16-17, 2007, a Technical Systems Audit (TSA) was conducted at the Crocker Nuclear Laboratory (CNL) located on the campus at the University of California in Davis, California (UC-Davis). The TSA was performed as part of the quality assurance oversight provided by the U.S. Environmental Protection Agency (EPA) for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. The Air Quality Group working at the CNL facility has been providing valuable and critical services for the IMPROVE program since the program began in 1987. More information about the program can be found at the IMPROVE web site at the following address. http://vista.cira.colostate.edu/improve

The audit was performed by Steve Taylor, Jewell Smiley, and Marc Pitchford. Steve and Jewell are physical scientists who work at EPA's National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. Marc is a meteorologist with the National Oceanic and Atmospheric Administration (NOAA), senior scientist with the EPA, and he also is the chairman of the IMPROVE steering committee. This TSA was a routine inspection of specific laboratory and support operations performed for the IMPROVE program by the Air Quality Group at UC-Davis. This was the second IMPROVE audit performed on-site at CNL by EPA's audit team. A similar audit was performed in March of 2005.

Summary of Audit Proceedings

A significant amount of planning and communication was necessary before the auditors actually traveled to UC-Davis. The most recent IMPROVE QA documents were reviewed and a preliminary list of questions was submitted to the Air Quality Group on April 26. Response to the advance questions was used to create an agenda for the on-site visit. The advance questions along with responses from UC-Davis are included as Appendix A to this report.

The audit team arrived at CNL before noon on May 16, and was greeted by Dr. Charles (Chuck) McDade. Chuck is the Principal Investigator for IMPROVE activities within the Air Quality Group. Since the audit was not scheduled to begin until 1 P.M., Chuck suggested a quick lunch at a nearby sandwich shop on campus before the audit activities began at CNL.

The first item on the agenda was to meet with some of the CNL staff and discuss the logistics for the audit. The audit team had brought data loggers and a set of filters and metallic weights with them to

capture and record experimental measurements during the audit. After the audit materials were transferred to the appropriate CNL staff, it was time for the audit team to visit specific areas of the laboratory to interview those technical staff who actually perform the analyses and provide other forms of support for the IMPROVE operations. At least one member of the staff was always available to escort and assist the auditors. The following areas were visited and reviewed.

- ✓ Sample Shipping, Receiving, and Handling - Steve Ixquiac and Tamera LaBelle
- ✓ Gravimetric Laboratory - Steve Ixquiac and Tamera LaBelle
- ✓ XRF Laboratory - Brian Perley, Paul Wakabayashi, and Krystyna Trzepla-Nabaglo
- ✓ HIPS and PESA - Brian Perley and Paul Wakabayashi

Besides the areas mentioned above, interviews were also conducted with the following staff.

- ✓ Chuck McDade - IMPROVE Principal Investigator
- ✓ Nicole Hyslop - Quality Assurance/Data Delivery
- ✓ Database Management – Jim Hughes
- ✓ Data Analysis - Warren White
- ✓ Method Testing and Development - Ann Dillner

The Air Quality Group at CNL currently processes about 8000 air filter samples per month which is equivalent to supplying filter packs for 200 field sites that collect Particulate Matter (PM) from the ambient air every third calendar day, and each collection event requires four filters. The group also provides critical initial and ongoing technical support for the field sites. This TSA focused on the laboratory operations listed above.

Sample Shipping, Receiving, and Handling

The laboratory staff, under the direction of Steve Ixquiac, is immediately responsible for shipping clean filters to the field sites and receiving loaded filters back at the lab. A large volume of filters must be mounted into cassettes which are shipped to the field sites for sample collection. Each field site receives a corrugated plastic box with new cartridges every three weeks. The typical field site will collect aerosol PM onto four different filters at each 24-hour sampling event which is scheduled every one-in-three calendar days. For each collection event, the "A" channel collects $PM_{2.5}$ onto a 25-mm Teflon® filter, the "B" channel collects $PM_{2.5}$ onto a 37-mm Nylon® filter, the "C" channel collects $PM_{2.5}$ onto a 25-mm quartz filter, and the "D" channel collects PM_{10} onto a 25-mm Teflon® filter. Some of the field sites will have an extra channel to collect co-located duplicate samples of a prescribed filter medium for precision data. The field operator visits the site every week on Tuesday at which time the operator will retrieve the loaded filter cartridges, install a fresh cartridge into each sampler channel, and also record sampling information onto a log sheet. In addition to the log sheet, specific sampling information is stored automatically by the sampler onto a removable memory stick. About every three weeks, the field operator will ship the exposed filters and the corresponding log sheets and memory stick back to the laboratory. IMPROVE filter samples are routinely shipped by FedEx, UPS, and US mail at ambient temperature.

All of the loaded filters that arrive back at the laboratory must be recovered from the filter holder cassettes and then scheduled for analysis. The process begins by inspecting the log sheets and memory stick information. Inputs are made into the electronic database as necessary. Both of the Teflon® filters from channel "A" and "D" are analyzed locally by the Air Quality Group. The gravimetric mass is always measured first, and followed by other determinations. The Nylon® filters from channel "B" must be shipped to RTI in Research Triangle Park, NC, for the Ion Chromatography analysis [see reference 1]. The quartz filters from channel "C" must be shipped to the Desert Research Institute (DRI) in Reno, NV, for the OC/EC carbon analysis [see reference 2].

It is important to evaluate each new batch of filters before they are used for sample collection, and this is accomplished by analyzing a few filters from each new batch as laboratory blanks. Field blanks are also analyzed periodically to assess the overall background contamination that includes exposure of the filter to routine shipping and handling. Field blanks are scheduled at a frequency of 1-2% for the Teflon® filters and 3-4% for Nylon® and quartz filters. The analytical results for the Nylon® and quartz samples are routinely adjusted for field blank contamination. The analytical results for the Teflon® samples are not adjusted for field blank contamination. A field blank is created by placing a representative clean filter into a cassette that is reserved for blanks, and then placing that cassette into the number three position of the sampling cartridge. The number three position is not used for sample collection, but the filter is constantly exposed to the immediately surrounding air. The filter is exposed to representative shipping and handling inside a zip-lock bag, and the cartridge is actually installed into the sampler so that it resides at the field site for a one-week period. The filter holder cassettes are expensive and are normally reused without cleaning beyond using a brush to remove visible particles and cleaning with alcohol. Each sample cassette is dedicated for use with the same type of filter, and will always be used at the same field site.

A request was made to see results for the last ten field blanks at two different field sites. The request also stipulated that one site should be east and one site should be west of the Mississippi River. Field blank results from the Brigantine, New Jersey (BRIG) and the Badlands, South Dakota (BADL) field sites are summarized in the Table 1.

Table 1. Summary of Field Blank Results from Two Field Sites – BRIG and BADL

Parameter	Concentration (µg/filter)				Number of Values	Sampling Dates		
	Average	Max	Min	Std. Dev.				
PM2.5 Mass	1.45	10	-4	3.47	20	06/09/99	to	07/13/06
Elemental Carbon	0.25	1.20	0.00	0.37	20	10/17/02	to	11/16/06
Organic Carbon	8.28	14.34	2.70	2.55	20	10/17/02	to	11/16/06
Chloride	6.38	35.27	0.19	12.09	20	03/13/03	to	08/24/06
Chloride (before Jan 2004)	29.56	35.27	24.74	5.49	4	03/13/03	to	09/18/03
Chloride (after Jan 2004)	0.58	1.05	0.19	0.27	16	04/15/04	to	08/24/06
Nitrite	0.58	2.05	0.00	0.55	20	03/13/03	to	08/24/06
Nitrate	0.73	1.82	0.00	0.77	20	03/13/03	to	08/24/06
Sulfate	0.68	4.54	0.00	1.14	20	03/13/03	to	08/24/06

The only parameter in Table 1 that changed dramatically over the identified time period was chloride. The chloride results are summarized over more than one time period to show the point of sudden change in concentration. The network changed to a new manufacturer for the Nylon® filters in January of 2004, and the level of chloride contamination has remained dramatically lower from that point forward.

