



TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS
FROM: Eric Boswell / NAREL
COPY: Dr. Richard Tropp / DRI
AUTHOR: Steve Taylor / NAREL
DATE: March 6, 2014
SUBJECT: DRI Laboratory Audit

Introduction

On October 29, 2013, a technical systems audit (TSA) was conducted at the Environmental Analysis Facility (EAF) located at the Desert Research Institute (DRI) in Reno, Nevada. This TSA was performed as part of the quality assurance oversight provided by the U.S. Environmental Protection Agency (EPA) for the PM_{2.5} Chemical Speciation Network (CSN) and also for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. This audit was a routine inspection of laboratory operations at the EAF.

DRI has provided the thermal/optical carbon analysis for the IMPROVE program since the program began in 1985. This support includes pre-treatment and analysis of 25-millimeter quartz-fiber filters to determine the organic carbon and elemental carbon (OC/EC) fractions present on the filter. IMPROVE carbon results are reported to the Crocker Nuclear Laboratory (CNL) located on the campus of the University of California at Davis. CNL is the coordinating laboratory for all field operations and speciation laboratory work for the IMPROVE program.

DRI has also been subcontracted by Research Triangle Institute (RTI) to provide OC/EC analysis for all CSN quartz filters. DRI has been providing OC/EC analysis of CSN samples using the IMPROVE_A method since 2007.

A significant contract for air monitoring support was awarded to DRI in 2004 by the Texas Commission on Environmental Quality (TCEQ). The TCEQ contract includes comprehensive laboratory support for their supplemental PM_{2.5} CSN sites, including micro-gravimetric mass, ions, XRF and carbon analysis. Support also includes sites that monitor PM_{2.5} mass using the federal reference method (FRM). DRI provides shipping and analysis of filter samples, data management, database development, training, and project management (reference 1 and 2).

The audit team included Steve Taylor, Jewell Smiley, and Joann Rice. Steve and Jewell are physical scientists at EPA's National Analytical Radiation Environmental Laboratory (NAREL) located in Montgomery, Alabama. Joann is a physical scientist at the EPA's Office of Air Quality Planning and Standards (OAQPS). This TSA was the fourth EPA inspection of the EAF laboratory operations at DRI. A report from the last TSA, conducted in 2010, is available on the web (reference 3).

Summary of Audit Proceedings

This TSA required a significant amount of advanced planning and communication before the auditors actually traveled to DRI. Auditors were provided copies of the laboratory standard

operating procedures (SOPs) and other quality assurance documents to study before the audit. A preliminary agenda was prepared and distributed so that DRI staff would be available for interviews and would also be available to participate in several experimental activities planned for the audit.

The first item on the agenda was a brief meeting with DRI senior staff and laboratory supervisors at which time the audit team gave an overview of the audit process. The agenda included inspection of the following operational areas.

- ✓ Sample Shipping, Receiving, and Handling
- ✓ Information Management
- ✓ Gravimetric Laboratory
- ✓ Organic Carbon/Elemental Carbon (OC/EC) Laboratory
- ✓ X-Ray Fluorescence (XRF) Laboratory
- ✓ Ion Chromatography (IC) Laboratory

Several experimental activities were on the agenda which were discussed with DRI staff during the briefing. Blind samples had been prepared at NAREL for each analytical area and brought to the audit so that analysts could be observed performing the analysis and results could be compared to expected values. The details of these experiments will be described later within the appropriate section of this report.

The following DRI managers were available to assist the audit team and also were invited to participate in the discussions with technical staff.

- ✓ Dr. Richard Tropp – TCEQ Principal Investigator and Project Manager
- ✓ Dr. Judith Chow – EAF Director and Senior Technical Advisor
- ✓ Dr. John Watson – EAF Quality Assurance Manager and Senior Technical Advisor
- ✓ Brenda Cristani – EAF Shipping, receiving and gravimetric laboratory
- ✓ Dana Trimble – EAF Assistant Research Scientist, carbon laboratory
- ✓ Steven Kohl – EAF Associate Research Scientist, XRF laboratory

Sample Shipping, Receiving and Handling Laboratory

DRI currently provides laboratory support for more than three hundred CSN and IMPROVE air monitoring sites. The majority of the samples received at the EAF are quartz filters from the IMPROVE and CSN programs that require the OC/EC analysis. Samples received from the TCEQ speciation sites require the OC/EC analysis and also elements by XRF, selected ions by IC, and measurement of the PM_{2.5} gravimetric mass. All CSN OC/EC analyses for TCEQ are performed using the IMPROVE_A method. The Texas supplemental CSN sites are unique in that Nylon® filters are not used to collect ions. TCEQ uses only Teflon® and quartz filters for PM_{2.5} sampling. Teflon® filters and R&P model 2025 samplers are paired with quartz filters and URG 3000N samplers to accomplish TCEQ's PM_{2.5} collection.

Ms. Brenda Cristani is responsible for coordinating the sample shipping and receiving activities. Brenda and Krista Phelps were available to explain how clean filters are prepared for shipment to the Texas field sites, and exposed filters are received back at the laboratory ready for analysis (reference 4 through 7). Tasha Pascal from the carbon analysis lab was also present to describe sample handling procedures used for quartz filters used by the IMPROVE program. Record books and other documentation were available for the auditors to examine in order to verify that standard operating procedures were being followed. After each sampling event is complete, the exposed filters are returned to the EAF where the quartz filter is scheduled for OC/EC analysis, and the exposed Teflon® filter is first scheduled for post-weighing to determine the PM_{2.5} mass after which it is scheduled for XRF analysis, and finally the Teflon® filter is extracted so that the extract can be analyzed for ions using IC.

The EAF 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. Results from the analyses performed at NAREL are shown in table 1.

Table 1. Results from Clean Filters Removed from DRI Stock

Filter ID	Filter Description	Analysis	Parameter	Concentration (µg/filter)
Q13-15021	25-mm quartz test filter #1	Carbon	EC	-0.02
Q13-15022	25-mm quartz test filter #2	Carbon	EC	0.00
Q13-15023	47-mm quartz test filter #1	Carbon	EC	0.12
Q13-15024	47-mm quartz test filter #2	Carbon	EC	1.66
Q13-15033	Quartz control filter #1	Carbon	EC	0.00
Q13-15034	Quartz control filter #2	Carbon	EC	0.01
Q13-15021	25-mm quartz test filter #1	Carbon	OC	2.01
Q13-15022	25-mm quartz test filter #2	Carbon	OC	1.02
Q13-15023	47-mm quartz test filter #1	Carbon	OC	1.70
Q13-15024	47-mm quartz test filter #2	Carbon	OC	0.86
Q13-15033	Quartz control filter #1	Carbon	OC	3.07
Q13-15034	Quartz control filter #2	Carbon	OC	2.90
T13-15025	Teflon® test filter #1	IC	Ammonium	-0.013
T13-15026	Teflon® test filter #2	IC	Ammonium	-0.012
T13-15029	Teflon® control filter #1	IC	Ammonium	-0.012
T13-15030	Teflon® control filter #2	IC	Ammonium	-0.012
T13-15025	Teflon® test filter #1	IC	Chloride	not detected
T13-15026	Teflon® test filter #2	IC	Chloride	not detected
T13-15029	Teflon® control filter #1	IC	Chloride	not detected
T13-15030	Teflon® control filter #2	IC	Chloride	not detected
T13-15025	Teflon® test filter #1	IC	Nitrate	0.016
T13-15026	Teflon® test filter #2	IC	Nitrate	0.017
T13-15029	Teflon® control filter #1	IC	Nitrate	not detected
T13-15030	Teflon® control filter #2	IC	Nitrate	not detected

