TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS
FROM: Eric Boswell / NAREL
COPY: Dr. Charles McDade / UC-Davis
AUTHOR: Jewell Smiley / NAREL
DATE: March 4, 2014
SUBJECT: UC-Davis Laboratory Audit

Introduction

On October 30-31, 2013, a Technical Systems Audit (TSA) was conducted at the Crocker Nuclear Laboratory (CNL) located on 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 1985. More information about the program can be found at the IMPROVE web site located at the following address. http://vista.cira.colostate.edu/improve

The audit was performed by Steve Taylor, Jewell Smiley, and Joann Rice. Steve and Jewell are physical scientists who work at EPA's National Analytical Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. Joann is also a physical scientist, and she works in EPA's Office of Air Quality Planning and Standards located in Research Triangle Park, NC. 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 fourth IMPROVE audit performed at CNL by EPA's audit team. A similar audit was performed in July of 2010 (see reference 1).

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 October 17. 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 just in time to begin the audit activities at 1 P.M. 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 so that experimental measurements could be made 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 – Anthony Kawamoto
- ✓ Gravimetric Laboratory – Anthony Kawamoto

- ✓ HIPS Laboratory – Margaret Cruz
- ✓ XRF Laboratory – Krystyna Trzepla, Sinan Yatkin, and Margaret Cruz

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

- ✓ Chuck McDade and Nicole Hyslop – IMPROVE Principal Investigators
- ✓ Xiaoya Cheng – Data Validation and Quality Assurance
- ✓ Rudi De Marco Ramey – Database Management and Application Development
- ✓ Warren White – Data Analysis
- ✓ Ann Dillner – Method Testing and Development

The Air Quality Group at CNL currently processes about 8000 air filter samples per month to support approximately 150 sampling stations that collect Particulate Matter (PM) from the ambient air every third calendar day. The workload includes supplying routine filter packs as well as quality control filters such as field blanks. 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 at CNL 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 $PM_{2.5}$ through a sodium carbonate denuder 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 collocated 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 the Research Triangle Institute (RTI) in Research Triangle Park, NC, for the Ion Chromatography analysis [see reference 2]. The quartz filters from channel "C" must be shipped to the Desert Research Institute (DRI) in Reno, NV, for the organic carbon/elemental carbon (OC/EC) analysis [see reference 3].

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 about 2% for the Teflon® and Nylon® filters and about 4% for quartz filters. The analytical results for the Nylon® and quartz samples are routinely adjusted for field blank contamination [see reference 4]. 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 active sampling since no air is drawn through the filter, but the filter is passively exposed to 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 be used repeatedly at the same field site.

A request was made to see the analytical results from recent field blanks. The auditors have carefully examined all of the field blank data from 2012 and prepared a summary of the field blank results shown in table 1.

Table 1. Summary of 2012 Field Blank Results

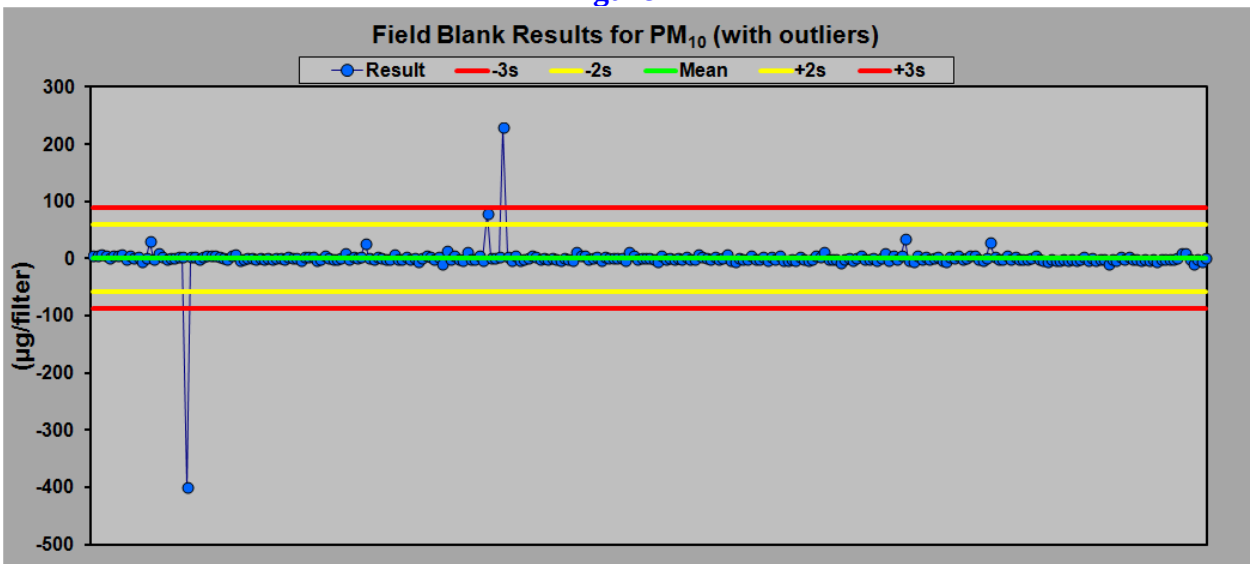
Analyte	Analysis	Concentration (µg/filter)							Number of Field Blanks
		Mean	Min	5th Percentile	95th Percentile	Max	Std. Dev.	MDL*	
Cl	IC	0.3	0.1	0.2	0.5	2.5	0.1	0.13	487
NO_2	IC	0.5	0.0	0.0	1.4	5.7	0.6	0.21	487
NO_3	IC	0.6	0.0	0.3	1.0	1.9	0.2	0.11	487
SO_4	IC	0.6	0.0	0.0	1.4	3.7	0.4	0.16	487
OC	Carbon	3.9	0.6	1.8	6.6	11.9	1.5	2.2	880
EC	Carbon	0.0	0.0	0.0	0.2	1.3	0.1	1.3	880
Na	XRF	0.03	-0.01	0.00	0.14	0.26	0.05	0.12	462
Mg	XRF	0.02	-0.10	-0.04	0.11	0.27	0.05	0.09	462
Al	XRF	0.02	-0.15	-0.05	0.18	1.18	0.10	0.06	462
Si	XRF	0.03	-0.06	-0.03	0.20	2.88	0.18	0.09	462
P	XRF	0.001	-0.002	0.000	0.006	0.012	0.002	0.007	462
S	XRF	0.002	0.000	0.000	0.010	0.320	0.016	0.008	462
Cl	XRF	0.002	-0.009	-0.004	0.013	0.041	0.006	0.008	462
K	XRF	0.008	-0.033	-0.010	0.049	0.377	0.029	0.036	462
Ca	XRF	0.018	-0.022	-0.015	0.107	0.757	0.065	0.062	462
Ti	XRF	0.002	-0.002	-0.001	0.007	0.095	0.007	0.010	462
V	XRF	0.000	-0.002	-0.002	0.003	0.007	0.002	0.003	462
Cr	XRF	0.000	-0.005	-0.003	0.004	0.032	0.003	0.004	462
Mn	XRF	0.000	-0.016	-0.009	0.010	0.017	0.005	0.008	462