Field blank results for the XRF elements are not presented in Table 1. CNL began publishing a series of quarterly reports in 2005 that contain the most recent QA/QC information for the XRF analysis [see reference 3]. These quarterly reports include a discussion of the analytical precision and bias for the XRF and PESA systems. Assessments are made by examining the results from calibration check samples, field and laboratory blanks, and replicate determinations of the same filter sample. Each report also serves another important purpose which is to document any significant change to the analytical system such as modifying an operational parameter for the instrumentation.

It was stated earlier that filter holder cassettes are expensive and must be reused. It is common practice for the audit team to randomly select a set of filter cassettes and then observe the analyst install clean filters into those cassettes using the standard procedures as closely as possible. After all the test filters have been installed, the analyst immediately retrieves the filters from the cassettes and transfers custody of the filters to the audit team. The audit team places the test filters into a zip-lock plastic bag along with a set of "clean" travel blanks that serve as control filters. All of the filters are hand-carried back to NAREL for analysis to determine any contamination that may be present on the filters. Table 2 shows results from the cassette assembly experiment performed during the audit at CNL.

Table 2. Results from Cassette Assembly & Filter Retrieval Experiment

Filter ID	Filter Description	Parameter	Instrument	Concentration (µg/filter)
T07-12136	Teflon® test filter #1	PM2.5 Mass	Balance	5
T07-12137	Teflon® test filter #2	PM2.5 Mass	Balance	0
T07-12138	Teflon® control filter #1	PM2.5 Mass	Balance	-2
T07-12139	Teflon® control filter #2	PM2.5 Mass	Balance	-1
Q07-12144	Quartz test filter #1	Elemental Carbon	Carbon Anal.	not detected
Q07-12145	Quartz test filter #2	Elemental Carbon	Carbon Anal.	not detected
Q07-12146	Quartz control filter #1	Elemental Carbon	Carbon Anal.	not detected
Q07-12147	Quartz control filter #2	Elemental Carbon	Carbon Anal.	not detected
Q07-12144	Quartz test filter #1	Organic Carbon	Carbon Anal.	1.52
Q07-12145	Quartz test filter #2	Organic Carbon	Carbon Anal.	1.09
Q07-12146	Quartz control filter #1	Organic Carbon	Carbon Anal.	0.85
Q07-12147	Quartz control filter #2	Organic Carbon	Carbon Anal.	0.72
N07-12140	Nylon® test filter #1	Chloride	IC	0.65
N07-12141	Nylon® test filter #2	Chloride	IC	0.61
N07-12142	Nylon® control filter #1	Chloride	IC	0.52
N07-12143	Nylon® control filter #2	Chloride	IC	0.45

Table 2. Results from Cassette Assembly & Filter Retrieval Experiment

Filter ID	Filter Description	Parameter	Instrument	Concentration (µg/filter)
N07-12140	Nylon® test filter #1	Nitrite	IC	0.46*
N07-12141	Nylon® test filter #2	Nitrite	IC	0.55*
N07-12142	Nylon® control filter #1	Nitrite	IC	3.05*
N07-12143	Nylon® control filter #2	Nitrite	IC	1.08*
N07-12140	Nylon® test filter #1	Nitrate	IC	not detected
N07-12141	Nylon® test filter #2	Nitrate	IC	not detected
N07-12142	Nylon® control filter #1	Nitrate	IC	<0.8
N07-12143	Nylon® control filter #2	Nitrate	IC	not detected
N07-12140	Nylon® test filter #1	Sulfate	IC	not detected
N07-12141	Nylon® test filter #2	Sulfate	IC	not detected
N07-12142	Nylon® control filter #1	Sulfate	IC	not detected
N07-12143	Nylon® control filter #2	Sulfate	IC	not detected
N07-12140	Nylon® test filter #1	Ammonium	IC	not detected
N07-12141	Nylon® test filter #2	Ammonium	IC	not detected
N07-12142	Nylon® control filter #1	Ammonium	IC	not detected
N07-12143	Nylon® control filter #2	Ammonium	IC	not detected

**** Nitrite values may be due to laboratory contamination at NAREL.***

It should be stated that all of the Nylon® and quartz filters identified in Table 2 were removed from CNL's stock of ready-to-use filters. All of the Teflon® filters were supplied by NAREL. Except for nitrite, no significant filter contamination is observed in Table 2. Low-level nitrite contamination is frequently observed in blanks that are extracted and analyzed at NAREL.

SOP's were available that describe filter procurement and acceptance testing, filter cassette construction, and sample handling [see reference 4, 5, and 6]. These documents have not been updated since 1997, and some of the information is no longer accurate and needs to be updated.

Gravimetric Laboratory

Steve Ixquiac and his technical staff supervise a small group of student employees that perform the gravimetric mass measurements. The audit team was able to interview Tammy and Steve while filters were being weighed. The weighing room was located next to the sample receiving area. Three micro balances were setup for weighing. There were lots of shelves inside the weighing room, and many of the corrugated plastic shipping boxes were placed on the shelves. Three main activities take place inside the weighing room to process Teflon® filter samples: (1) clean filters are mounted into cassettes, (2) loaded filters are removed from cassettes, and (3) the micro balances are used to measure the mass of each filter before and after the sample collection event. It should be noted that the weighing room was not used to equilibrate filters by placing them into open containers for several hours.

The weighing room did not have the tight control of humidity and dust that is typically observed at other weighing labs. Temperature and humidity control is through a central heating/air conditioning unit used for the entire Air Quality Group annex building. The weighing room was equipped with a single door that was not closed during the audit even though filters were being weighed. The audit team brought two Dickson data loggers which were placed in the weighing room at about 1:30 P.M. to monitor the temperature and relative humidity (RH). Dickson#1 was placed immediately near CNL's sensors for temperature and humidity so that measurements from both devices could be compared. The Dickson loggers were set up to automatically log values every minute, but the CNL measurements were recorded manually every five minutes. Results from the Dixon#1 logger are presented in Figure 1 along with the official temperature and RH values provided by CNL.