Filter ID	Filter Description	Analysis	Parameter	Concentration (µg/filter)
T13-15025	Teflon® test filter #1	IC	Potassium	not detected
T13-15026	Teflon® test filter #2	IC	Potassium	0.008
T13-15029	Teflon® control filter #1	IC	Potassium	not detected
T13-15030	Teflon® control filter #2	IC	Potassium	not detected
T13-15025	Teflon® test filter #1	IC	Sodium	0.015
T13-15026	Teflon® test filter #2	IC	Sodium	0.014
T13-15029	Teflon® control filter #1	IC	Sodium	0.009
T13-15030	Teflon® control filter #2	IC	Sodium	0.009
T13-15025	Teflon® test filter #1	IC	Sulfate	not detected
T13-15026	Teflon® test filter #2	IC	Sulfate	not detected
T13-15029	Teflon® control filter #1	IC	Sulfate	not detected
T13-15030	Teflon® control filter #2	IC	Sulfate	not detected
T13-15027	Teflon® test filter #1	Mass	PM2.5 Mass	-10*
T13-15028	Teflon® test filter #2	Mass	PM2.5 Mass	2*
T13-15031	Teflon® control filter #1	Mass	PM2.5 Mass	-1
T13-15032	Teflon® control filter #2	Mass	PM2.5 Mass	0

**Pre-mass determined at DRI and Post-mass determined at NAREL (corrected for buoyancy)*

No significant contamination was observed on the filters taken from DRI's stock. Please note that XRF analysis was not performed for the Teflon® filters listed in table 1. Also note that the PM_{2.5} mass concentration of the test filters was determined by using the pre-mass value determined at DRI and the post-mass value determined a few days later at NAREL. Both values were corrected for the buoyant lifting force of the air as discussed later in the gravimetric section of this report.

There is a potential to contaminate filters due to sample handling in the laboratory and in the field. Field blanks are included with every shipment of filters to monitor for contamination. The field blank is handled with the same procedures as routine samples except that no air is sampled through the field blank. The audit team made a request to examine recent field blank results from the TCEQ program. A summary of those results is presented in table 2 covering a period from the first quarter of 2012 through the second quarter of 2013.

Table 2. Summary of Recent TCEQ Field Blank Data

Parameter	Analysis Method	Concentration (µg/filter)						Number of Field Blanks
		Average	Min	Max	Std. Dev.	LQL*	MDL **	
PM _{2.5} Mass	Gravimetric	4	-19	40	9	28	15	94
OC (TOR)	IMPROVE_A Method with URG 3000N samplers and 25-mm filters implemented in January of 2010	4.40	1.33	15.49	2.06	6.17	2.91	99
EC (TOR)		0.04	0	0.70	0.12	0.35	2.40	99
OC1		0.61	0	2.43	0.50	1.49	0.42	99
OC2		1.32	0.47	2.76	0.49	1.48	0.55	99
OC3		2.31	0.70	11.94	1.38	4.13	1.69	99
OC4		0.16	0	1.24	0.23	0.70	1.86	99
PyroIC (TOR)		0.01	0	0.70	0.07	0.22	1.61	99
Nitrate	IC	0.20	0	0.88	0.25	0.74	0.52	94

Parameter	Analysis Method	Concentration (µg/filter)						Number of Field Blanks
		Average	Min	Max	Std. Dev.	LQL*	MDL**	
Sulfate	IC	0.15	-0.05	1.91	0.23	0.70	0.24	94
Ammonium	IC	0.03	0	0.75	0.11	0.34	0.25	94
Potassium	IC	0.17	0	0.77	0.19	0.57	0.21	94
Sodium	IC	0.34	0.16	2.20	0.25	0.75	0.18	94
Aluminum	XRF	0.23	0.00	1.05	0.31	0.92	1.08	94
Antimony	XRF	0.02	0.00	0.11	0.03	0.10	0.09	94
Arsenic	XRF	0.00	0.00	0.02	0.00	0.01	0.02	94
Barium	XRF	0.03	0.00	0.23	0.06	0.18	0.30	94
Bromine	XRF	0.00	0.00	0.03	0.01	0.02	0.02	94
Cadmium	XRF	0.00	0.00	0.03	0.00	0.01	0.04	94
Calcium	XRF	0.08	0.00	0.95	0.14	0.41	0.10	94
Cerium	XRF	0.10	0.00	0.50	0.15	0.45	0.55	94
Cesium	XRF	0.04	0.00	0.20	0.06	0.18	0.26	94
Chlorine	XRF	0.02	0.00	0.45	0.06	0.18	0.02	94
Chromium	XRF	0.02	0.00	0.09	0.02	0.05	0.03	94
Cobalt	XRF	0.00	0.00	0.01	0.00	0.01	0.01	94
Copper	XRF	0.01	0.00	0.17	0.03	0.08	0.02	94
Europium	XRF	0.12	0.00	0.67	0.20	0.60	0.82	94
Gallium	XRF	0.00	0.00	0.03	0.00	0.01	0.04	94
Gold	XRF	0.00	0.00	0.02	0.01	0.02	0.04	94
Hafnium	XRF	0.00	0.00	0.00	0.00	0.00	1.00	94
Indium	XRF	0.01	0.00	0.05	0.01	0.04	0.05	94
Iridium	XRF	0.00	0.00	0.00	0.00	0.00	0.43	94
Iron	XRF	0.08	0.00	0.31	0.08	0.23	0.08	94
Lanthanum	XRF	0.03	0.00	0.26	0.07	0.22	0.35	94
Lead	XRF	0.01	0.00	0.07	0.02	0.05	0.03	94
Magnesium	XRF	0.70	0.00	4.35	0.99	2.97	2.12	94
Manganese	XRF	0.01	0.00	0.10	0.02	0.05	0.05	94
Mercury	XRF	0.00	0.00	0.01	0.00	0.01	0.02	94
Molybdenum	XRF	0.01	0.00	0.06	0.01	0.04	0.03	94
Nickel	XRF	0.01	0.00	0.02	0.01	0.02	0.01	94
Niobium	XRF	0.01	0.00	0.03	0.01	0.03	0.02	94
Phosphorous	XRF	0.01	0.00	0.07	0.02	0.05	0.06	94
Potassium	XRF	0.02	0.00	0.55	0.06	0.18	0.04	94
Rubidium	XRF	0.00	0.00	0.05	0.01	0.02	0.02	94
Samarium	XRF	0.09	0.00	0.90	0.19	0.58	1.09	94
Scandium	XRF	0.06	0.00	0.33	0.09	0.27	0.43	94
Selenium	XRF	0.01	0.00	0.03	0.01	0.03	0.03	94
Silicon	XRF	0.07	0.00	0.37	0.08	0.23	0.14	94
Silver	XRF	0.00	0.00	0.03	0.01	0.03	0.03	94
Sodium	XRF	3.15	0.00	17.14	4.22	12.65	9.38	94
Strontium	XRF	0.00	0.00	0.03	0.01	0.02	0.02	94
Sulfur	XRF	0.00	0.00	0.00	0.00	0.00	0.05	94
Tantalum	XRF	0.00	0.00	0.00	0.00	0.00	1.00	94
Terbium	XRF	0.29	0.00	1.63	0.45	1.34	1.12	94
Tin	XRF	0.01	0.00	0.07	0.02	0.06	0.07	94
Titanium	XRF	0.01	0.00	0.10	0.02	0.07	0.07	94
Vanadium	XRF	0.00	0.00	0.03	0.00	0.01	0.01	94