Analyte	Analysis	Concentration (µg/filter)							Number of Field Blanks
		Mean	Min	5th Percentile	95th Percentile	Max	Std. Dev.	MDL*	
Fe	XRF	0.007	-0.045	-0.034	0.055	0.687	0.058	0.043	462
Ni	XRF	0.000	-0.004	-0.002	0.004	0.013	0.002	0.003	462
Cu	XRF	0.000	-0.011	-0.005	0.007	0.021	0.004	0.007	462
Zn	XRF	0.002	-0.007	-0.004	0.010	0.216	0.012	0.008	462
As	XRF	0.001	0.000	0.000	0.008	0.014	0.003	0.006	462
Se	XRF	0.000	-0.007	-0.005	0.007	0.012	0.004	0.007	462
Br	XRF	0.000	-0.006	-0.004	0.006	0.019	0.003	0.007	462
Rb	XRF	0.000	-0.010	-0.007	0.009	0.020	0.005	0.009	462
Sr	XRF	0.001	-0.007	-0.005	0.009	0.015	0.004	0.008	462
Zr	XRF	0.001	-0.064	-0.034	0.041	0.087	0.024	0.038	462
Pb	XRF	0.001	-0.029	-0.016	0.019	0.040	0.011	0.020	462
$PM_{2.5}$	Gravimetric	0.5	-8	-4	5	38	3.3	~5	481
PM_{10}	Gravimetric	1.4	-400	-4	10	229	29.6	~5	259

MDL = Average Method Detection Limit for the year 2012 field blanks

Table 1 includes several statistical parameters that were calculated from the pool of values reported for each analyte. Table 1 also includes an estimate of the laboratory MDL. It is interesting to compare each statistical parameter to the MDL. For example, the standard deviation and the MDL are approximately the same size for most analytes, but not for PM_{10}. On further inspection, the minimum and maximum values for PM_{10} are also extremely different from the MDL. Figure 1 is a graph of all the PM_{10} field blank values, and this graph shows at least three suspicious values.

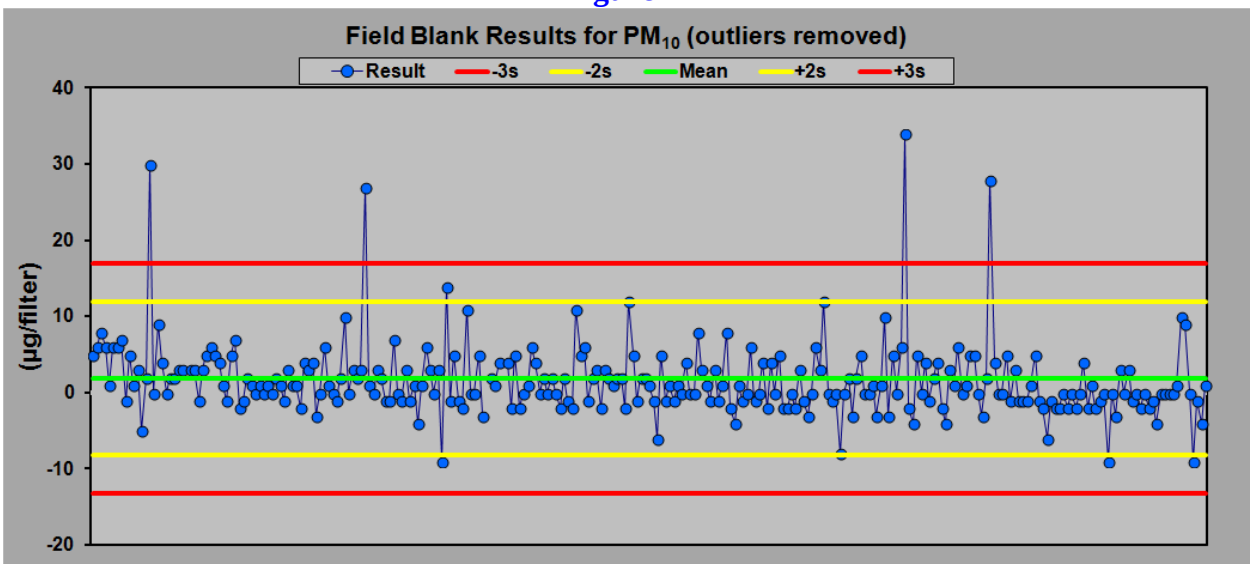
Figure 1



If the three suspicious values are removed from the pool of PM_{10} data, then the minimum, maximum, and standard deviation of the remaining values would be much closer to the MDL as shown in figure 2. The auditors were allowed to observe several different aspects of the data validation performed at CNL, and they were favorably impressed with the systems in place and the

level of effort used to identify errors in processing samples so that appropriate flags are placed on the affected results.

Figure 2



CNL maintains a supply of unexposed filters that are ready to send to the field sites for sampling. A request was made during the audit to remove a few filters from this supply for testing at NAREL. Two filters of each type were randomly selected and carried to NAREL for analysis. The audit team placed 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 were hand-carried back to NAREL for analysis to determine any contamination that may be present on the filters. Table 2 shows results from the analyses performed at NAREL.

Table 2. Results from Clean Filters Removed from CNL Stock.