Figure 1

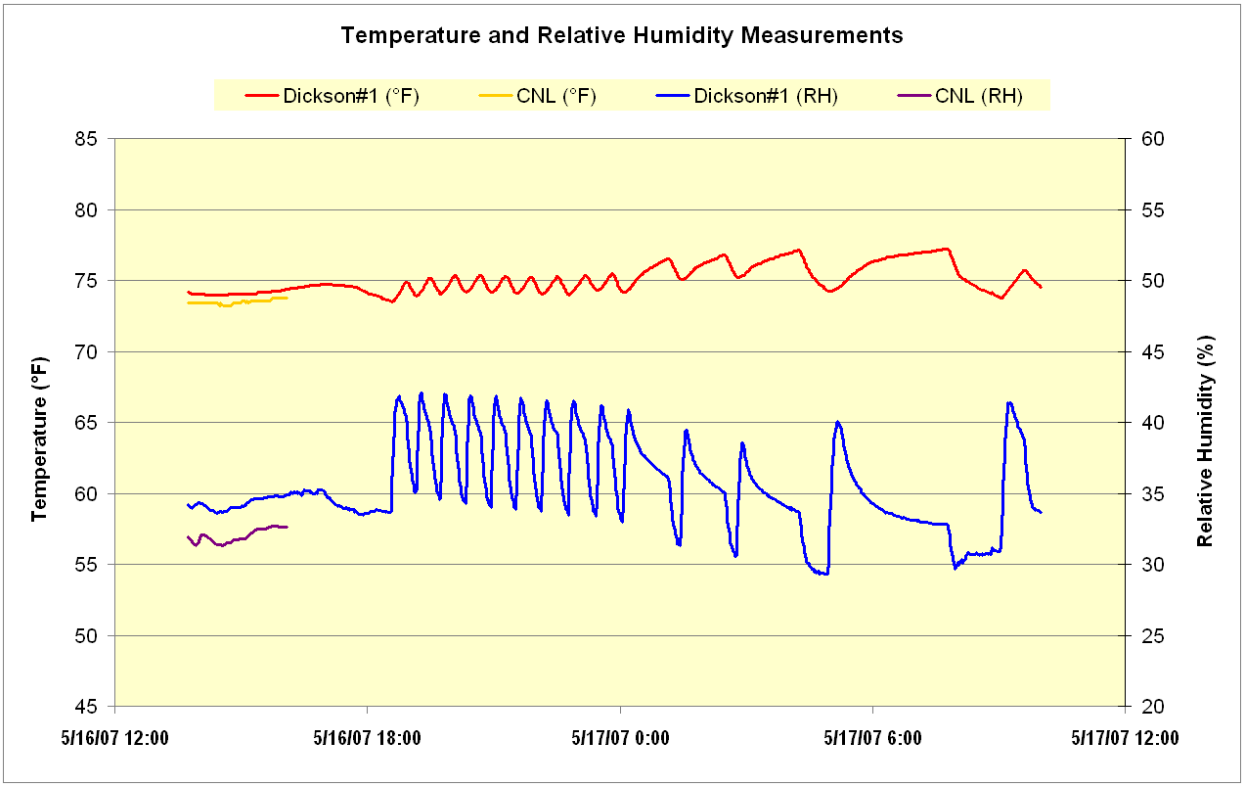

Figure 1 presents continuous data from the Dickson#1 logger that was collected over the course of about eighteen hours beginning during the afternoon of May 16. Only about two hours of data (40 data points) were recorded from each CNL sensor since the temperature and humidity values were recorded manually. Reasonably good agreement is observed for the temperature measurements and also for the humidity measurements taken during the first two-hour period shown in the graph. The Dickson#1 logger has an expected accuracy of ± 0.5 °F for temperature and ± 2 % for relative humidity, and it is compared to a NIST reference every year. It is unclear why the temperature and humidity became cyclic after about 6 P.M. on May 16.

The filter handling process inside the weighing room has been organized for efficiency, and computer programs keep track of all gravimetric mass measurements. Three different balances are available to deal with the large volume of work, and a correlation equation has been developed for each balance so that the actual mass value determined on one balance can be converted to the equivalent mass of another balance.

The correlation equations are developed by measuring the same set of twenty control filters on all of the balances. By having all of the balances calibrated in this manner, it is common practice to measure the tare mass of a filter on one balance and measure the loaded filter mass on a different balance. New equations are developed when QC checks indicate a problem.

A set of QC filters is kept inside the weighing room and weighed more than once to determine precision. These filters provide a daily record of weighing performance. The individual filters that make up this collection are constantly changing. Every day a new filter is weighed on every balance and added to the collection, while the oldest filter is weighed on every balance and removed. Each filter remains in the collection for about six weeks, and during that time it is assembled into a cassette for storage. Loaded filters returned from the field are not routinely weighed more than once to develop precision data.

Several steps must be completed before a new filter is ready to ship to the field site. A supply of new filters is kept in the weighing room. Each new filter must be visually inspected for obvious defects such as a torn or punctured membrane. A filter's identification is assigned by the computer during the tare mass measurement. Since there is no serial number on the filter itself, the filter is immediately placed into a cassette which can be assembled into a labeled cartridge.

Loaded filters are received from the field inside a zip-lock bag, and normally kept inside the bag until time to POST-weigh the filter. It has already been mentioned that a long equilibration time of several hours inside the chamber humidity is not provided for each filter before the mass is determined. During a weigh session, the loaded filter is taken out of the zip-lock bag inside the weighing room, removed from the cassette, and the POST-mass is determined almost immediately with only a few minutes of exposure to the humidity in the weighing room. During the previous EPA audit conducted in 2005, it was stated that prior tests conducted at CNL demonstrated that loaded samples equilibrate to laboratory conditions in less than four minutes. Some data was provided at that time to support the rapid equilibration of loaded filters. More recently, experiments have been performed at NAREL that also provides evidence for a rapid mass equilibration of the loaded 25-mm Teflon® filter.

Two clean 25-mm Teflon® filters and two metallic transfer weights were hand-carried to the audit so that CNL staff could weigh them during the audit. All four of these items had previously been weighed at NAREL so that comparisons could be made immediately. Each item was weighed on three of the CNL balances. The results from both labs are presented in Table 3.

Table 3. Results from Weighing Teflon® Filters and Metallic Units During Audit

Sample ID	Sample Description	NAREL Value (mg)	CNL Balance ID	CNL Value (mg)	Difference (mg)
T07-12162	25-mm filter	38.859	Cahn30a	38.855	-0.004
			Cahn31a	38.855	-0.004
			Cahn31	38.854	-0.005
T07-12163	25-mm filter	41.905	Cahn30a	41.902	-0.003
			Cahn31a	41.901	-0.004
			Cahn31	41.901	-0.004
MW07-12148	metallic standard	41.818	Cahn30a	41.818	0.000
			Cahn31a	41.816	-0.002
			Cahn31	41.817	-0.001

Table 3. Results from Weighing Teflon® Filters and Metallic Units During Audit

Sample ID	Sample Description	NAREL Value (mg)	CNL Balance ID	CNL Value (mg)	Difference (mg)
MW07-12149	metallic standard	38.534	Cahn30a	38.532	-0.002
			Cahn31a	38.533	-0.001
			Cahn31	38.533	-0.001

Table 3 shows very good agreement between the NAREL and the CNL mass values. Excellent agreement is also observed among the three different CNL balances. Cahn31 is the primary balance at CNL. The original mass values from the Cahn 30a and Cahn31a balances were converted to the Cahn31 equivalent values that are presented in Table 3. Good performance was also observed from the CNL weighing lab during a multi-laboratory inter-comparison study sponsored by EPA in 2006 [see reference 7].

The procedures for measuring gravimetric mass at CNL are included within *SOP 251 Sample Handling* [see reference 6]. Even though this document contains some information that is outdated, such as the number of balances discussed, the procedures for measuring gravimetric mass are still quite accurate.

X-Ray Fluorescence (XRF) Laboratory

Brian Perley is the resident spectroscopist, and Paul Wakabayashi is responsible for data processing and programming. Krystyna Trzepla-Nabaglo is responsible for certain aspects of the XRF quality assurance. The XRF laboratory currently has three instruments that represent two slightly different instrument designs. All of the instruments were designed and built in-house by CNL staff. All three instruments are energy dispersive spectrometers using an x-ray tube to excite the sample and using a lithium drifted silicon detector cooled with liquid nitrogen. XRF#1 was designed and built first. It uses an x-ray tube with a molybdenum anode to excite the sample without providing a vacuum or helium purge for the optical bench, and therefore the sample is analyzed in the presence of air. XRF#2 and XRF#3 have the same more recent design. They both use an x-ray tube with a copper anode and provide a vacuum for the optical bench. None of the instruments are set up to rotate the sample during the analysis.

At least two XRF spectra are needed to complete the analysis of each Teflon® filter sample. XRF#1 must be used to produce a spectrum for the heavier elements that include Ni, Cu, Zn, As, Se, Br, Rb, Sr, Ar, and Pb. A second spectrum produced by either XRF#2 or XRF#3 is needed to determine the lighter elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, and Fe. This analytical scheme offers good sensitivity for the twenty-four elements that are normally reported from the XRF analysis.

Calibrations are performed in the normal manner using thin film standards supplied by Micromatter Company in Deer Harbor, WA. It was interesting to note that both instruments were operated remotely using automation. A camera was available to observe some of the instrument functions, and a safety interlock switch was present to remove power from the x-ray tube if anyone approached the instruments.

There is one more unique feature of the XRF laboratory at CNL. For the past several years, it has been the only speciation lab that routinely reports XRF elements from a 25-mm filter. All of the other labs are set up to analyze either 37-mm or 47-mm filters. This simple fact has been a problem for EPA's speciation quality assurance program. EPA has established a program that provides single-blind samples to the participating speciation XRF labs. In some cases, all of the participating labs analyze the same filter and report results to EPA. In other cases, EPA creates several replicates and submits some of the replicates to

each participating lab for analysis. Thus far EPA has not been able to sponsor an inter-laboratory study that includes the XRF analysis of a 25-mm filter. There are two logical reasons for this problem: (1) if 25-mm filters are used for the study, there is currently no other lab identified that can submit reliable results for comparison, and (2) if the popular 47-mm filters are used for the study, the CNL lab will need to use modified analytical procedures to accommodate the larger filter. This subject was discussed during the last EPA audit in 2005, and the CNL staff has responded to this problem by investing considerable time and effort to develop new procedures for analyzing the popular 47-mm filter. The success of CNL's investment can be seen in their very good performance as a participating XRF lab in the last inter-laboratory comparison study sponsored by EPA in 2006 [see reference 7].