Parameter	Analysis Method	Concentration (µg/filter)						Number of Field Blanks
		Average	Min	Max	Std. Dev.	LQL*	MDL**	
Wolfram	XRF	0.01	0.00	0.07	0.02	0.06	0.11	94
Yttrium	XRF	0.00	0.00	0.04	0.01	0.02	0.02	94
Zinc	XRF	0.01	0.00	0.15	0.02	0.06	0.02	94
Zirconium	XRF	0.01	0.00	0.08	0.02	0.05	0.04	94
* LQL is estimated from the long term precision of field blanks.								
** MDL is estimated from the long term precision of lab blanks.								

Table 2 also includes current estimates for the lower quantifiable limit (LQL) and method detection limit (MDL) for most parameters. Fresh estimates of the LQL are calculated each quarter as part of the ongoing data quality assessment.

Critical bookkeeping is required to insure sample integrity and keep track of data as it is generated. SOPs were in place, barcodes were used extensively, and critical data was maintained within an electronic database as well as on hand-written forms. No deficiencies were noted for this area of laboratory operations.

Gravimetric Weighing Laboratory

Brenda Cristani is the weighing lab supervisor, and Krista Phelps was the weighing lab technician on duty during the audit. Both were available to participate in the interview. The auditors were familiar with DRI's most recent SOP for weighing air filters (reference 8). The procedures are consistent with EPA guidance (reference 9).

The weighing room is configured to satisfy conditions of cleanliness, constant temperature, and constant humidity required by the program. All of the air entering the room has been scrubbed using a HEPA filter. Accurate control of the climate inside the weighing room is important because the balance calibration is very sensitive to temperature, and the mass of an exposed filter is sensitive to humidity. The weighing room is used to equilibrate filters before they are weighed. Criteria for temperature and humidity control are stated in the SOP as well as EPA guidance. Temperature must be held constant at 20-23 °C, controlled to ± 2 °C for 24 hours, and the average relative humidity (RH) must be between 30-40% controlled to ± 5% RH over 24 hours. DRI uses a Dickson digital hydrometer/thermometer data logger to monitor and record the weighing room conditions. The temperature and humidity sensors are checked for accuracy semi-annually by DRI staff using standards traceable to the National Institute of Standards and Technology (NIST).

Dickson temperature/humidity data loggers were brought from NAREL to independently measure conditions inside DRI's weighing room. NAREL's data loggers were placed into the weighing room on the morning of the audit and remained there for several hours. The EPA logger #11 was placed near the balance, and EPA logger #10 was placed near the room temperature/humidity sensor, which is located several feet away from the balance. Figure 1 shows the comparison of the temperature and humidity measurements inside the weighing room as recorded by DRI and the EPA #11 data logger. EPA's Dickson #10 malfunctioned and did not record data.

Figure 1

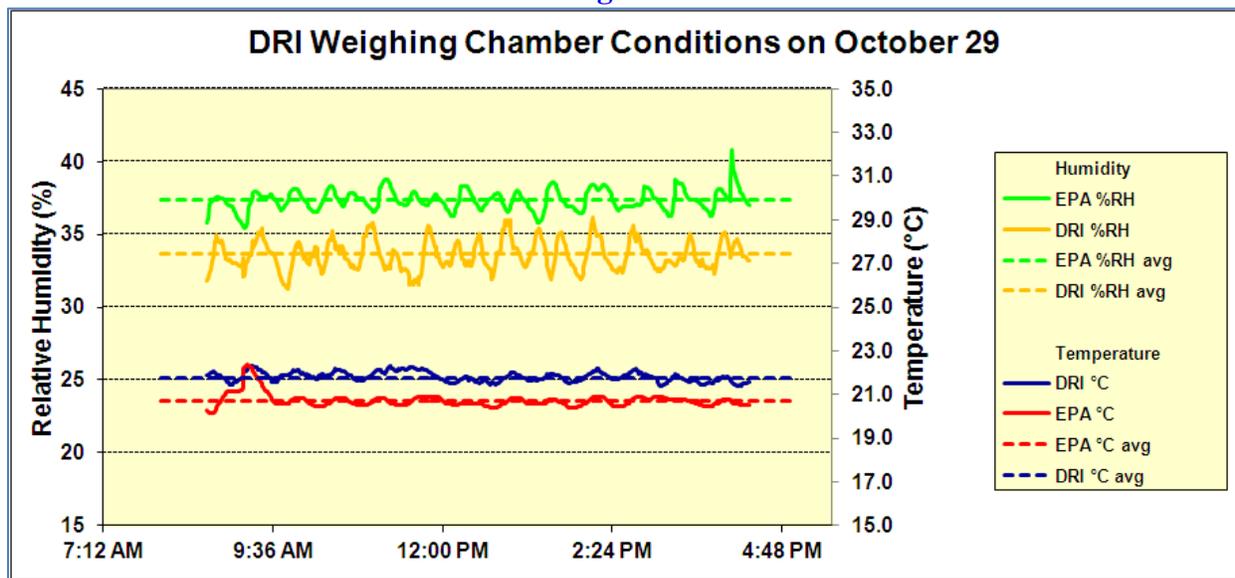


Figure 1 shows reasonably good agreement between the loggers for temperature and humidity. During the period of simultaneous measurements, the average temperature recorded by the EPA logger and the DRI logger was 20.7 °C and 21.8 °C respectively. The average relative humidity (RH) recorded by the EPA logger and the DRI logger was 37.4 and 33.6 % respectively. Both devices show that the room conditions are within the criteria stated above. Part of the differences seen between devices could be attributed to the placement of the devices; however, the measurement differences are within acceptable limits based on the accuracy for each device.

Prior to the audit, the auditors had planned for experimental demonstrations that could be performed by DRI analysts. In preparation for the gravimetric demonstrations, two Teflon® filters were inspected, equilibrated and weighed in NAREL’s weighing chamber. Two stainless steel mass standards that had been slightly altered from their nominal mass were also weighed at NAREL. All four samples were placed into individual labeled petri slides and brought to the TSA where they were used to demonstrate DRI’s weighing procedures in the gravimetric lab.