Filter ID	Filter Description	Analysis	Parameter	Concentration (µg/filter)
Q13-15040	Quartz test filter #1	Carbon	EC	0.01
Q13-15041	Quartz test filter #2	Carbon	EC	0.03
Q13-15033	Quartz control filter #1	Carbon	EC	0.00
Q13-15034	Quartz control filter #2	Carbon	EC	0.00
Q13-15040	Quartz test filter #1	Carbon	OC	0.42
Q13-15041	Quartz test filter #2	Carbon	OC	1.01
Q13-15033	Quartz control filter #1	Carbon	OC	0.91
Q13-15034	Quartz control filter #2	Carbon	OC	0.86
N13-15042	Nylon® test filter #1	IC	Chloride	0.03
N13-15043	Nylon® test filter #2	IC	Chloride	0.05
N13-15048	Nylon® control filter #1	IC	Chloride	not detected
N13-15049	Nylon® control filter #2	IC	Chloride	not detected
N13-15042	Nylon® test filter #1	IC	Nitrite	0.60*
N13-15043	Nylon® test filter #2	IC	Nitrite	0.36*
N13-15048	Nylon® control filter #1	IC	Nitrite	0.40*

Filter ID	Filter Description	Analysis	Parameter	Concentration (µg/filter)
N13-15049	Nylon® control filter #2	IC	Nitrite	0.21*
N13-15042	Nylon® test filter #1	IC	Nitrate	not detected
N13-15043	Nylon® test filter #2	IC	Nitrate	not detected
N13-15048	Nylon® control filter #1	IC	Nitrate	not detected
N13-15049	Nylon® control filter #2	IC	Nitrate	not detected
N13-15042	Nylon® test filter #1	IC	Sulfate	not detected
N13-15043	Nylon® test filter #2	IC	Sulfate	not detected
N13-15048	Nylon® control filter #1	IC	Sulfate	not detected
N13-15049	Nylon® control filter #2	IC	Sulfate	not detected
T13-15044	Teflon® test filter #1	Gravimetric	PM2.5 Mass	1**
T13-15045	Teflon® test filter #2	Gravimetric	PM2.5 Mass	4**
T13-15046	Teflon® control filter #1	Gravimetric	PM2.5 Mass	-1
T13-15047	Teflon® control filter #2	Gravimetric	PM2.5 Mass	0

**** Nitrite values may be due to laboratory contamination at NAREL.***
*****Pre-mass determined at CNL and Post-mass determined at NAREL.***

No significant contamination was observed on the filters taken from CNL's stock. Please note that XRF analysis was not performed for the Teflon® filters listed in table 2. Also note that the $PM_{2.5}$ mass concentration of samples T13-15044 and T13-15045 was determined by using the pre-mass value determined at CNL and the post-mass value determined a few days later at NAREL. It should be stated that all of the test filters identified in table 2 were removed from CNL's stock of ready-to-use filters. All of the control 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.

SOPs were available that describe data processing and validation [see reference 4], filter procurement and acceptance testing [reference 5], filter cassette construction [reference 6], and sample handling [reference 7]. Two of these documents have not been updated since 1997, and some of the information is no longer accurate. Please note that CNL is in the process of updating all of its SOPs along with the IMPROVE Quality Assurance Project Plan (QAPP).

Gravimetric Laboratory

Anthony Kawamoto works with a small group of student employees that perform the gravimetric mass measurements. The audit team was able to interview Anthony while filters were being weighed. CNL has built a new weighing room since the last audit, and many of the procedures have been updated. Two Mettler XP-6 micro balances were setup for weighing. 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 building. The audit team brought a Dickson data logger which was placed in the weighing room at about 1:48 P.M. during the first day of the audit to monitor the temperature and relative humidity (RH). Dickson #11 was placed immediately near CNL's sensors for temperature and humidity so that measurements from both devices could be compared. The Dickson logger was set up to automatically record measurements every minute, and the CNL logger recorded measurements every five minutes. Results from the EPA logger are presented in figure 3 along with the official temperature and RH values provided by CNL.

Figure 3

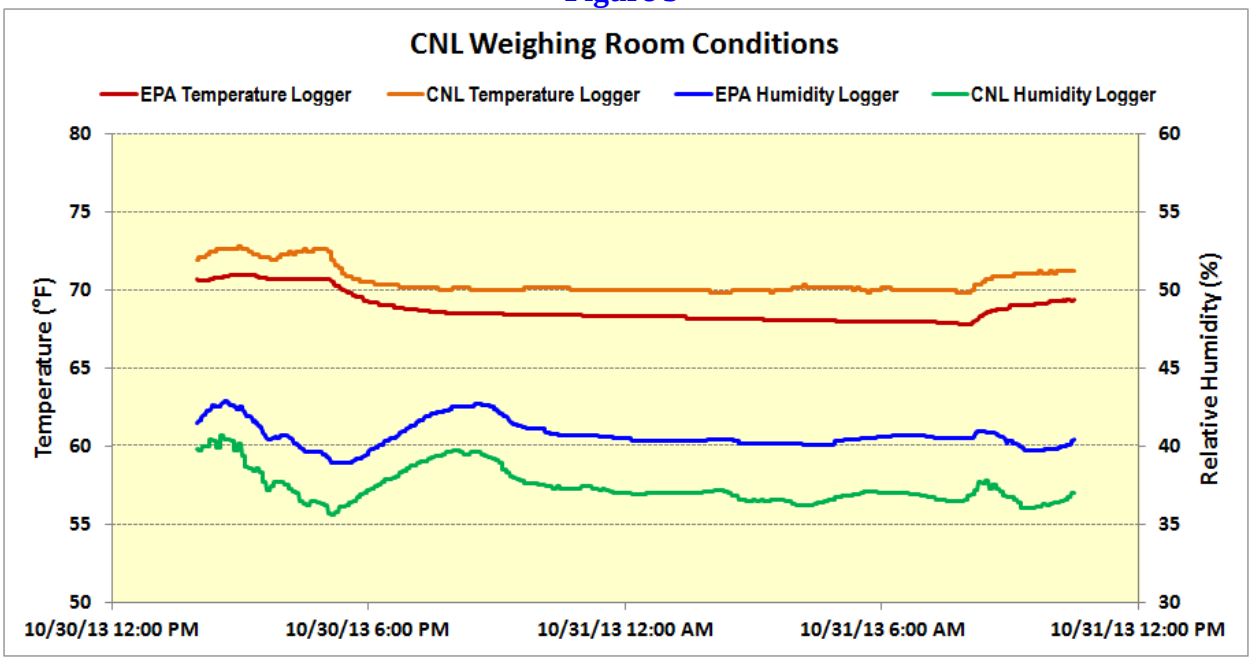


Figure 3 presents continuous data from the EPA and CNL loggers that were collected over the course of about twenty hours beginning during the afternoon of October 30. Only a small bias is observed between the EPA and CNL loggers for the temperature measurements and also for the humidity measurements. The EPA's Dickson logger has an expected accuracy of about ±1 °F for temperature and about ±2 % for relative humidity. It is compared to a NIST reference at least annually.