The XRF lab produces an incredible amount of data and many changes have been observed in recent years with the development and implementation of the latest XRF design. Krystyna has been busy looking at results from calibration standards and filter sets that were analyzed multiple times using either the same or a different instrument. She showed the audit team several spreadsheet plots that had been used to examine data for trends, instrument comparability, and correlations such as sample vacuum versus detector response. Krystyna explained that this type of data analysis was useful for developing QC criteria and for spotting problems.

An SOP for the XRF analysis was available [see reference 8], and it contained the appropriate level of detail for operating a non-commercial instrument. It was last modified in 1997, and some of the information is not current. It needs to be updated, and it needs to include information for XRF#2 and XRF#3 which is not mentioned in the current version.

Analysis by HIPS and PESA

The Hybrid Integrating Plate/Sphere (HIPS) system and the Proton Elastic Scattering Analysis (PESA) were briefly discussed with Brian Perley. The HIPS analysis provides a quantitative measure of the optical light that is absorbed by the $PM_{2.5}$ deposit. PESA is used to determine the amount of hydrogen present in the captured PM. An SOP is available that describes both of these analytical techniques [see reference 9 and 10].

CNL is the only speciation laboratory that performs the HIPS analysis. Most of the optical measurements for the IMPROVE program are made at the field site using a transmissometer, a nephelometer, or a camera. HIPS is the only optical analysis that is performed inside the laboratory where attention can be paid to quality controls that are not practical in the field. Only the "A" channel Teflon® filters are measured by HIPS.

CNL is also the only speciation laboratory that measures hydrogen by PESA. Very few labs have the necessary facility, equipment, and expertise. PESA measurements are taken by placing the filter into an evacuated target chamber, and then exposing the filter to a beam of 4.5 MeV protons. Scatter is produced by the elastic collisions between the incident protons and the particles in the filter deposit. The scatter, measured at the proper angle, is proportional to the amount of hydrogen present in the filter deposit. Filter samples were once staged for a simultaneous analysis using PESA and Particle Induced X-ray Emissions (PIXE) until 2001 at which time PIXE was discontinued in favor of expanding the number of elements determined by XRF.

The SOP document for PESA has not been updated since 1997, and it still describes the discontinued PIXE analysis. No other critical observations were noted regarding the PESA and the HIPS analysis.

Other Staff Interviews

Chuck McDade has been the central facilitator for this audit. He has provided rapid response to requests and questions from the audit team. As principal investigator for the air monitoring group, Chuck has the best overall perspective for lab operations, service and data delivery, and the quality of those deliverables. He was provided with the details of all the experimental measurements performed at NAREL that relate to this audit so that he could distribute those details to members of the CNL staff as needed. He has been a good host for this audit!

The audit team was told before this TSA that many QA documents still need to be updated. It was important to know this early in the planning stage since the audit team normally spends a great deal of time reading SOP's and other QA documents to prepare for the on-site visit. Checking compliance with the SOP documents is always a principle mission of the audit team. Since many of the QA documents still need to be updated, the audit team decided to use an advance audit questionnaire to fill the information gap. This approach was taken for the last EPA audit performed in 2005. The audit questionnaire with updated responses has been added as Appendix A to this report.

Nicole Hyslop was present as QA officer for most of the interviews with the laboratory staff. Nicole took center-stage for several minutes to explain the importance of co-located data derived from a few of the field sites that have an extra filter channel. She explained that the overall analytical precision could be calculated from the co-located data, and depending upon the level of analyte present in the samples, the co-located data might be useful for estimating the Method Detection Limit (MDL). Her comments were well received. Warren White spends most of his time performing data analysis with a serious mathematical toolbox. He has suggested reporting a more dynamic uncertainty for each data set which implies that the uncertainty and the MDL would probably change from one data set to the next.

Jim Hughes has been working to help design and implement numerous improvements for the electronic database at CNL. The goal is to provide better access to the laboratory and field data along with modern security features such as an audit trail. Some of the information technology at CNL is new and efficient, but some of the computer resources are quite dated such as the VAX/VMS system that is largely used in the XRF lab. Jim identified several specific tasks that are planned for the near future. The XRF spectra and metadata should be moved into a relational database. Automation will be developed to import and examine flash card data delivered from the field sites. The capability to automatically record the temperature and humidity of the weighing room will be restored. Numerous other improvements were mentioned which could broaden the horizon for CNL operations.

Ann Dillner has been working on a project that makes an aerosol in the laboratory from known materials. After the aerosol has been generated, it can be captured by an air filter. If the method can be perfected, it will offer new options for filter spiking. As mentioned earlier, XRF instrument calibration is normally accomplished by using standards purchased from the Micromatter Company. The Micromatter standards are not accurate for elemental concentrations less than approximately 20 $\mu g/cm^2$ of filter material. Yet there is a need to have accurate standards at much lower concentrations. Furthermore there is a need to have accurate multi-element standards. The spike method used at Micromatter deposits each element onto the filter in separate layers, and this is a problem for the XRF analysis. Ann's project could potentially offer a valuable filter spiking method to the XRF community and beyond.

Conclusions

This TSA has produced the following findings, recommendations, and comments.

1. Many of the QA documents are not current and need to be updated. The revised documents need to include current procedures, equipment, objectives, policy, personnel, and other information that documents the actual work performed. This is a problem that was identified during the last EPA audit performed in 2005.

   Recommendation: The Air Quality Group at CNL should work with the IMPROVE Steering Committee to set priorities and establish a schedule for updating the QA documents.

2. Currently blank filters are weighed more than once to generate precision data, but loaded filters are not routinely weighed more than once. This audit has demonstrated that large swings in humidity occur inside the weighing room which could affect loaded filters more than blank filters. This is a potential problem that was identified during the last EPA audit.

   Recommendation: A small percentage of loaded filters should be weighed more than once to generate new precision data. The repeat measurement should not be made immediately but it should not be delayed for more than a few hours. NAREL has observed loaded filters to gradually lose mass over time possibly due to the vapor pressure of the captured semi-volatile components of the PM.

References

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Appendix A

Advanced Questions and Responses for the
Technical Systems Audit of the IMPROVE Program at UC-Davis
Scheduled for May 16-17, 2007

1. Can we get a list of the staff at UC Davis that perform work for the IMPROVE program?

   Crocker Lab Director – Bob Flocchini
   IMPROVE Principal Investigator – Chuck McDade
   Data Validation & Special Studies – Lowell Ashbaugh
   Quality Assurance – Nicole Hyslop
   Method Testing & Development – Ann Dillner
   Data Analysis – Warren White
   Database Management – Jim Hughes
   Computer Support – Dan Shadoan
   XRF Data Processing – Paul Wakabayashi
   XRF Quality Assurance – Krystyna Trzepla-Nabaglo
   Spectroscopist – Brian Perley
   Sample Collection & Handling – Steve Ixquiac
   Field Siting – Pete Beveridge
   Lab Operations – Tamera LaBelle
   Field Operations – Jose Mojica, Kevin Goding, Ciara Remillard, Ted Scharfen
   Student Employees (lab, instrumentation, and field support)

2. What are the routine analytical measurements currently performed at CNL for the IMPROVE program? Gravimetric mass, XRF, PESA, HIPS, (PIXE ?)

   All except PIXE, which was discontinued in 2001.

3. Will the laboratory staff be available for interviewing during the TSA?

   Yes.

4. Will the labs be operational and analyzing samples during the audit?

   Yes.

5. Will there be opportunity to take experimental measurements during the audit? For example, the audit team may bring a data logger to record temperature and humidity during the audit.

   Yes.

6. Will the audit team be allowed to select and remove a few filters from the IMPROVE archive for the purpose of performing an independent analysis?

   Probably not during the audit visit. Before releasing filters for external analysis we prefer to review the protocol for the analyses that are to be performed, including sample handling, analytical plans, chain of custody documentation, and plans for data analysis. During the

audit, however, we expect to discuss at length our ongoing work in comparing our XRF system to that at RTI. As part of that discussion we can decide how NAREL might participate and thereby receive filters from us.

7. How much time will we need during the audit to discuss future PE samples for the laboratories at CNL?

   See question 6. We expect to spend an hour or two on this discussion. We can devote more time if needed.

8. Is access to the facility limited and controlled?

   Yes. Both the main Crocker building and the Annex have locked entrances, with card key access by employees.