Krista was ready to start the gravimetric demonstration once the auditors arrived at the weighing lab. The filters and metallic weights had been placed in a laminar flow hood with the petri slides open to facilitate sample equilibration. Krista started the weighing session using a Mettler Toledo XP6 microbalance. The session began with a zero check and a calibration check using three metallic weight standards. ²¹⁰Po was used to neutralize electrical static charge from each filter sample immediately before it was weighed. In addition to the ²¹⁰Po, a U-shaped electrostatic ionizer manufactured by Haug was used to further remove static charge from the filters. The auditors noted that Krista’s technique for using the U- ionizer involved lightly touching the filter to the device while dragging it across the device. The U-ionizer operating instructions states that the most favorable distance from the device to the material is approximately 20 – 30 mm, with a minimum of 10 mm and a maximum of 80 mm. It is the auditor’s opinion that the filter should not come in contact with the device since there is the potential to contaminate or damage the Teflon® filter. In addition to the two filters and two metallic weights provided by NAREL, DRI provided two fully equilibrated filters and two filters randomly selected by the auditors from DRI’s stock of filters. Table 3 shows results from the gravimetric demonstration expressed as conventional mass (displayed by the balances) and also

expressed as true mass that includes a correction for the buoyant lifting force acting on an object weighed in air.

Table 3. Initial Results from Gravimetric Demonstration

Sample ID	Sample Description	Conventional Mass (mg)			True Mass (mg)		
		NAREL	DRI	Difference	NAREL	DRI	Difference
MW13-15007	Metallic weight provided by NAREL	496.649	496.648	0.001	496.649	496.648	0.001
MW13-15008	Metallic weight provided by NAREL	83.533	83.534	-0.001	83.533	83.534	-0.001
T13-15009	Teflon filter provided by NAREL	402.450	402.489	-0.039	402.601	402.615	-0.014
T13-15010	Teflon filter provided by NAREL	385.514	385.548	-0.034	385.659	385.669	-0.010
T13-15011	Teflon filter provided by DRI	380.781*	380.814	-0.033	380.924	380.933	-0.009
T13-15012	Teflon filter provided by DRI	379.158*	379.189	-0.031	379.301	379.308	-0.007
T13-15027	Teflon filter removed from DRI stock	145.850*	145.892	-0.042	146.037	146.047	-0.010
T13-15028	Teflon filter removed from DRI stock	145.086*	145.115	-0.029	145.272	145.269	0.002

**This value was determined at NAREL a few days after the audit.*

Modern microbalances are programmed to display "conventional mass", not the "true mass" described by Newton's second law of motion. All of the conventional mass values in table 3 were taken directly from the balance display. Direct conventional mass comparison between two balances is not generally a useful test unless both balances are located together and tested under the same conditions. Table 3 also shows the [true] mass of each sample which was calculated using the following equation (reference 10 and 11).

$$m_x = m_c \times (1 - \rho_{air}/\rho_{std}) \div (1 - \rho_{air}/\rho_x) \quad \text{equation 1}$$

where

- m_x is the [true] mass of the sample
- m_c is the conventional mass indicated by the balance display
- ρ_{air} is the air density
- ρ_{std} is the density of the balance calibration standard, 8 g/cm³
- ρ_x is the density of the sample, 0.85 g/cm³ and 2.3 g/cm³ used for Whatman and MTL filters respectively

The [true] mass values were needed because DRI's location is approximately 5000 feet above sea level compared to NAREL's location at 300 feet above sea level. At the higher elevation the air density is less resulting in less buoyant lifting force operating on objects that displace air. Teflon® filters are significantly less dense than the stainless steel weights used to establish the balance calibration curve. The "true mass" shown in tables 3 and 4 is the balance reading corrected to account for a significant difference in the buoyant lifting force at two locations, NAREL and DRI. Since the density of the metallic samples (MW13-15007 and MW13-15008) is essentially the same as the balance calibration weights, the displayed conventional and [true] masses are equal (see equation 1). It should be stated that even though a calculated [true] mass was needed during this TSA to compare the filter mass determined at NAREL with the filter mass determined at DRI, [true] mass values are not required for routine PM_{2.5} determinations. Measuring the pre-weight and post-weight of a filter on the same balance at the same location eliminates the need for a buoyancy correction.

Although the samples brought from NAREL were allowed only a few minutes to equilibrate, the corrected [true] mass values in table 3 shows excellent agreement with the metal weight samples and reasonably good agreement between DRI and NAREL for the filter samples. The auditors and DRI staff were concerned that some of the true mass measurement differences were larger than expected, e.g. 0.014 mg and 0.010 mg for samples T13-15009 and T13-15010 respectively. A decision was made for DRI to reweigh the two NAREL supplied filters after overnight equilibration in the DRI weighing room. Additionally, the auditors were to reweigh all samples after returning to NAREL. Table 4 shows that the true mass comparisons for the two NAREL supplied test filters did improve with the added filter equilibration time. Filter T13-15009 changed from 0.014 mg to 0.008 mg difference while filter T13-15010 changed from 0.010 mg to 0.006 mg difference. The auditors consider the results shown in table 4 acceptable considering the variables involved with directly comparing mass measurements taken at different locations.

Table 4. Final Results from Gravimetric Demonstration

Sample ID	Sample Description	Conventional Mass (mg)			True Mass (mg)		
		NAREL	DRI	Difference	NAREL	DRI	Difference
MW13-15007	Metallic weight provided by NAREL	496.648	496.648	0.000	496.648	496.648	0.000
MW13-15008	Metallic weight provided by NAREL	83.533	83.534	-0.001	83.533	83.534	-0.001
T13-15009	Teflon filter provided by NAREL	402.454	402.487	-0.033	402.605	402.613	-0.008
T13-15010	Teflon filter provided by NAREL	385.517	385.547	-0.030	385.662	385.668	-0.006
T13-15011	Teflon filter provided by DRI	380.781	380.814	-0.033	380.924	380.933	-0.009
T13-15012	Teflon filter provided by DRI	379.159	379.189	-0.030	379.302	379.308	-0.006
T13-15027	Teflon filter removed from DRI stock	145.850	145.892	-0.042	146.037	146.047	-0.010
T13-15028	Teflon filter removed from DRI stock	145.087	145.115	-0.028	145.273	145.269	0.003

Good laboratory practices and good documentation were in place for the gravimetric weighing laboratory and Brenda and Krista were very knowledgeable about all procedures used in the gravimetric lab. No deficiencies were noted during the gravimetric laboratory inspection.

Ion Chromatography (IC) Laboratory

Mr. Matt Tompkins is responsible for the analysis of ions. The auditors were familiar with Matt's SOPs for extracting filter samples (reference 12) and subsequently using IC to determine selected anions (reference 13) and cations (reference 14) present in the extract.

The laboratory is equipped with an automated Dionex ICS 3000 instrument running Chromeleon® software. One channel is optimized for the analysis of anions, and another channel is optimized for the analysis of cations. The lab also has equipment for cleaning and extracting Teflon®, Nylon®, and quartz filters. Ions are collected on Teflon® filters for the Texas samples. As stated earlier, the gravimetric and XRF analyses must be performed and results validated before the Teflon® filters are extracted. Extractions are performed using an ultrasonic bath and a shaker table. The entire filter is placed into a 15-mL polystyrene tube and 100 µL of ethanol is added to the filter as a wetting agent. The extraction solvent for the Teflon® filters is distilled-deionized water. Multilevel standards are used to develop calibration curves and establish retention times. New calibration curves are checked against a standard from

a secondary source. Fresh curves are prepared daily or when the routine check samples indicate excessive calibration drift. Matt allowed the audit team to view recent calibration curves and the associated quality control elements on the instrument's data system. No deficiencies were noted in reviewing the data.