The filter handling process inside the weighing room has been organized for efficiency, and computer programs keep track of all gravimetric mass measurements. Two balances are available to deal with the large volume of work, and both balances are checked for weighing performance using the same sets of check standards and check samples. It is important to assess the performance between the two balances since it is common practice at CNL to pre-weigh a filter using one balance and post-weigh it using the other balance. A set of external metallic weights are measured by both balances at least three times daily and must be within three micrograms of the expected value for results to be accepted.

Performance is also monitored by weighing the laboratory control filters. CNL maintains a unique set of rotating filter blanks inside the weighing lab. This filter set includes thirty-two Teflon® filters assembled into labeled IMPROVE cassettes which do not leave the weighing lab. The individual filters that make up this collection are constantly changing. Each working day a new filter is

randomly selected from the CNL stock and added to the collection after it has been pre-weighed twice (once in the morning and again in the afternoon) using both balances. Each time a new filter is added to the set, the oldest filter is removed from its cassette and post-weighed in the morning and again in the afternoon using both balances. The pre-mass and post-mass values measured for a lab blank usually differ by about three micrograms, but if the difference exceeds ten micrograms, prescribed action must be performed to investigate the outlier. Furthermore, each filter measurement must be performed using both balances, and if the difference between balances exceeds three micrograms, the problem is noted and metallic check weights are immediately weighed to investigate the outlier. Weighing lab blanks from this collection provides a daily record of weighing performance.

A second set of experimental filters is kept inside the weighing room and reweighed every week. This filter collection contains ten blank filters and four "test" filters that have undergone special sampling. The ten lab blanks and four exposed "test" filters are weighed on both balances, and the weights are recorded in an Excel file. These filters are tracked to see how the mass differs over time for clean and sampled filters. Regular sampled filters returned from the field are not typically weighed more than once to develop precision data.

Several steps must be completed before a new 25-mm Teflon® filter is ready to ship to the field site. The Pall Corporation currently supplies new filters with a serial number already printed on the outer support ring of each filter. The new filters are kept in the weighing room. Each new filter must be visually inspected for obvious defects such as a torn or punctured membrane. After inspection the filter is pre-weighed using software that assigns that filter to a specific sampling event (date, location, and module). After the sampling event has been assigned, 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 the weighing room is not used to equilibrate filters by placing them into open containers for several hours. Post-weighing the filter is simply a step in the filter recovery, inspection, and documentation process. During the filter recovery process, 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 first 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. Following that audit, a few experiments were performed at NAREL that also provided 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 one of the CNL balances. The results from both labs are presented in table 3. Table 3 shows good agreement between the NAREL and the CNL mass values.

Table 3. Gravimetric Results from Audit Test Samples

Sample ID	Sample Description	NAREL Value (mg)	CNL Value (mg)	Difference (mg)
T13-15037	25-mm filter	41.909	41.906	-0.003
T13-15038	25-mm filter	42.490	42.488	-0.002

Sample ID	Sample Description	NAREL Value (mg)	CNL Value (mg)	Difference (mg)
MW13-15035	metallic standard	92.960	92.957	-0.003
MW13-15036	metallic standard	54.938	54.935	-0.003

The general procedures for measuring gravimetric mass at CNL are included within *SOP 251 Sample Handling* [see reference 7], with details provided in a separate document [reference 8]. These SOPs were updated last year to reflect the numerous changes in procedures due to building a new weighing lab and replacing all of the balances.

Analysis by HIPS

The Hybrid Integrating Plate/Sphere (HIPS) system provides a quantitative measure of light that is absorbed by the $PM_{2.5}$ deposit on a Teflon® filter. The instrument uses a helium-neon laser as the light source to illuminate the sample. The integrating sphere is used to collect light that is reflected from the sample, and the integrating plate is used to collect light that transmits through the sample. When the instrument is properly calibrated, a clean filter shows essentially zero light absorption.

Margaret Cruz was available to demonstrate the instrument for the auditors and answer any questions. She explained that results from the HIPS analysis have been used to help validate the OC/EC analysis performed at DRI. The OC/EC instrument also uses a helium-neon laser to illuminate the quartz filter sample so that changes in the reflected or transmitted light are recorded during the analysis to determine the total EC and total OC present in the sample.

CNL is the only speciation laboratory that performs the HIPS analysis. Only the IMPROVE module "A" filters are measured using the HIPS technique. A new SOP has been written that describes this analytical technique. Two documents are posted on the IMPROVE website that include the SOP itself and a technical information document that supplements the SOP [see reference 9 and 10].

X-Ray Fluorescence (XRF) Laboratory

Krystyna Trzepla, Sinan Yatkin, and Margaret Cruz were available to discuss the XRF operations with the auditors. Krystyna is the laboratory manager, Sinan is the resident spectroscopist, and Margaret demonstrated how samples are scheduled for the XRF analysis.

The XRF lab contains three PANalytical Epsilon 5 instruments: Froya, Odin, and Thor. Each instrument is set up to report a set of twenty-four elements previously listed in table 1. Samples are excited to fluoresce by using an x-ray tube to interact with a secondary target which in turn excites the sample. Seven spectra are sequentially generated for each filter sample by using seven different secondary targets mounted in the instrument. This analytical scheme offers good sensitivity for the range of elements reported. Calibrations are performed in the normal manner using thin film standards.

A loaded 25-mm Teflon® test filter was hand-carried from NAREL to CNL so that it could be analyzed by the XRF staff during the audit. The filter was submitted for analysis as a single-blind sample. The test filter had previously been analyzed at CNL in September of 2012, however, this information was not provided to the CNL staff. A decision was made to analyze the test filter three times so that the analytical precision could be demonstrated. Results from the three determinations made during the audit are presented in figures 4-6 along with the results from the 2012 analysis.

Please note that a 3-sigma uncertainty and MDL were available for the 2012 results and have been included in the figures.