9. Are samples maintained in a secure area at all times after being delivered to the facility?

   Yes, they remain in Crocker Lab or the Annex until all analyses and data delivery have been completed. Long-term archival storage is in another locked facility elsewhere on the Davis campus.

10. Who is authorized to halt program activities due to inadequate quality?

    Chuck McDade, the Principal Investigator (PI), has final authority to halt program activities. However, anyone in the program is authorized to halt their activities to solve a problem. For example, XRF analysis is periodically halted to refurbish or replace a failing detector. Most of these temporary outages are brief and are conducted unilaterally. More serious or long-term problems are discussed with the PI and/or raised in our weekly staff meetings.

11. How are records of critical consumables (such as filter lot numbers) maintained?

    All filter lot numbers are maintained in a file called lotnums.dbf. In the future this information will be maintained in SQL database tables.

12. Are reports available from previous audits (internal or external)?

    Annual site maintenance visits represent our internal audits. Complete records are maintained from each visit, including calibration records, maintenance comments, and site photos. External audits have been rare and infrequent, but the reports are available.

13. Are reports available for recent preventive or corrective actions?

    All preventive and corrective actions are documented in our Problems File. We can demonstrate this file during the audit.

14. Are there periodic summary reports of quality measurements and if so, what information does the report contain?

    Beginning this year we have begun producing quarterly XRF QA reports that summarize the quality control test data that support our measurements, principally through control charts. We can provide copies of these reports.

15. How are QA documents controlled at CNL?

    The most current SOPs have been delivered to CIRA and are posted on the IMPROVE

website. They are available from the website in read-only form and thus cannot be corrupted.

16. How often are QA documents reviewed for accuracy?

    Many of our SOPs are outdated and we are in the process of reviewing and updating them. Once we are finished, we will revise them whenever our procedures are changed. Since we are a trends network, we try to avoid changes and, when necessary, try to implement several changes at once.

17. Are obsolete documents such as the old version of an SOP retained?

    Old versions of SOPs are retained at CNL, but they are not obsolete. IMPROVE is a long-term trends network, and the old SOPs serve as documentation for the data that were collected when they were in use.

18. How long are technical records maintained before they are disposed?

    We keep the paper field log sheets for at least five years. In addition, the data from the log sheets are hand-entered into an electronic file that we keep indefinitely. We have considered scanning the log sheets and retaining the electronic file, but we have not yet begun doing so.

19. How are electronic records backed-up to prevent loss?

    Backup of all files on the network occurs each day via several mechanisms

    a. Real-time file copies of files changed on a daily basis (incremental) are done twice a day, once at 7:00am and once at 12:00pm
    b. Incremental backup to magnetic tape every day at midnight
    c. Full backup of the entire system every Sunday at midnight

20. Do the records for each analytical test contain sufficient information to enable the test to be repeated under conditions as close as possible to the original?

    Yes, data are recorded in notebook and data files.

21. Are the records sufficiently complete to identify the personnel responsible for sampling, receiving, testing, calibration, and checking of results?

    Yes, initials are recorded in data files for all steps. Our new relational database has the additional feature of auditing (recording) every database manipulation.

22. How are corrections/amendments made to hand-written records?

    Using pen or pencil on paper, and initialed.

23. How are corrections/amendments made to electronic records?

    Entered by keyboard, and initialed; comments added as appropriate. Our new relational database will document changes, and it also can place restrictions on who is allowed to make changes.

24. How are instrument maintenance records maintained?

Complete records are maintained in the calibration records, maintenance comments in the problems file, and site data sheets. In the future these records will be maintained as part of the relational database.

25. Has all computer equipment been installed in accordance with manufacturer's recommendation? If not, why? If so, how is this documented?

    All computer equipment is installed according to manufacturer's specifications and recommendations. No documentation is currently kept on the installation of computer equipment maintained by the CNL IT staff.

26. Is there a user's manual for each software program in use? If the program was written in-house, the minimum documentation should include a user guide and the source code.

    All software developed in house has a guide for the users or has sufficient on-line help files to make a written guide unnecessary.

27. Is there an approval process for testing and validating either purchased or in-house analytical software before it is used to generate data?

    No formal review process exists for validating or testing analytical software. Currently, the testing and validation process may be described by "Does it do what we require?" concept.

28. Are there adequate acceptance procedures for software changes?

    Yes. Group level discussions are held as to the efficacy of the software modifications and whether to incorporate those changes in the "released" versions. We are in the process of formalizing our software testing protocols so that any changes are fully documented and rigorously tested before implementation.

29. Is it required that audit trails be produced showing all data entered, changed, or deleted? If so, are these reports reviewed thoroughly by appropriate personnel?

    Our new database electronically documents every data entry and data edit, indicating when and by whom the changes were made.

30. Is there manual rechecking of data entered against source documents at any point? How is this accomplished and documented?

    All hand-entered data are entered twice, by two different people.

31. Are there procedures that ensure that the data collection system is secured so that the data integrity can be protected against unintentional error or intentional fraud?

    Specific procedures and safeguards are employed at all levels in the data collection systems. Many of these safeguards are under software control and many are methods employed by the spectroscopist during the collection and analysis processes. Our new database provides additional data security protection.

32. Is there adequate storage capability of the automated data collection systems or of the facility itself to provide for retention of raw data, including archives of computer-resident data?

No raw data is ever deleted or lost. Archives on magnetic tape are kept of all data produced since the beginning of the system. Data storage capability has never been inadequate or lacking.

33. Are there policies governing conditions of raw data storage and retention times?

    Raw data are never deleted. Our new database enforces strict rules against deleting raw data.

34. Does each instrument have a bound logbook? If not, how is instrument usage, calibration, and maintenance documented?

    All instruments have Computer records; the XRF systems also have a written record as specified by UC Davis EH&S.

35. Are corrections to data and logbook entries made correctly, one line through the data and initialed and dated? (e.g. no whiteout or masking of original entry)

    Yes.

36. Is there a document control program in place? Is it fully and correctly implemented?

    We are in the process of updating all of our SOPs. When completed, we will incorporate them into a document control system.

37. Are all QMPs, QAPPs, SOPs, and other technical documents in the document control system?

    No (see # 36)

38. Does the Document Control Record contain a revision history for controlled documents?

    No (see # 36)

39. Are there pen-and-ink revisions on copies of controlled documents that have not been approved by the responsible official(s)?

    No (see # 36)

40. If pen-and-ink changes have been approved, has the same change been made to every copy of the document in distribution?

    N/A

41. Is a copy of the approved QAPP available for review by the laboratory analysts? If not, briefly describe how and where QA requirements and procedures are documented and are made available to them.

    Yes

42. Are there deviations from the QAPP?

    Yes. In some cases, procedures have been changed but the changes haven't been documented. We will address this issue in the revisions to our SOPs.

43. How are any deviations from the QAPP noted?

    They aren't documented.

44. What are the critical measurements in the program as defined in the QAPP?

    Those measurements required for reconstructed extinction as described on Page 4-29 of the QAPP.

45. Does the QAPP list measurement quality objectives (MQOs) for each critical measurement clearly and explicitly?

    Yes

46. Are the MQOs based either on documented performance criteria or on actual QC data compiled for the measured parameter?

    Our MQOs and DQOs are currently under review. Any changes will be driven by the need to discern long-term trends, not by the specifics of a particular measurement. Collocated data have been collected for approximately three years now, and we will be using these data along with laboratory QA data to evaluate our performance in achieving our MQOs. Initial analysis of the collocated data suggest that we have been underreporting the uncertainties associated with some species.

47. Are there established procedures for corrective or response actions when MQOs are not met? If yes, briefly describe them.

    No, in our review of the SOPs/QAPP, we will develop tests to evaluate whether the MQOs are being met and actions to remedy any failures.

48. Have any such corrective actions been taken during the program?

    No

49. To what extent is CNL responsible for performing annual calibrations, adjustments, and major repair of the field samplers?

    Audits and calibrations of our samplers are done every year, weather permitting, by UCD staff. Missed sites are handled using a mail Audit/Calibration kit, performed by the operator, and coordinated by a field technician. Adjustments are handled as a mail Audit/Calibration and coordinated by a field technician. Repairs are done by the site operator, using equipment sent by UCD.

50. Is there a Quality Management Plan (QMP) in place?

    Yes

51. Is the QMP current?

    No, but we will be working with EPA to revise this document.