Matt was given the opportunity to demonstrate his ability to analyze an unknown solution during the audit. The auditors had brought two solutions with them for Matt to analyze. He was advised to dilute each solution by a factor of ten before his analysis, and that he should use his own pipettes, containers, and the local reagent water to perform the dilution. He was given the unknown solutions during the initial briefing so there was plenty of time to perform his analysis. Results are presented in table 5 which shows excellent agreement with the expected values.

Table 5. Demonstration of Anion and Cation Analysis During the Audit

Sample_ID	Sample Description	Parameter	Expected Value (ppm)	DRI Result (ppm)
SS13-15013	Anion solution provided by NAREL	Fluoride	1.00	not reported
		Chloride	1.00	0.99
		Nitrite	1.00	not reported
		Nitrate	2.00	1.97
		Sulfate	3.00	3.05
SS13-15014	Cation solution provided by NAREL	Lithium	0.25	0.25
		Sodium	1.00	0.98
		Ammonium	2.00	1.95
		Potassium	1.00	1.99
		Magnesium	1.00	1.03
		Calcium	5.00	5.24

Matt was asked to give the auditors a sample of his calibration solutions so that they could be analyzed at NAREL. The results from NAREL's analyses are shown in table 6. Very good agreement between labs was observed for all of the ions tested.

Table 6. DRI Calibration Standards Analyzed at NAREL After the Audit

Sample_ID	Sample Description	Parameter	Expected Value (ppm)	NAREL Result (ppm)
SS13-15015	Anion standard provided by DRI	Fluoride	0.20	0.20
		Chloride	0.30	0.32
		Nitrite	1.00	0.99
		Bromide	1.00	not determined
		Phosphate	1.50	not determined
		Nitrate	1.00	1.03
		Sulfate	1.50	1.53
SS13-15016	Cation standard provided by DRI	Lithium	0.25	0.25
		Sodium	1.01	1.00
		Ammonium	1.25	1.26
		Potassium	2.49	2.40
		Magnesium	1.26	1.24
		Calcium	2.51	2.49

Good laboratory practices and good documentation were in place for the analysis of ions by IC. Based upon these observations and results from the demonstration experiments, no problems were seen with this area of the laboratory.

X-Ray Fluorescence (XRF) Analysis

Teflon® filters returned from the speciation field sites are first analyzed in the weighing lab to determine the gravimetric mass of particulate captured by the filter. After the gravimetric analysis is complete, the filter is then submitted for analysis using energy dispersive XRF to determine the elements present in the particulate matter captured by the filter.

Mr. Steve Kohl is responsible for the XRF analysis. Steve's lab has a PANalytical Epsilon 5 instrument equipped with a high purity germanium detector cooled with liquid nitrogen. Samples are excited to fluoresce using an X-Ray tube with a gadolinium anode along with a set of secondary targets. The SOP describes instrument conditions that are used to produce seven different spectra for each sample, and forty-eight elements are routinely reported (reference 15).

Instrument calibration is performed using two concentration levels of thin film standards from Micromatter. Polymer film standards and NIST standards are used as calibration verification QC checks. A multi-element Micromatter standard is analyzed daily to check for instrument drift. A criterion of $\pm 5\%$ is used to determine if re-calibration is necessary. Energy calibration of the germanium detector is performed weekly using an automated program supplied with the operating software. For each batch of samples analyzed, laboratory blanks are analyzed and the average concentration of each element is used for background subtraction. MDLs are determined quarterly from the analysis of a series of twenty-four Teflon® laboratory blanks. The MDL for each element is computed as three times the standard deviation of the element concentration. The lower quantifiable limits (LQLs) are determined quarterly from the analysis of field blanks (see table 2). The XRF measurement uncertainty of each element in a sample is calculated by adding the standard deviation of lab blank measurements to the absolute sample concentration multiplied by the relative standard deviation of multiple measurements of the low standard. Replicate analyses are performed at a frequency of approximately one per ten samples. Corrective action is taken if a difference greater than 10% or three times the analytical uncertainty is observed in repeated analysis. No attenuation corrections are made for PM_{2.5} samples. Control charts are maintained to monitor instrument performance.

A single exposed Teflon® test filter and five unexposed Teflon® filters were brought to the audit and submitted to Steve during the initial audit briefing. He was asked to analyze the exposed filter along with the unexposed filters for use as background correction. The test filter had been previously analyzed at DRI as part of NAREL's annual inter-laboratory comparison study of 2012 (reference 16). Results from Steve's demonstration are presented in figures 2-4 along with results from the 2012 analysis for comparison. The figures also show 3 sigma uncertainty bars and the MDL for each element. The figures show that the analysis performed on the day of the audit compares very well with the previous DRI analysis for majority of the elements.