Figure 4

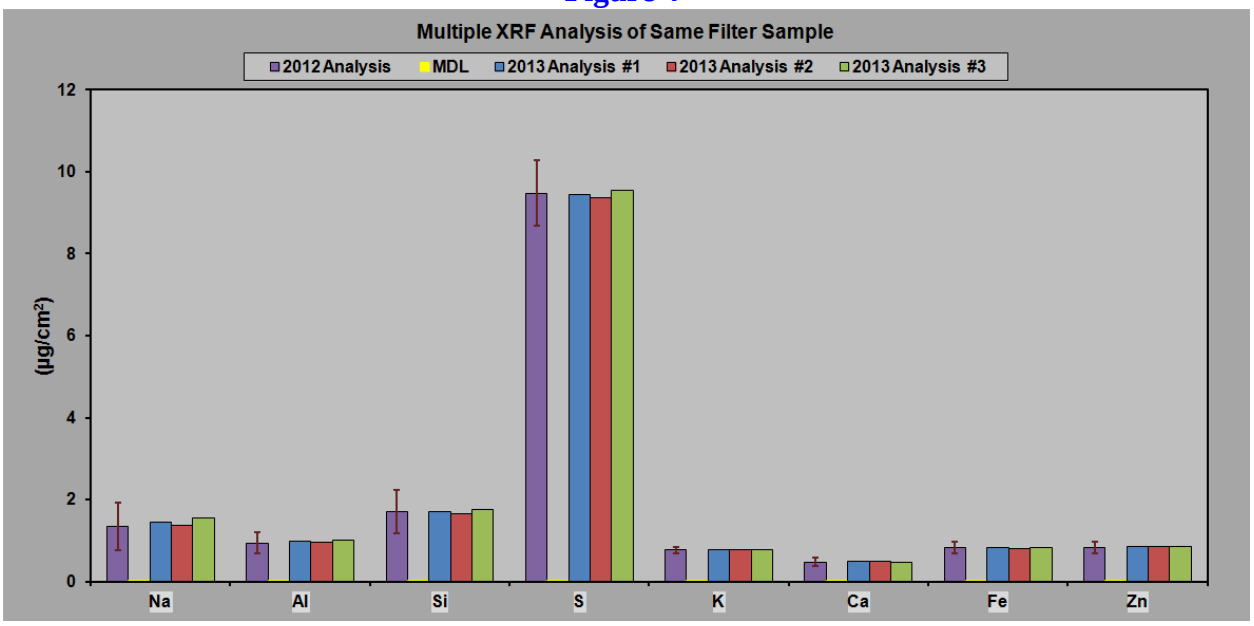


Figure 4 presents those eight elements that were most abundant in the test sample. All eight of the abundant elements show excellent precision and the audit results show excellent agreement with the 2012 analysis.

Figure 5

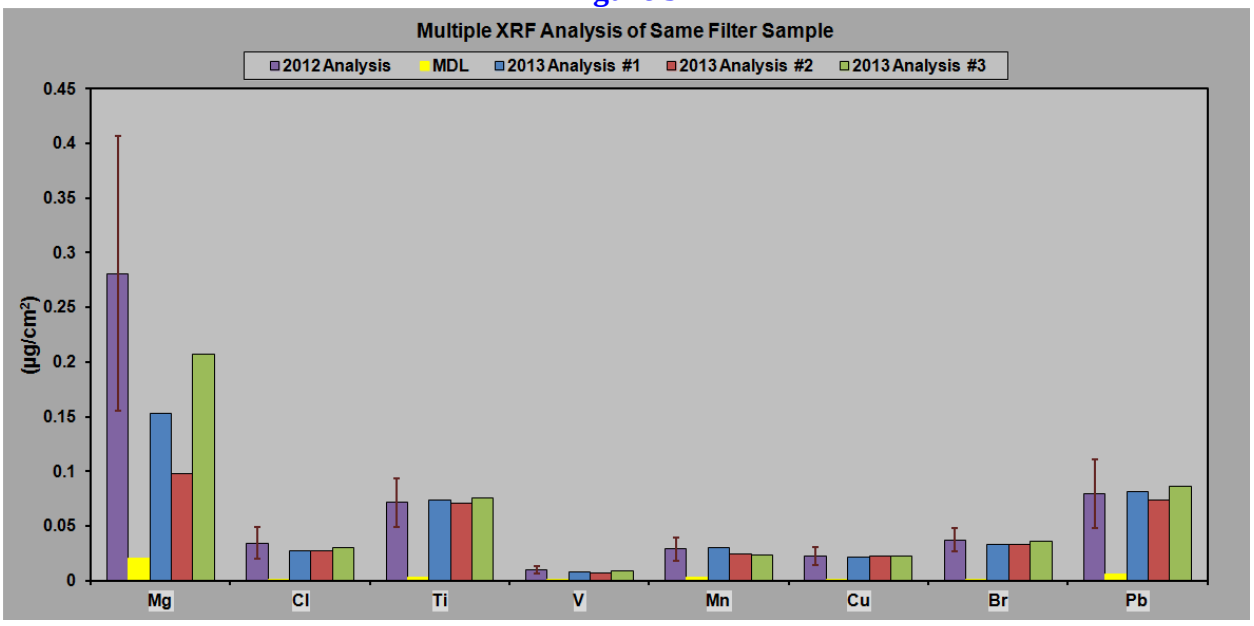


Figure 5 shows eight more elements that were less abundant in the test sample than those presented in figure 4. Some elements such as magnesium (Mg) are approaching the MDL and have relatively large uncertainty.