52. Are there regular staff meetings to discuss quality issues and problems?

    We meet every Tuesday afternoon.

53. Does the QA manager have direct access to the highest level of management at which decisions are made on lab policy and resources?

    Chuck McDade is responsible for IMPROVE project decisions, and Bob Flocchini for Crocker Lab resources. Both are freely available to anyone working on the program.

54. Are written job descriptions available for each member of the staff?

    There is a job description in each individual's personnel file.

55. How are new staff members trained?

    Field staff are trained using equipment repair procedures, group training sessions and individual training sessions at UCD and in the field.

56. Is there an adequate initial training program for new employees which covers health and safety, quality assurance policies and procedures, CNL policies, and analytical or other job-related responsibilities?

    There is a new employee orientation given to all university staff members. Specific job related responsibilities are given by individual training sessions.

57. How is training for a new job responsibility done? Is there a process of training, testing, and validation for a new job responsibility?

    Training for a new responsibility is conducted just as it is for a new staff member. The most common transition is from a weighing lab position to a field maintenance position.

58. Are Standard Operating Procedures in place for all analytical methods, general procedures and policies, and other processes which have an impact on data quality?

    SOPs are in place for most procedures. There is no finalized SOP for the Copper XRF system.

59. Are the SOPs complete, up-to-date, and followed?

    We are working with a technical editor to revise and update the SOPs.

60. Do the SOPs address calibrations and their frequency?

    Yes, although they are lacking detail in some cases.

61. Do the SOPs include QC acceptance limits and associated corrective actions when such limits are surpassed?

    Some do, see Page 5-45 of the QAPP.

62. Do the SOPs include preventive and remedial maintenance?

    Yes

63. How are data quality assessments made for precision and accuracy?

    We will be developing these procedures as part of the QAPP review process.

64. How are measurement uncertainties calculated?

    See Section 5.8 of the QAPP for discussions of the uncertainty calculations for each analytical technique.

65. Are SOPs accessible to the persons who need to use them, and available at all appropriate work sites?

    Yes

66. Are SOPs in place covering system security, training, hardware and software changes, data changes, procedures for manual operations during system downtime, disaster recovery, backup and restore procedures, and general system safety?

    The sampler software and hardware is documented and tracked with version numbers. Documentation is sparse for the other systems/procedures mentioned.

67. Is there an SOP for software development, maintenance, and changes?

    Not currently, although we are planning to formalize our software management system.

68. How are new filter lots tested before they are used to collect routine field samples?

    Duplicate samples are collected for several days using filters from the new filter lot and the current filter lot. The resulting concentrations are compared using the Student's T-test. XRF (Teflon) or IC (nylon) analyses are performed for several blank filters from the new and current lot. The pressure drop across several filters is measured and compared to filters from the current lot. The acceptance criteria for these tests are in the process of being refined.

69. How are filter lots tracked and documented?

    Depending on the type, they are given a lot number if they do not already have a usable number from the supplier. Each change in lot number is recorded with the first filter (Site, Samdat) used in that lot. The time and date are recorded at upload for each filter (Site, Samdat).

70. When a new individual filter is inspected for use, what are the acceptance criteria for using it?

    That it looks clean and has no tears or holes.

71. Have maximum holding times been established for the critical steps of the overall sample analysis?

    No.

72. Are out-of-control events properly documented, tracked, and followed up?

    Yes.

73. Have records been identified as quality control records? Have retention times been established?

    Various computer files are used to maintain quality control records. These files are retained indefinitely.

74. Are quality control records stored in such a manner to protect against damage, deterioration, and loss?

    Yes. Computer files are backed up routinely. Paper files are stored at Crocker Lab, and then archived at a facility elsewhere on campus.

75. If a QC analysis fails, is the entire batch re-analyzed?

    Sometimes, but more often the problem is isolated and only a subset of filters requires

reanalysis. Our new quarterly XRF QA reports provide details.

76. Is there a formal health and safety program in place at CNL?

    Yes. The documentation is on file in the cyclotron control room in Crocker Lab.

77. Are Performance Evaluation samples from an external source prepared and analyzed on a regular basis?

    Yes, XRF foils produced by Micromatter are used for calibration purposes.

78. Does the QA staff provide single blind and/or double blind samples for analysis on a regular basis? If so, for what tests?

    No.

79. Is a complete systems audit performed by the QA staff at some established minimum frequency?

    No, this type of audit will be implemented once the SOPs and QAPP have been updated.

80. Are external audits conducted of the CNL facility or any part of the IMPROVE operations on a regular basis? Give details.

    EPA now has an active audit program that checks sampler flowrates at a subset of the IMPROVE sites every year.

81. Are records of all audits, findings, responses, and corrective actions easily accessible for review during this TSA?

    Yes.

82. What action will be taken if a comment on the field log sheet states that the grass around the shelter was mowed during a collection event?

    The event would be commented in the logs database and a full detailed description given in the corresponding problems file.

83. Which staff members are authorized to amend the primary records received from the field operator? How are amendments documented?

    Jose Mojica, Kevin Goding, Ciara Remillard, Ted Scharfen, and Tamera LaBelle are authorized to amend field records under the supervision of Steven Ixquiac.

84. A memory stick has been returned to the lab, and it is unreadable. What action is taken?

    The Flashcard contacts are cleaned with alcohol and another download is attempted using the primary program. If this fails, another download is attempted using a secondary download program. If this fails, the card ID number is used to research the integrity of the card, and the operator is contacted to verify proper installation of the card.

85. How often are data from the memory stick downloaded? How long are those data retained?

    Flashcard data are downloaded with every new Bluebox received, containing 3 weeks of filters. The data are retained indefinitely.

86. How are filters conditioned before gravimetric mass measurements are taken?

They are not. Testing at UCD has demonstrated that we are able to meet our data quality goals without conditioning.

87. Are the temperature and relative humidity (RH) inside the conditioning environment recorded on a continuous basis during filter conditioning?

N/A

88. Describe the temperature and RH measurement devices and data recording system, including the sampling frequency.

RH and Temperature are monitored continuously in the weighing room. The values are checked several times each day.

89. Is the calibration of the temperature and RH devices verified on a regular basis?

Yes. They are compared against a mercury thermometer and sling psychrometer, respectively.

90. Do laboratory records indicate that the mean RH during postsampling conditioning is within 5 percent the RH value during presampling conditioning?

No. Our tests have demonstrated that our weighing results are not measurably affected by the range of RH and temperature typically encountered in our laboratory.

91. What is the manufacturer and model of each microbalance used to weigh sample filters?

Cahn models 25, 30, and 31

92. Has the microbalance been modified in any way since it was received from the manufacturer? If so, what was the modification?

No.

93. Does the weighing laboratory have a service agreement for periodic microbalance calibration and servicing?

No. We provide our own minor maintenance. Major maintenance has never been required.

94. Is the microbalance located in an area that is free from vibration, contamination, drafts, and temperature gradients?

Yes.

95. Is the microbalance mounted on a sturdy base?

Yes.

96. Is the microbalance located in the filter conditioning environment?

N/A

97. According to the SOP, different balances are used for the PRE and POST mass measurements. Why not use the same balance for PRE and POST filter weighing?

There is no significant advantage to that and many disadvantages, the main one being disruption of the flow of filters through the laboratory.

98. Does the range of the mass reference standards bracket the mass of PM2.5 filters?

    Yes.

99. Does the weighing laboratory have laboratory primary standards as well as working standards?

    Yes.

100. Are the mass reference standards handled using clean, smooth, nonmetallic forceps?

    Yes.

101. Are the mass reference standard forceps different from the filter-handling forceps?

    Yes.

102. How and where is a filter lot stored when it is first received by the weighing laboratory?

    They remain in the boxes that they were supplied to us in.

103. Are filters kept in their original, sealed containers until they are inspected?

    Yes.

104. Are all filters visually inspected for defects immediately before both presampling and postsampling conditioning?

    Yes, before pre weight and post weight.

105. What happens when a defective filter is discovered during presampling inspection?

    They are set aside to be returned to the manufacturer.

106. What happens when a defective filter is discovered during postsampling inspection?

    They are tagged with a status that reflects the observation.