Figure 2. Demonstration of XRF Analysis

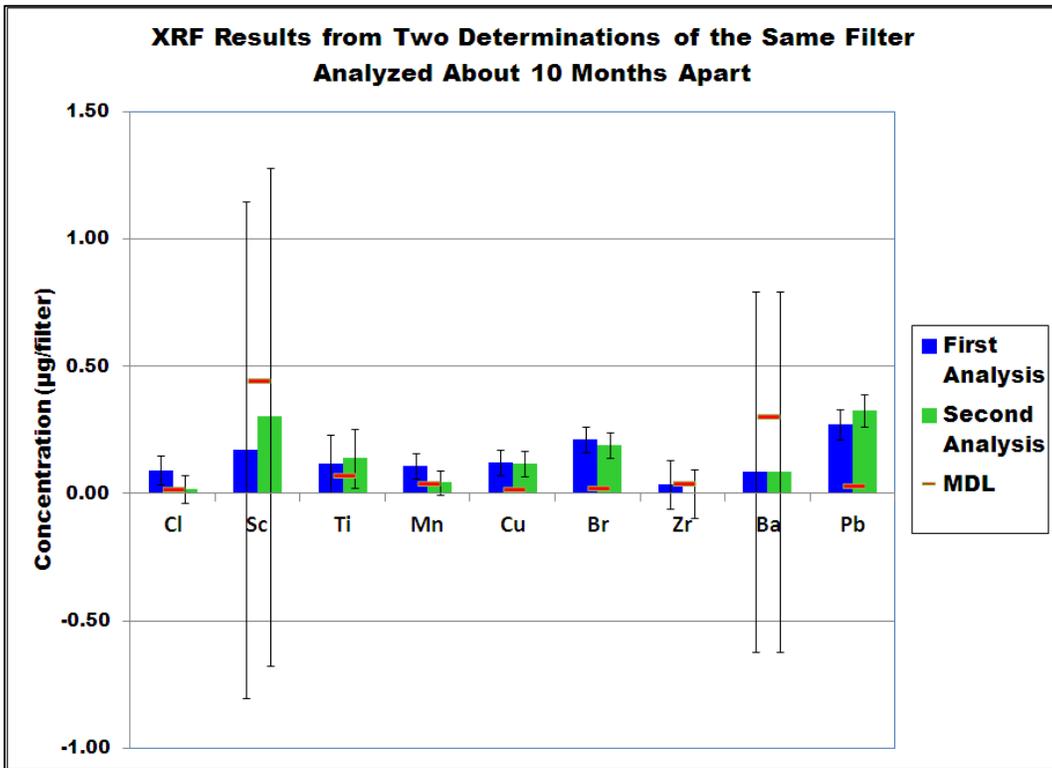
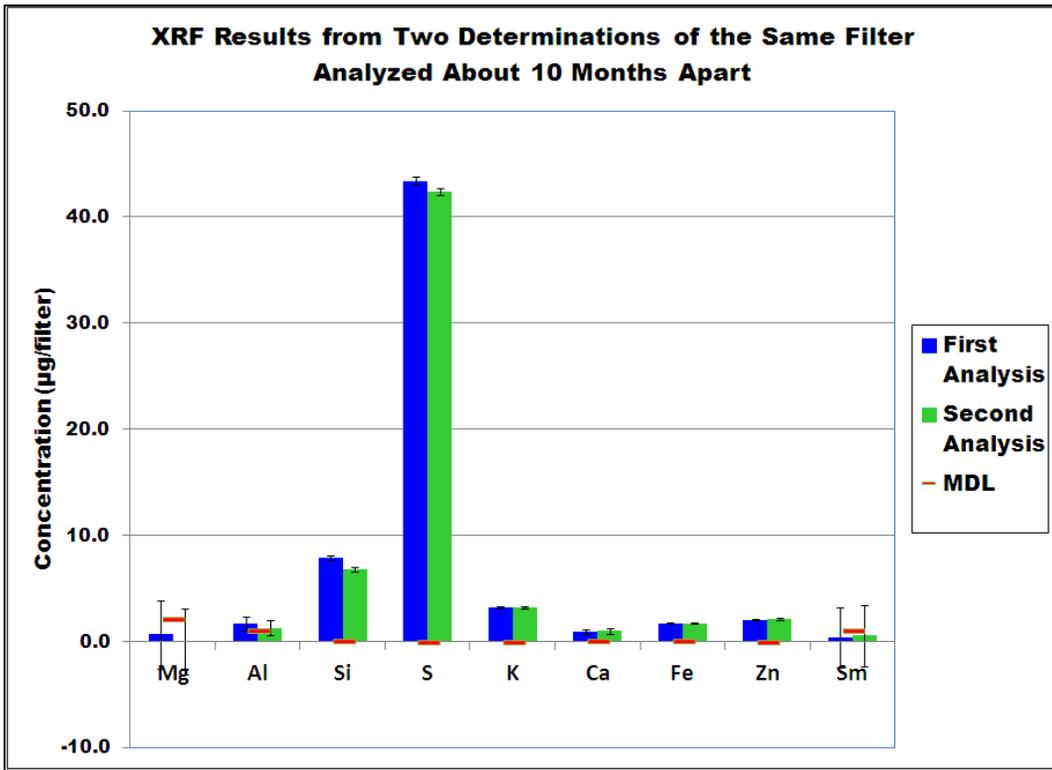


Figure 3 Demonstration of XRF Analysis

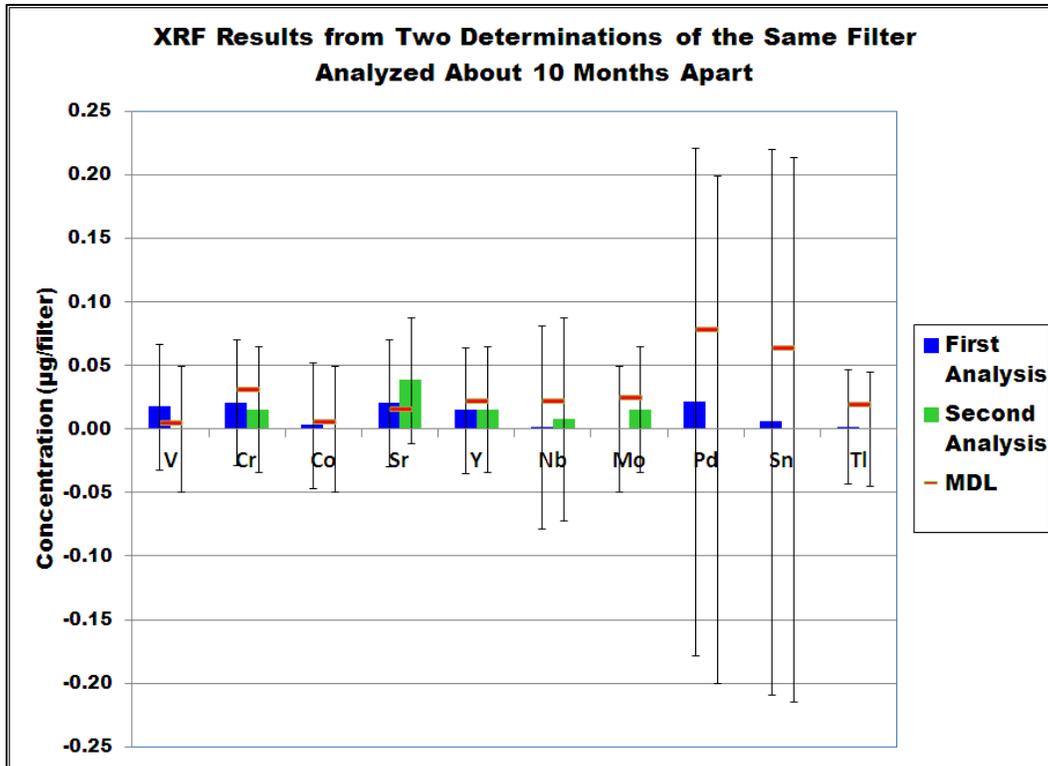


Figure 4 Demonstration of XRF Analysis

Table 7 is a comprehensive list of results that includes all of the elements reported. The data in table 7 also includes the uncertainty reported with each analysis and a current estimate of the MDL.

Table 7. XRF Results from Demonstration Filter

Z	Element	First Analysis (µg/filter)		Second Analysis (µg/filter)		MDL (µg/filter)
		Sample Conc.	Uncertainty	Sample Conc.	Uncertainty	
11	Na	0.000	4.442	0.000	4.468	9.84
12	Mg	0.691	1.071	0.000	1.051	2.20
13	Al	1.677	0.232	1.299	0.231	1.12
14	Si	7.887	0.071	6.790	0.068	0.147
15	P	0.000	0.032	0.000	0.032	0.061
16	S	43.408	0.120	42.370	0.118	0.050
17	Cl	0.092	0.018	0.016	0.018	0.020
19	K	3.204	0.035	3.203	0.035	0.042
20	Ca	0.898	0.080	0.979	0.080	0.100
21	Sc	0.173	0.325	0.301	0.326	0.448
22	Ti	0.117	0.038	0.139	0.038	0.075