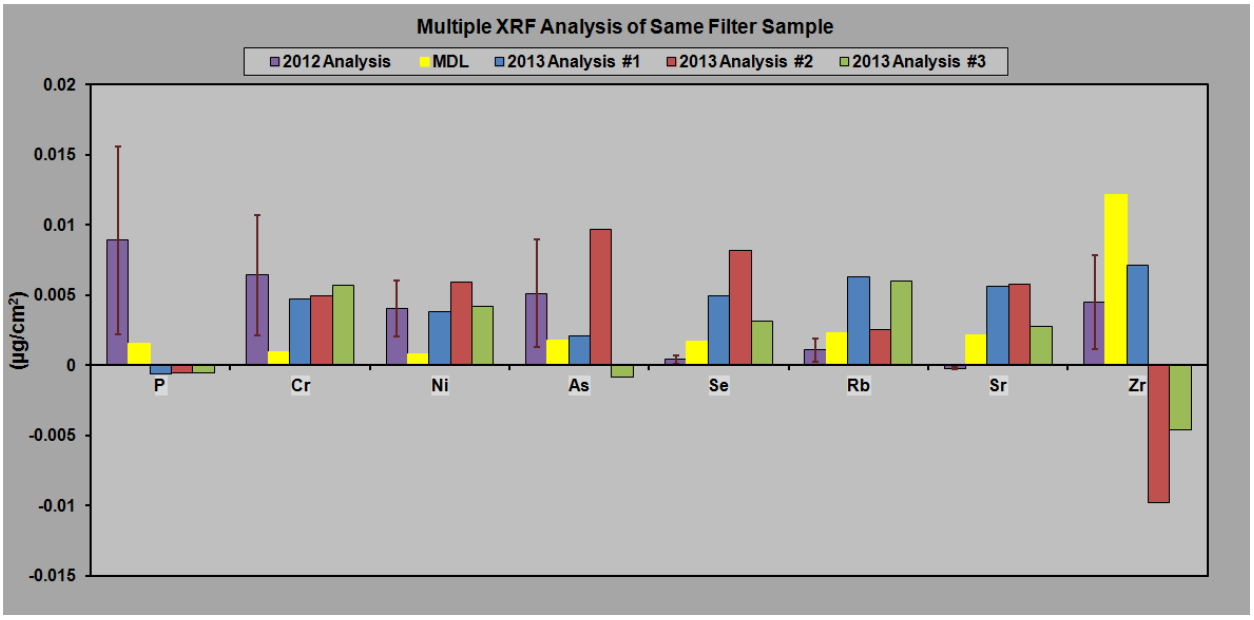


Figure 6

The eight elements at the lowest abundance in the test sample are presented in figure 6. Some of the results are actually negative values, but that is perfectly acceptable when the concentration is near the MDL. It is interesting to notice that the 3-sigma uncertainty reported for strontium (Sr) is significantly smaller than the MDL. It is useful to know that the MDL values were determined empirically, based on the observed distribution of field blank loadings from the IMPROVE network. The expressed uncertainties were calculated as a prescribed proportion of the measured filter value, and the uncertainty proportion for each element was determined empirically, based on observed differences between collocated measurements in the IMPROVE network.

The XRF lab has changed dramatically since the last EPA audit. Previously all of the instruments were designed and built in-house, and now a popular commercial instrument is being used. The XRF lab produces an incredible amount of data, and it was good to see that excellent quality controls were in place and significant work is being done to carefully examine the data before it is released. A new SOP for the XRF analysis has been completed, and it will be posted on the IMPROVE web site soon.

Other Staff Interviews

Chuck McDade has been the central facilitator for this audit. He has provided rapid response to requests for information from the audit team both preceding the audit as well as during the follow-up. Chuck has been a principal investigator for the air monitoring group for many years, and now Nicole Hyslop is also a principal investigator. As principal investigators, both are familiar with the overall operations and both are familiar with the wide range of tools that are used to examine the huge data sets generated by the IMPROVE network.

Xiaoya Cheng spends most of her time validating data and looking at quality control plots. For example, time series plots were being used to examine popular items such as sulfate ion versus three times the XRF sulfur. The auditors were very impressed with the variety of plots that are routinely examined to monitor trends and spot problems (see reference 4).

Ann Dillner has been working on a new method for measuring the ambient particulate organic matter (OM) as it appears on the IMPROVE channel "A" Teflon® filter. The method uses mid-infrared (MIR) spectroscopy to quantify alkanes, alcohols, carboxylic acids, and carbonyl containing compounds that are present in the captured $PM_{2.5}$. The OM is estimated by summing these functional groups in the sample. Calibrations have been developed using a multivariate regression technique. The new method offers an alternative approach to estimating the OM for visibility assessments under the Regional Haze Rule. Historically the OM has been estimated by multiplying the thermal optical OC by a factor (usually ~1.8). The multiplier is needed because the thermal optical method only measures carbon, and the OM contains other elements such as hydrogen, oxygen, and nitrogen that are bonded to the carbon. The thermal optical method does not account for the dynamic temporal and spatial variation in the OM/OC ratio which has already been observed using the new method.

Conclusions

This audit has produced many positive findings that were described earlier in this report. Only a few negative findings were observed all of which are in the realm of documentation. The audit team was told before this inspection that some 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 some 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 same approach was taken for previous audits performed in 2005, 2007, and 2010. The audit questionnaire with updated responses has been added as Appendix A to this report.

The following QA documents must be updated to accurately reflect the current procedures, equipment, objectives, policy, and personnel.

- SOP TI 101A Filter Procurement and Acceptance Testing (reference 5)
- SOP TI 101D Filter Cassette Construction (reference 6)
- IMPROVE Quality Assurance Project Plan (QAPP) http://vista.cira.colostate.edu/improve/Publications/QA_QC/IMPROVE_QAPP_R0.pdf

Please note that the IMPROVE QAPP is actively under revision at this time, and the new version should be ready to release later this year.

References

1. EPA/NAREL. January 11, 2011. Technical Memorandum: UC-Davis Laboratory Audit. U.S. Environmental Protection Agency. [currently available on the web] http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/UCD_2010_audit_report.pdf
2. RTI. October 26, 2005. *Standard Operating Procedures for National Park Service Filter Preparation, Extraction, and Anion Analysis*, Research Triangle Institute, Research Triangle Park, NC. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/RTI_SOPs/RTI_IonSOP102605.pdf

3. DRI. October 22, 2012. *DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A*, Desert Research Institute, Reno, NV. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/DRI_SOPs/2012/IMPROVEA_2-216r3_20121022small.pdf

4. IMPROVE. July 16, 2008. SOP 351, *Data Processing and Validation,* Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdavis_sops/sop351_V2.pdf

5. IMPROVE. February 12, 1997. SOP TI 101A, *Filter Procurement and Acceptance Testing*, Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdavis_sops/ti101a.pdf

6. IMPROVE. February 12, 1997. SOP TI 101D, *Filter Cassette Construction,* Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdavis_sops/ti101d.pdf

7. IMPROVE. April 23, 2013. SOP 251, *Sample Handling Laboratory*, Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/UCDavis_SOPs/SOP251_Sample_Handling_2013.pdf

8. IMPROVE. April 23, 2013. SOP TI 251, *Sample Handling Laboratory*, Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/UCDavis_SOPs/SOP251_TI_2013.pdf

9. IMPROVE. July 18, 2013. SOP 276, *Optical Absorption Analysis of $PM_{2.5}$ Samples*, Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdavis_sops/SOP276_Optical_Absorption_2013.pdf

10. IMPROVE. July 18, 2013. SOP TI 276, *Optical Absorption Analysis of $PM_{2.5}$ Samples*, Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently available on the web] http://vista.cira.colostate.edu/improve/Publications/SOPs/UCDavis_SOPs/SOP276_TI_2013.pdf

11. IMPROVE. January 17, 2014. SOP 301, *IMPROVE Standard Operating Procedure for the X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*, Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, CA. [currently not yet available on the web]

Appendix A

Advanced Questions and Responses for the
Technical Systems Audit of the IMPROVE Program at UC-Davis
Scheduled for October 30-31, 2013

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

   Crocker Lab Director – Tony Wexler
   IMPROVE Principal Investigators – Chuck McDade, Nicole Hyslop
   Operations Manager – Nicole Hyslop
   Data Validation & Quality Assurance – Chuck McDade, Xiaoya Cheng
   Method Testing & Development – Ann Dillner
   Data Analysis – Warren White
   Database Management & Application Development– Rudi De Marco Ramey
   Application Development/QC Analyst – Sean Raffuse
   Laboratory Manager – Krystyna Trzepla
   Spectroscopist/XRF QA – Sinan Yatkin
   Lab Operations – Anthony Kawamoto, Margaret Cruz
   Field and Shop Operations Manager – Jose Mojica
   Field Operations –Reuben Krofft, Michael Truong
   Design Engineers – Doug Gordon, Chris Wallis
   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. PESA was discontinued effective January 2011 (sample date).