107. How are filters stored during conditioning?

    N/A

108. What is the filter conditioning period and how was it determined?

    N/A

109. Are laboratory blanks weighed routinely during weighing sessions? If so, what warning/control limits are applied?

    Yes, Reweights have a standard deviation of about 1 microgram and lab controls are less than 3 micrograms.

110. Are field blanks weighed routinely along with PM2.5 filters during presampling and postsampling weighing sessions? If so, what warning/control limits are applied?

    Yes, field blanks weights are routinely comparable to the lab controls. The control limit is approximately 3 ug/filter.

111. How frequently do laboratory records indicate that field blanks are collected and weighed?

    Teflons 1-2%, Nylons and Quartz 3-4%.

112. What action is taken if laboratory or field blank acceptance criteria are exceeded?

We investigate, usually initially by contacting the filter manufacturer to inquire about contamination in manufacturing.

113. Are polonium antistatic units used to remove static from filters?

Yes.

114. Are the polonium antistatic units replaced every six months?

Yes.

115. Is at least one working standard reweighed after approximately every tenth filter?

No. Standards are reweighed twice a day, or a) when the instrument zero drifts or b) When the magnetic field in the lab changes significantly (influenced by the cyclotron next door).

116. Do verified and measured values of the working standard agree to within 3 micrograms? What action is taken if this acceptance criterion is exceeded?

Yes. Procedures are repeated and investigated until resolved.

117. If exposed filters are stored at ambient temperature from retrieval to conditioning, is the postsampling weighing completed within 10 days after the end of the sample period?

No, but the postsampling weighing is completed well within 10 days after the filter is received in Davis.

118. Are routine filter loadings corrected by weight gains in laboratory or field blanks?

No. Weight gains are monitored but they are not used to correct the data because their magnitude is insignificant.

119. How are cassettes currently recycled?

Cassettes cycle back to the same site in the routine.

120. You are the technician removing a filter from the cassette, and you discover that a filter is missing. What action do you take?

An appropriate status flag is assigned.

121. You are the technician weighing a filter already loaded with PM2.5, and you accidentally drop the filter onto the floor before the mass measurement is taken. What action do you take?

An appropriate status flag is assigned and a supervisor notified. The measurement is made and further investigation occurs.

122. After reading the SOP, it appears that no specific conditioning period is required to allow filter mass to reach an equilibrium? What has CNL learned over the past several years about filter mass stability?

The Teflon filters we use do not need conditioning. We are able to routinely satisfy our QC criteria without filter conditioning. The pre weight is in equilibrium out of the box.

123. Exactly what data are reported to CIRA? to AIRS?

No data are currently reported to AIRS. The data reported to CIRA consist of a file for each month. There is record for each sampling site for each sampling day of the month, whether or not a sample is collected. The only exception to this is that no data are reported for the period prior to operation or after the site is removed.

The data consists of site name, sampling date, start time, flow rate and elapsed time for each module, status flags for each module, $PM_{2.5}$ and PM_{10} mass, eight carbon fractions, sulfate, nitrate, nitrite, and chloride ions, and the elements H, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Se, Br, Rb, Sr, Zr. Each reported species includes the concentration, uncertainty, and minimum detectable limit.

124. Exactly what data are reported to CNL from DRI and RTI?

DRI reports the following data:

Field name	Description
QID	Quartz filter ID
OETF	TOR analysis flag
SITE	Site Name
SAMDAT	Sampling Date
FILTYPE	Filter type (primary or secondary)
STRTIM	Sampling Start Time
STATUS	Filter Sampling Flags
CA	Carbon analyzer number
O1TC	Organic carbon fraction 1 concentration (µg/filter)
O1TU	Organic carbon fraction 1 concentration (µg/filter) uncertainty
O2TC	Organic carbon fraction 2 concentration (µg/filter)
O2TU	Organic carbon fraction 2 concentration (µg/filter) uncertainty
O3TC	Organic carbon fraction 3 concentration (µg/filter)
O3TU	Organic carbon fraction 3 concentration (µg/filter) uncertainty
O4TC	Organic carbon fraction 4 concentration (µg/filter)
O4TU	Organic carbon fraction 4 concentration (µg/filter) uncertainty
OPTTC	Pyrolyzed organic carbon, transmittance concentration (µg/filter)
OPTTU	Pyrolyzed organic carbon, transmittance concentration (µg/filter) uncertainty
OPTRC	Pyrolyzed organic carbon, reflecance concentration (µg/filter)
OPTRU	Pyrolyzed organic carbon, reflecance concentration (µg/filter) uncertainty
OCTRC	Organic carbon, reflecance concentration (µg/filter)
OCTRU	Organic carbon, reflecance concentration (µg/filter) uncertainty
E1TC	Elemental carbon fraction 1 concentration (µg/filter)
E1TU	Elemental carbon fraction 1 concentration (µg/filter) uncertainty
E2TC	Elemental carbon fraction 2 concentration (µg/filter)
E2TU	Elemental carbon fraction 2 concentration (µg/filter) uncertainty
E3TC	Elemental carbon fraction 3 concentration (µg/filter)
E3TU	Elemental carbon fraction 3 concentration (µg/filter) uncertainty
ECTRC	Elemental carbon, reflecance concentration (µg/filter)

Field name	Description
ECTRU	Elemental carbon, reflecance concentration (µg/filter) uncertainty
TCTC	Total carbon concentration (µg/filter)
TCTU	Total carbon concentration (µg/filter) uncertainty
DEPAREA	Deposit area (cm^2)
LRINIT	Laser reflectance initial value (mV)
LRMIN	Laser reflectance minimum value (mV)
LRFINL	Laser reflectance final value (mV)
LTINIT	Laser transmittance initial value (mV)
LTMIN	Laser transmittance minimum value (mV)
LTFINL	Laser transmittance final value (mV)
COMMENT	Carbon analysis and data validation comments

RTI reports the following data:

Field name	Description
SITE	Site Name
SAMDAT	Sampling Date
STATUS	Filter Sampling Flag
IC	IC Analyzer Number
CL	Chloride, µg/filter
NO2	Nitrite, µg/filter
NO3	Nitrate, µg/filter
SO4	Sulfate, µg/filter
Comment	IC analysis and data validation comments

Both laboratories have recently added a data column indicating which of their multiple instruments was used for each analysis. This column is shown as CA for carbon analysis and IC for ion analysis.

125. What are the elements of data validation performed at CNL before the analytical results are reported to CIRA?

The following checks are performed (this is not a comprehensive list):

a. Filter weights are examined during weighing to ensure that the post-weight is greater than the pre-weight.

b. Flow rate and elapsed time measurements are examined to ensure they are within bounds.

   i. Flow rates are flagged in stages if they differ from nominal, and may cause a sample to be invalidated. We are currently reviewing this and may make changes to the bounds,

   ii. Elapsed time less than 18 hours invalidates a sample. For elapsed times 18-24 hours, the reason for the short time is noted.

c. For each pair of parameters listed below, time trend plots and scatter plots for each site are examined. The plots are examined for potential swapped filters, fine mass > total mass, and agreement between data pairs. Corrective action is taken if data are identified as incorrect, a mechanism can be identified as to how it occurred, and the assumed correction improves internal consistency. If necessary, time trends from nearby sites are examined to aid in this analysis. Corrective action may entail changing the dates on two (or even three) adjacent samples, or realigning pre-weights or post-weights, as appropriate. It may also be necessary to swap a sample labeled as a field blank with one labeled as a sample.

   i. Sulfur(x3)/Sulfate

   ii. $PM_{10}/PM_{2.5}$

   iii. Reconstructed mass/gravimetric mass

   iv. Organic mass by hydrogen (OMH)/Organic mass by carbon (OMC)

   v. Light absorbing carbon (LAC)/Laser absorption (LRNC)

d. Flow rates are examined again during the site-by-site data review when necessary to resolve a discrepancy. Review of 15-minute flashcard data is sometimes necessary to correct a flow rate or elapsed time error.