Z	Element	First Analysis (µg/filter)		Second Analysis (µg/filter)		MDL
		Sample Conc.	Uncertainty	Sample Conc.	Uncertainty	(µg/filter)
23	V	0.018	0.017	0.000	0.017	0.006
24	Cr	0.021	0.017	0.016	0.017	0.032
25	Mn	0.107	0.017	0.043	0.017	0.046
26	Fe	1.705	0.018	1.713	0.018	0.083
27	Co	0.003	0.017	0.000	0.017	0.007
28	Ni	0.000	0.017	0.009	0.017	0.007
29	Cu	0.122	0.017	0.116	0.017	0.021
30	Zn	2.060	0.023	2.123	0.023	0.023
31	Ga	0.000	0.032	0.000	0.032	0.040
33	As	0.000	0.017	0.000	0.017	0.019
34	Se	0.000	0.017	0.000	0.017	0.025
35	Br	0.213	0.017	0.190	0.017	0.024
37	Rb	0.000	0.017	0.000	0.017	0.017
38	Sr	0.021	0.017	0.038	0.017	0.017
39	Y	0.015	0.017	0.015	0.017	0.023
40	Zr	0.034	0.032	0.000	0.032	0.044
41	Nb	0.001	0.027	0.008	0.027	0.023
42	Mo	0.001	0.017	0.015	0.017	0.026
46	Pd	0.022	0.067	0.000	0.067	0.080
47	Ag	0.000	0.033	0.000	0.033	0.036
48	Cd	0.000	0.027	0.000	0.027	0.043
49	In	0.000	0.047	0.034	0.047	0.048
50	Sn	0.006	0.071	0.000	0.071	0.065
51	Sb	0.000	0.128	0.000	0.128	0.097
55	Cs	0.000	0.206	0.000	0.205	0.250
56	Ba	0.086	0.235	0.087	0.236	0.307
57	La	0.000	0.274	0.000	0.273	0.356
58	Ce	0.000	0.506	0.000	0.506	0.545
62	Sm	0.352	0.942	0.546	0.944	1.11
63	Eu	0.000	0.682	0.000	0.684	0.82
65	Tb	0.010	1.638	1.324	1.638	1.15
72	Hf	0.000	0.111	0.000	0.111	1.00
73	Ta	0.000	0.111	0.000	0.111	1.001
74	W	0.000	0.071	0.000	0.071	0.107
77	Ir	0.000	0.028	0.000	0.028	0.426

Z	Element	First Analysis (µg/filter)		Second Analysis (µg/filter)		MDL (µg/filter)
		Sample Conc.	Uncertainty	Sample Conc.	Uncertainty	
79	Au	0.000	0.023	0.000	0.023	0.041
80	Hg	0.000	0.015	0.000	0.015	0.024
81	Tl	0.002	0.015	0.000	0.015	0.021
82	Pb	0.273	0.020	0.326	0.021	0.033
92	U	0.000	0.028	0.000	0.028	0.043

The XRF laboratory documentation was in good order, and good quality control practices were in place. No deficiencies were noted for this area of laboratory operations.

Carbon Analysis Laboratory

The carbon analysis laboratory is supervised by Ms. Dana Trimble. Ms. Tasha Pascal and Dr. Tropp were also present to answer questions about the carbon analysis and assist with the inspection of this laboratory.

DRI has an SOP for pre-firing and acceptance testing of quartz fiber filters that are subsequently distributed to the field sites for sampling (reference 17). A batch of one hundred new quartz filters from the same lot is placed into a furnace and thermally cleaned at 900 °C for at least four hours. After cooling, the filters are visually inspected for imperfections such as holes or uneven texture, and the blemished filters are discarded. Two filters from the batch are scheduled for analysis to test for residual contamination. Criteria for acceptance of the batch is for an OC concentration of less than 1.5 µg/cm² and EC concentration less than 0.5 µg/cm².

The laboratory has twelve DRI Model 2001 instruments. Eight analyzers are setup for routine analyses while four are used for research experiments. Most of the samples are 25-mm filters received from either CNL or RTI with a request for analysis using the IMPROVE_A method (reference 18). In the past, DRI supplied 47-mm quartz filters to TCEQ for speciation sampling, and those filters required analysis using the CSN method (reference 19). TCEQ has now fully implemented URG 3000N samplers along with IMPROVE_A method of analysis for carbon. The carbon lab is in continuous operation 24 hours a day, seven days a week in order to keep up with demand.

Instruments are calibrated at least twice per year using four different sources of carbon: methane gas, carbon dioxide (CO₂) gas, sucrose, and potassium hydrogen phthalate (KHP). The most recent SOP for carbon analysis by the IMPROVE_A method (reference 18) shows that DRI has added extra daily QC checks to the procedure. Table 8 is taken from the DRI carbon SOP and details a strict daily calibration and instrument performance check schedule. Notice that both sucrose and KHP calibration solutions are now used to check instrument response in addition to the methane and CO₂ calibration gases. In the past version of the SOP, only the calibration gases were used for daily checks. The auditors also learned that the analysis program used for the daily checks is the same program used for the analysis of actual air samples.

Table 8. From DRI's Carbon SOP

Daily Calibration Schedule (Based on 24/7 operation)							
	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Morning (Startup)	System Blank Lab Blank Autocalib	Lab Blank Sucrose	Lab Blank Autocalib KHP	Lab Blank Sucrose	Lab Blank Autocalib KHP	Lab Blank Sucrose	Lab Blank Autocalib KHP
Evening.	CO2 inject	Autocalib	CO2 inject	Autocalib	CO2 inject	Autocalib	CO2 inject
Note: Sucrose and KHP – Total Carbon (TC) must be between 17.1 – 18.9 ug C/filter in order to pass. System and Lab Blanks should be < 0.2 ug C/cm ²							

An automatic injection of methane gas is performed at the end of every sample analysis to serve as an internal standard. Additional quality control elements practiced by the DRI carbon laboratory include the following.

- ✓ System blanks are analyzed daily to check for contamination of the analyzers.
- ✓ Method detection limits (MDLs) are determined from the analysis of lab blanks. Frequency of MDL determinations depends upon project requirements. MDLs are determined quarterly for TCEQ and annually for the IMPROVE program. MDLs are also determined after major instrument maintenance.
- ✓ The lower quantifiable Limits (LQLs) are determined from the analysis of field blanks. Frequency of LQL determinations depends upon project requirements. LQLs are determined quarterly for TCEQ and annually for the IMPROVE program.
- ✓ Mid-level precision is evaluated by analyzing ten percent of the filter samples in duplicate. The duplicates are performed using an analyzer chosen at random.
- ✓ Peak area of the internal standard is plotted on control charts and used to monitor instrument performance.
- ✓ Temperature calibration of the sample oven is performed every six months or when the temperature sensor is replaced.
- ✓ A gas chromatograph/mass spectrometer (GC/MS) is used to determine oxygen levels inside the instrument during the helium stage of analysis. This is performed semi-annually to ensure oxygen levels are below 100 parts per billion.

Prior to the TSA, PT samples were prepared at NAREL to use as test samples for carbon analysis at DRI. One sample was prepared from a thermally cleaned quartz filter from which several circular 0.5 cm² subsamples were removed using a punch tool. The samples were placed into a labeled Petri-dish with a tight fitting lid. A second sample was prepared exactly like the first except that each subsample was spiked with 20 µg (40 µg/cm²) of carbon from a sucrose solution. The spiked samples were air dried in a separate labeled Petri-dish. Except for the labels, the two samples were visibly indistinguishable. During the initial audit briefing, the samples were given to Dana and Tasha with a request to analyze them.