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?

   Unexposed (fresh) filters will be readily available, but exposed filters cannot be released without prior authorization. Before releasing exposed 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.

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

We expect to spend an hour or less on this discussion. We have participated in several analyses of PE samples and the existing protocol seems to work well.

8. Is access to the facility limited and controlled?

   Yes. The main Crocker building and the Annex are always locked. Both buildings have 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 and Nicole Hyslop, the Principal Investigators (PI), have 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 for repairs. 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. Filter inventory is also tracked using a separate Excel spreadsheet for each type of filter. 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 (visits are now once every two years to accommodate recent budget cuts). Complete records are maintained from each visit, including calibration records, maintenance comments, and site photos. External audits have been 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. We are making the transition to a new ticketing system called Jira. This new system will allow us to better track our progress on addressing problems, but the information contained will be similar to that in the Problems File.

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

    All summaries of quality measurements by XRF contain monitoring (daily/weekly/monthly) with blanks, ME samples and reanalysis samples are located on U:\IMPROVE_Lab\XRF_Epsilon5\QA in appropriate folders.

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?

SOPs are revised every few years as needed, when significant and broad-based changes have been made to our operations. During the intervening periods we issue data advisories to alert data analysts to specific changes in procedures that may affect their analyses. The objective of the data advisories is to alert data users to non-atmospheric influences on the data. The data advisories can be found on the IMPROVE website at:

http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm

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

    Old versions of SOPs are retained at CNL and are available on the VIEWS website, 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.

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 three times a day: 7:00am, 12:30pm, and 3:00pm.

    b. Incremental backups of user files to our backup server every Wednesday and Saturday with a full backup the first Saturday of the month.

    c. Backups of SQL database are done every night at 2:00am.

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 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 database also documents changes electronically, 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. Many of these records are maintained electronically 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. .

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 database electronically documents every data entry and data edit, indicating when and by whom the changes were made. These records are reviewed as necessary during data validation.

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 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 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?

    The final versions of all SOPs and other formal project documentation are archived in the "Publications" section of the IMPROVE website:

    http://vista.cira.colostate.edu/improve/Publications/publications.htm

    With SOPs, for example, the most current version of the SOP is shown at the left margin (with its version number) and older archived versions are listed at the bottom of the page.

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

    Yes, all are archived in the "Publications" section of the IMPROVE website (see above).

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

    Yes. As described above, the most current version of documents that have been revised is shown at the left margin and older archived versions are shown below it.

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

    No. All of our revisions are made electronically. The use of pen-and-ink is rare.

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?

    The most significant deviation from the QAPP lies in our Measurement Quality Objectives (MQOs). Since initiating collocated sampling in 2003 we have come to understand that we have been underreporting the uncertainties associated with some species (see question #46, below). We expect to recommend revised MQOs to be incorporated into the QAPP.

    Other deviations from the QAPP reflect specific changes in procedures. For example, the QAPP still refers to PIXE, which has been replaced by XRF for elemental analysis.

43. How are any deviations from the QAPP noted?

    During the past few years we have begun issuing data advisories to alert data analysts to changes in procedures or in data quality that may affect their analyses. The objective of the data advisories is to alert data users to non-atmospheric influences on the data. The

data advisories can be found on the IMPROVE website at:

http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm

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

    Those measurements required for reconstructed extinction as described in Section 4.5 of the QAPP. The species shown in Equation 1 of that section are the species of interest to the Regional Haze Rule data analysts.

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

    Yes, in Section 4.6.

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

    Collocated data have been collected for almost 10 years now, and we use these data along with laboratory QA data to evaluate our performance in achieving our MQOs. Analysis of the collocated data suggests 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.

    XRF recalibrations are performed when established limits were exceeded, based upon routine calibration checks. For gravimetric analysis, standard metal weights and blank filters are weighed to test balance performance, and recalibrations are performed as needed. Flow rate data are evaluated on a regular schedule, based on the flashcard data, and sites are identified that exceed specifications. Samplers at these errant sites are recalibrated as needed.

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

    Yes, all of the actions described in #47 have been performed as needed.

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 other 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. It is posted on the IMPROVE website at:

    http://vista.cira.colostate.edu/improve/Publications/publications.htm

51. Is the QMP current?

    The QMP was last revised in 2002. Revision of this document is at the discretion of EPA/OAQPS.

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

We meet every Thursday morning.

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 and Nicole Hyslop are responsible for IMPROVE project decisions, and Tony Wexler for Crocker Lab resources. All 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?

    The IMPROVE SOPs for the UC Davis field, laboratory, and data processing operations can be found on the IMPROVE website at:

    http://vista.cira.colostate.edu/improve/Publications/SOPs/ucdsop.asp

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

    Most are, and others are under revision to reflect changes in equipment and procedures. As noted previously, SOPs are revised every few years, when significant and broad-based changes have been made to our operations, and data advisories are issued as needed to alert data analysts to specific changes in procedures that may affect their analyses.

60. Do the SOPs address calibrations and their frequency?

    Yes. SOP 176 covers calibration of the IMPROVE aerosol sampler. The SOP for each analytical method contains a section on calibration of that method.

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

    Yes. As an example, see Sections 6 and 7 in SOP 276 (Optical Absorption Analysis).

62. Do the SOPs include preventive and remedial maintenance?

    Yes. As an example, see SOP 226 (Annual Site Maintenance).

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

    These procedures are described in SOP 351 (Data Processing and Validation).

64. How are measurement uncertainties calculated?

    The calculation procedure is described in SOP 351 (Data Processing and Validation). See, in particular, Section 5.3.

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?

    This information is covered for field site operators in SOP 201 (Sampler Maintenance by Site Operators), which was revised in 2005. For operations performed in Davis, this information is contained in each system's SOP (e.g., XRF, sampling handling, etc.).

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?