126. Do the current IMPROVE data flags sufficiently communicate critical information to the data users?

The current list of flags is posted on the VIEWS website at:

http://vista.cira.colostate.edu/views/Web/Program/IMPROVE/IMPROVEInfoPanel.htm

This list is shown below:

Flag	Flag Type	Flag Description
AA	Data Flag	ORGANIC ARTIFACT CORRECTED. A value of 0 is reported.
AP	Data Flag	POSSIBLE ORGANIC ARTIFACT. A value is reported.
BI	Data Flag	Incorrect installation of sample cartridge during weekly change. A value is not reported.
CG	Data Flag	Clogging Filter, Flow rate less than 18 L/min for more than 1 hour. This affects the cut point of the particle but the concentrations are correct. A value is reported.
CL	Data Flag	Clogged Filter, Flow rate less than 15 L/min for more than 1 hour. A value is not reported.
DE	Data Flag	Derived or calculated value
EP	Data Flag	Equipment Problem. A value is not reported
LF	Data Flag	Moderately low/high flow rate. The average flow rate results in a cyclone cut point outside of the 2-3 micro-m range. This corresponds to flow rates < 21.3 L/min or > 24.3 L/min. A value is reported.

Flag	Flag Type	Flag Description
NA	Data Flag	Not Applicable. This is used for missing modules with non-protocol samplers with less than four modules. A value is not reported.
MV	Data Flag	Missing Value. A value is not reported.
NM	Data Flag	NORMAL. A value is reported.
NR	Data Flag	Not Reprocessed, Carbon data between 2000 – 2004 which were not Reprocessed to account for negative OP that had originally been reported as zero. A value is reported.
NS	Data Flag	Operator did not install the samples or installed them too late to acquire a valid time. All filters involved. A value is not reported.
OL	Data Flag	Off Line. In some cases, this is used when the sampler is inoperable due to hurricane or fire. For year 2000, this is used for the period after the Version 1 sampler is removed and before the Version 2 samples begins operation. A value is not reported.
PO	Data Flag	Power Outage. All filters involved. A value is not reported.
QA	Data Flag	QA problems suspected. Value held back for further investigation. A value is not reported
QD	Data Flag	QUESTIONABLE DATA. A value is reported.
RF	Data Flag	High flow rate. The flow rate is greater than 27 L/min for more than 1 hour. This affects the cut point of the particle but the concentrations are correct. A value is reported.
SA	Data Flag	Sampling Anomaly. A value may be reported
SP	Data Flag	An artifact filter was swapped with a sample filter. A value is reported
SW	Data Flag	Suspected filter swap. A value is reported.
UN	Data Flag	The concentrations failed the data validation for unknown reasons. A value may be reported.
XX	Data Flag	The filter is damaged. A value may be reported.

127. How is completeness calculated?

    For Regional Haze Rule analysis, a sampling period is considered complete only if data have been reported from all four IMPROVE modules.

128. What are the most common reasons for declaring a sample invalid? What is the most unusual reason?

    The most common reasons are equipment problems, bad installation of filters, and clogged filters. The most unusual reason would probably be an unknown pre-weight.

129. What studies are available that compare PIXE to XRF data?

    Multiple data sets (~2000 samples) were analyzed using both PIXE and XRF. The samples represented several quarters in the year 2000.

130. How many spectra are normally required to complete the XRF analysis and what are the conditions for each?

    Two spectra, one from the analysis of sample exposed to a Copper anode tube and another

exposed to a Molybdenum tube.

131. How is the XRF energy calibration performed for the multi-channel analyzer, and how often is it repeated?

    A set of Micromatter foils is analyzed at least once a month. In addition, a set of 30 IMPROVE samples are analyzed at least once a month. Both the Micromatter foils and IMPROVE samples are analyzed following any event that requires a physical change to the system. Details of our current procedures are described in our quarterly XRF QA reports.

132. What minimum detector resolution is required before acceptable qualitative analysis can be achieved?

    Copper tube – Iron Kα <10.5 channels wide (~.18 KeV)
    Molybdenum tube – Iron Kα < 5.5 channels wide (~ .19 KeV)

133. How many elemental standards are used to develop the calibration curves for quantitative analysis? Are some elements determined by interpolation?

    24 separate foils. Yes, Hg, Zr, and Y

134. How closely does the matrix and presentation geometry match for XRF samples and standards?

    The beam geometry is the same for both samples and standards. The matrix and mass per unit area are different between standards and filter samples and are acquired at different x-ray tube current settings to maintain established dead times and maximize sensitivity.

135. Are any of the standards multi-element? If so, how were they prepared?

    Yes, 10 of the standards have two or more elements. They were prepared by Micromatter.

136. How are blank subtractions performed, and what is the history of blank filters that are used for spectral subtractions?

    A laboratory blank is analyzed and the spectrum collected is "floated" against the spectrum of each sample.

137. Are attenuation corrections made for the lighter elements? If so, how are the corrections made?

    Yes, they are corrected using a theoretical calculation based on the element's x-ray strength and sample loading.

138. What are the components of uncertainty for XRF results?

    They are based on the relative background x-ray counts (see SOP 351).

139. How is the XRF uncertainty calculated?

    See SOP 351.

140. Do the measurement quality objectives need to be changed for those elements previously analyzed by PIXE but currently analyzed by XRF?

    Our MQOs and DQOs are currently under review. Any changes will be driven by the need to discern long-term trends, not by the specifics of a particular measurement. Results from

our collocated samper tests are being used to identify elements for which our uncertainties appear to be underreported.

141. What is the maximum acceptable dead time? What action is taken when this level of dead time is exceeded?

~10%. The current is reduced until acceptable dead time is achieved.

142. Are negative concentrations reported?

Negative concentrations are reported for species which are artifact corrected (ions and carbon). Negative values represent legitimate information, reflecting measurement uncertainty for near-zero concentrations.

143. Are the raw data files stored as ASCII text?

Yes.

144. Is there a visual or audible warning device to indicate that the x-ray tube is energized?

Yes, "x-ray on" lights.

145. Is CNL the only lab that performs the HIPS analysis? Are there any recommendations for challenging your instrument with a PE or comparing with another instrument?

Our HIPS system was designed at UCD and is unique. We are currently assessing the proper interpretation of the raw HIPS data. Once we have reached a decision we may choose to participate in a comparison, but we have not done so yet.

146. Will the sample interaction with laser light be different from the interaction with sunlight?

Yes, it is wavelength dependent.

147. Has evidence of living bacteria ever been observed on filters during storage?

No, our measurements are not designed to and do not directly measure bacteria. Furthermore, the measurement data do not typically differ significantly when samples are reanalyzed.

148. How do data sets from HIPS compare to data derived from Nephelometers, Transmissometers, Aethalometers, and OC/EC measurements?

We have not conducted formal comparisons of HIPS with other measurements. The mass loading correction (if any) that needs to be applied to HIPS data is under review. Once we reach a decision regarding the loading correction we can begin comparisons with other methods.

149. How are results from the HIPS measurements most useful to the program?

HIPS data provide a surrogate for elemental carbon, which is useful as a quality control cross-check and as a data analysis tool. However, as noted in question 148 our HIPS data are not formally certified, and thus provide only a broad-based check against other data.

150. Is CNL the only lab that performs PESA? Are there any recommendations for challenging your instrument with a PE or comparing with another instrument?

Our PESA system is unique. We have not undertaken comparisons with other laboratories,

but we use the hydrogen data in cross-comparisons with other IMPROVE species.

151. How are results from the PESA measurements most useful to the program?

    PESA measurements yield an independent measurement of hydrogen, providing a quality control cross-check for hydrogen-containing species.

152. Are all of the field sites visited for audit purposes at least once per year?

    Yes. Those that are missed for reasons out of our control are done by mail audit.

153. How often are flow rate devices calibrated with the spirometer at CNL? How is the spirometer evaluated for accuracy?

    The spirometer is no longer used. UCD Audit devices are now calibrated with a BIOS Drycal (DC-2 Flow Calibrator).

154. What action is taken when the annual site visit reveals a problem with the siting requirements such as overgrown trees or a newly constructed roadway?

    Siting criteria violations are documented in the site data sheets, and operators and/or site contacts are questioned on the violation details. If the violation is repairable (such as trees to be trimmed), it is coordinated with the site operator and/or contacts.

155. What are the most common mistakes made by the field operators?

    Sample change scheduling violations and upside down cartridge installations.

156. How important is it to know the local time at every field site?

    Very important. Clocks are reset at maintenance visits if they are >10 minutes off.

157. What additional training, if any, do the field operators need?

    Operators receive additional training during every Maintenance visit dependent on any equipment changes and/or program changes.