The auditors were able to observe different stages of the carbon analysis procedure during the inspection of the carbon lab. Analyses of some of the audit samples were in progress which

allowed the auditors to examine thermograms as they were produced. Tasha demonstrated the loading and analysis of one of the spiked test filters as well as the method for spiking a sucrose solution into the analyzer for an initial calibration check. The auditors were also able to review the raw data and discuss the details of the analyses. The results from DRI's analyses are presented in table 9 along with spike levels and results from the independent analyses performed at NAREL.

Table 9. Demonstration of Carbon Analysis

Sample ID	Sample Description	Carbon Fraction	Spike Level ($\mu\text{g}/\text{cm}^2$)	DRI Result ($\mu\text{g}/\text{cm}^2$)	NAREL Result ($\mu\text{g}/\text{cm}^2$)
Q13-15017	Spiked Quartz	OC	40.0	37.61 ± 3	40.94 ± 2.15
		EC	0.00	2.08 ± 0.1	0.00 ± 0.10
Q13-15018	Blank Quartz	OC	0.00	0.20 ± 0.3	0.51 ± 0.13
		EC	0.00	0.00 ± 0.1	0.02 ± 0.10

Table 9 shows good agreement between labs. Sucrose was selected for the spike material because it chars readily during the analysis, like many ambient air samples, and it offers a good challenge for how well the analysis can distinguish the OC and EC originally present in the sample. DRI's EC result for sample Q13-15017 shows a small EC concentration illustrating this challenge since there is no EC in the sample. NAREL's carbon analyzer also occasionally reports small concentrations of EC when analyzing sucrose or KHP solutions. For this reason, only the TC concentration is used for calibration purposes.

Table 10 contains results from sucrose and KHP calibration check solutions provided by DRI. Dana was asked to give the auditors the solution so they could be analyzed at NAREL. NAREL's analysis results of the solutions agree very well with DRI's expected concentrations.

Table 10. DRI Calibration Standards Analyzed at NAREL

Sample ID	Sample Description	Carbon Fraction	Spike Level ($\mu\text{g}/\text{cm}^2$)	NAREL Post-Audit Result ($\mu\text{g}/\text{cm}^2$)
SS13-15019	Sucrose solution provided by DRI	OC	18.00	17.91 ± 1.00
		EC	0.00	0.29 ± 0.10
SS13-15050	KHP solution provided by DRI	OC	18.00	18.54 ± 1.03
		EC	0.00	0.00 ± 0.10

Good laboratory practices, good QC practices, and good record keeping are performed in the carbon analysis laboratory. No deficiencies were observed for this area of laboratory operations.

Conclusions

This TSA was the fourth inspection of DRI's Environmental Analysis Facility conducted as part of the EPA quality assurance oversight for the PM_{2.5} Chemical Speciation Network and the IMPROVE Network. Observations made by the audit team on this inspection again found the DRI Laboratory to be a modern facility with state of the art instrumentation, good documentation, and well qualified staff. Good laboratory practices were in place throughout the lab, and relevant SOPs were current and being followed. The audit team appreciates the professionalism they observed during this audit.

Results from NAREL's most recent inter-laboratory study were available for discussion with DRI staff during the audit (reference 16). Results from that study indicated overall good performance from DRI. Several experimental activities conducted during this audit also gave objective evidence for the good work at DRI.

Further discussion among audit team members following the audit has resulted in a recommendation for the gravimetric lab. As previously stated during the gravimetric section of this report, the auditors observed the analyst's technique to remove static from a filter involved dragging the filter across the surface of the electronic anti-static device. The auditors believe that there is the potential to contaminate or damage the Teflon® filter by this procedure. The auditors recommend following the ionizing unit's manufacturer's instructions to maintain a small distance between the material and unit. Other than the recommendation, there were no negative findings produced from this audit.

References

1. DRI August 2012. Quality Assurance Project Plan, PM_{2.5} Filter Laboratory Analysis Program, prepared by DRI for the Texas Commission of Environmental Quality.
2. DRI April 2011. Quality Management Plan for Laboratory Support for PM_{2.5} Ambient Air Monitoring Programs, prepared by DRI for the Texas Commission of Environmental Quality.
3. EPA/NAREL June 1, 2011. Technical Memorandum: DRI Laboratory Audit. U.S. Environmental Protection Agency. [currently available on the web]
<http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/20110601DRITSA.pdf>
4. DRI October 2012. Standard Operating Procedure, PM_{2.5} FRM Sample Shipping, Receiving, and Chain-of-Custody, DRI SOP #2-113r4, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
5. DRI July 2007. Standard Operating Procedure, PM_{2.5} FRM Filter Pack Assembly, Disassembly, and Cleaning, DRI SOP #2-112r3, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
6. DRI October 2012. Standard Operating Procedure, URG 3000N Sample Shipping, Receiving, and Chain-of-Custody, DRI SOP #2-115r1, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
7. DRI November 2011. Standard Operating Procedure, URG 3000N Filter Pack Assembly Disassembly, and Cleaning, DRI SOP #2-116r1, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
8. DRI October 2012. Standard Operating Procedure, PM_{2.5} FRM Gravimetric Analysis, DRI SOP #2-114r9, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
9. EPA 1998. Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods. Quality Assurance Guidance Document 2.12. U.S. Environmental Protection Agency. Office of Research and Development, Research Triangle Park, NC. 1998. [currently available on the web]
<http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212cova.pdf>

10. DOE/ORNL September 1997. SOP 21, Air Buoyancy Correction, Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge National Laboratory, U.S. Department of Energy. [currently available on the web] <http://cdiac.ornl.gov/ftp/cdiac74/sop21.pdf>
11. NBS March 1974. Monograph 133, Mass and Mass Values, National Bureau of Standards, U.S. Department of Commerce. [currently available on the web] <http://digicoll.manoa.hawaii.edu/techreports/PDF/NBS133.pdf>
12. DRI July 2007. Standard Operating Procedure, Extraction of Ionic Species from Filter Samples, DRI SOP #2-109r6, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
13. DRI June 2010. Standard Operating Procedure, Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography, DRI SOP #2-203r8, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
14. DRI June 2010. Standard Operating Procedure, Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography, DRI SOP #2-208r3, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
15. DRI December 2010. Standard Operating Procedure, X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (PANalytical Epsilon 5), DRI SOP #2-209r6, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
16. EPA/NAREL June 26, 2013. Technical Memorandum: Experimental Inter-comparison of Speciation Laboratories. U.S. Environmental Protection Agency. [currently available on the web] <http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/MultilabSpeciationPT2012.pdf>
17. DRI July 2007. Standard Operating Procedure, Pre-firing and Acceptance Testing of Quartz-Fiber Filters for Aerosol and Carbonaceous Material Sampling, DRI SOP #2-106r6, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.
18. DRI October 2012. Standard Operating Procedure, DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples — Method IMPROVE_A, DRI SOP #2-216r3, Division of Atmospheric Sciences, 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
19. DRI August 2008. Standard Operating Procedure, DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples — Method STN - DRI SOP #2-201r4, Division of Atmospheric Sciences, Desert Research Institute, Reno NV.