    XRF (Teflon) or IC (nylon) analyses are performed for several blank filters from the new lot, and the results are compared against results from the current lot and from prior lots. The results are plotted to identify any deviations from expected behavior. In addition to these tests for chemical contamination, the pressure drop across several filters is measured and compared to filters from the current lot.

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?

    Quartz (carbon) and nylon (ions) filters are shipped to DRI and RTI, respectively, several times a month, so filters are typically shipped to these labs within about a week after receipt at UC Davis. Multiple reanalysis by XRF has demonstrated that elemental measurements remain stable over long periods, months to years. Thus, there appears to be no effective maximum holding time for XRF analysis.

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.

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?

    We have developed an aerosol generation chamber for the preparation of samples of known composition. The loadings on these filters are determined independently through gravimetric analysis. These samples are submitted to our XRF lab for analysis.

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

    Formal systems audits are not conducted. However, system performance is monitored regularly (approximately weekly) through calibration checks and reanalysis of selected samples.

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 flow rates 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, Reuben Krofft, Michael Truong, and Anthony Kawamoto are authorized to amend field records. Amendments are logged in the Problems file.

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

A second 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. The calibration has been recertified by the manufacturer.

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?

Mettler XP-6

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?

Yes, Mettler services our balances as needed.

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?

    Both of our balances are Mettler XP-6. We no longer have different model balances in our 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 pre-sampling and post-sampling conditioning?

    Yes, before pre weight and post weight.

105. What happens when a defective filter is discovered during pre-sampling inspection?

    They are set aside to be returned to the manufacturer.

106. What happens when a defective filter is discovered during post-sampling inspection?

    They are flagged 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 pre-sampling and post-sampling 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?

Teflon and Nylon, 2%, and Quartz 3%.

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 post-sampling weighing completed within 10 days after the end of the sample period?

Not necessarily, but the post-sampling 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 network.

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?

The data reported to CIRA and to AIRS 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 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)
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 also report 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. Network metrics (95%ile, median, etc.) comparison

v. Al/Fe, Si/Fe, …….

vi. 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 data flags were chosen to assist data analysts in interpreting data collected under a variety of measurement conditions. The current list of flags 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 2.25-2.75 micro-m range. This corresponds to flow rates < 19.7 L/min or > 24.1 L/min. A value is reported.
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.
TU	Data Flag	Time differs from typical midnight-to-midnight schedule.
XX	Data Flag	The filter is damaged.

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. More recently we have analyzed by XRF a 15-year sequence of samples from 3 sites – MORA1, PORE1, and GRSM1. PIXE represented a portion of the original 15-year record.

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

    The PANalytical Epsilon 5 collects spectra for IMPROVE using each of seven secondary targets – CaF_2, Fe, Ge KBr, SrF_2, Mo, and Al_2O_3.

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

    The XRF energy calibration process consists of repeated measurements of the Tungsten beam stop permanently installed in the Epsilon 5. During the process, the signals coming from the detector to the DSP (Digital Signal Processor) are placed into the appropriate energy channels. The calibration is typically performed on a weekly basis, following the

weekly LN2 fill on Thursdays. The analysis needs to be stopped to perform the energy calibration.

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

Epsilon 5 utilizes a PAN-32 Ge X-ray detector. Resolution of 135 eV or less (@2000 cps, Mn Ka) is requeried for acceptable analysis.

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

Currently 136 single and multi-elemental foils.
Yes, a few elements for which the standards are non-stoichiometric

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

XRF standards and samples are introduced to the X-rays in the same geometry.

All IMPROVE samples are collected on PTFE filters, while standards have Nuclepore and PTFE as backing material.

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

A few multi-elemental standards were prepared for us on Nuclepore by Micromatter utilizing layered vacuum deposition.

In addition, we prepared multi-elemental standards from certified ICPMS solutions utilizing an aerosol chamber and IMPROVE sampler developed in our lab.

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

All spectra from IMPROVE samples and field blank are processed with the PANalytical Epsilon 5 peak deconvolution software, and peak intensities are determined for all elements identified by the instrument. Sample peak intensities are then blank corrected to account for background contamination from the filter substrate and spectral noise. The blank correction is performed by subtracting from each element's sample intensity the median value of the intensities from the most current 25 field blanks.

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

No attenuation corrections are made.

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

See question 139.

139. How is the XRF uncertainty calculated?

The analytical uncertainty of XRF measurements is estimated according to the Guide to the Expression of Uncertainty in Measurement using Equation 1.

$$U_{ci} = 2\sqrt{\frac{u^2(I_{raw,i})}{b_{cal,i}^2} + \frac{u^2(I_{blank,i})}{b_{cal,i}^2} + \left(\frac{(I_{raw,i} - I_{blank,i})}{b_{cal,i}^2}\right)^2 u^2(b_{cal,i})}$$ where, $b_{cal,i}$

is the calibration factor of element i [(cps/mA)/(μg/cm^2)] calculated as the slope of linear regression between elemental concentrations of calibration standards and their blank corrected intensities (intercept was set to zero), $I_{raw,i}$ is the raw intensity of element i (cps/mA) in the sample and $I_{blank,i}$ is the raw intensity of element i (cps/mA) in the blank. The $u(b_i)$ values were estimated including the lack of linear fit between mass loadings of standards and their raw intensities, uncertainty of standards and repeatability of instrumental response. For $u(I_{raw,i})$ and $u(I_{blank,i})$, the repeatability was calculated as the standard deviations of multiple replicated analyses of samples and blanks.

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

    SOP 351 was updated in 2008, after PIXE had been discontinued, and the equations represent our most current knowledge of the measurements. In ongoing work, results from our collocated sampler tests are being used to identify elements for which our uncertainties appear to be underreported. Any changes will be driven by the need to discern long-term trends, not by the specifics of a particular measurement.

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

    The system is setup to correct automatically for dead times up to 50%. The current and real time of analysis are adjusted accordingly.

142. Are negative concentrations reported?

    Negative concentrations are reported for species which are artifact or blank corrected. 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. Warren White has been comparing HIPS optical absorption data to elemental carbon (EC) data. EPA has an interest in estimating historical levels of EC and they have considered measuring HIPS optical absorption on archived Teflon filters as a surrogate.

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?

    As noted above, Warren White's data analysis has investigated the reliability of HIPS data as a surrogate for EC. His results suggest some promise in this approach.

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.

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?

    PESA was discontinued in 2011.

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

    PESA was discontinued in 2011.

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

    Due to budget reductions each site is now visited once every two years.

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. During this past year we have produced a series of training videos for the site operators.