TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS
FROM: Eric Boswell / NAREL
COPY: Dr. Richard Tropp / DRI
AUTHOR: Jewell Smiley / NAREL
DATE: June 1, 2011
SUBJECT: DRI Laboratory Audit

Introduction

On July 27, 2010, 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.

Over time DRI has expanded its laboratory support activities so that today the EAF still performs all of the carbon analyses for the IMPROVE program and most of the carbon analyses for the CSN as well. Over the past three years EPA has been switching to a new IMPROVE-like air sampler, the URG-3000N, at the CSN field sites. Quartz filters taken from the URG-3000N samplers are analyzed at DRI through a subcontract with the Research Triangle Institute (RTI) located in North Carolina. RTI has been the national contract laboratory for CSN since the urban speciation network began in 2000.

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 ten supplemental $PM_{2.5}$ CSN sites within the state and eighteen sites that monitor $PM_{2.5}$ mass using the federal reference method (FRM sites). 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 Dave Maxwell. Steve and Jewell are physical scientists at EPA's National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, Alabama. Dave works for the National Park Service as an air quality monitoring specialist, and he works closely with the funding that supports the IMPROVE program. Dave attended the audit as an observer. This TSA was the third EPA inspection of the EAF laboratory operations at DRI. A report from the last TSA, conducted in 2007, 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 – Brenda Cristani
- ✓ Gravimetric Laboratory – Brenda Cristani
- ✓ Organic Carbon/Elemental Carbon (OC/EC) Laboratory – Dana Trimble
- ✓ X-Ray Fluorescence (XRF) Laboratory – Steven Kohl
- ✓ Ion Chromatography (IC) Laboratory – Ed Hackett

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 immediately. 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

Sample Shipping, Receiving and Handling Laboratory

DRI currently provides laboratory support for approximately three hundred fifty air monitoring sites. Most of the samples received at the EAF are quartz filters that require the OC/EC analysis, but some samples require a more comprehensive suite of analyses. For example, 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. The auditors were especially interested in the TCEQ samples since several different analytical techniques were involved with that work.

Ms. Brenda Cristani is responsible for coordinating most of the sample shipping and receiving activities, and she was available to explain how clean filters are prepared for shipment to the field sites, and later the exposed filters are received back at the laboratory ready for analysis (reference 4 through 7). The supplemental chemical speciation sites in Texas are unique in one respect. TCEQ has chosen to not use Nylon® filters at those sites. TCEQ uses only Teflon®

and quartz filters for $PM_{2.5}$ sampling, and DRI is responsible for providing the clean pre-weighed Teflon® and pre-fired quartz filters to the sites. 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 PM2.5 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.

TCEQ has used the R&P Partisol-Plus model 2025 sequential sampler for many years to collect $PM_{2.5}$ air samples. Until recently, a pair of the Model 2025 units has been used at each speciation site so that both filter media, Teflon® and quartz, were simultaneously exposed at each sampling event. Starting in January of 2010 however, two changes were implemented regarding the quartz filter sampling and the OC/EC analysis. URG 3000N samplers were installed at the field sites to replace the Model 2025 units that previously performed the quartz filter sampling. Also the thermal/optical carbon analysis was switched from the CSN method to the IMPROVE_A method.

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	Instrument	Parameter	Concentration
T10-13565	Teflon® test filter #1	IC	Nitrate	1.9 µg/filter
			Sulfate	<0.5 µg/filter
			Ammonium	<0.5 µg/filter
			Potassium	0.7 µg/filter
			Sodium	0.7 µg/filter
T10-13566	Teflon® test filter #2	IC	Nitrate	5.1 µg/filter
			Sulfate	<0.5 µg/filter
			Ammonium	<0.5 µg/filter
			Potassium	<0.5 µg/filter
			Sodium	0.7 µg/filter
Q10-13561	25-mm quartz test filter #1	OC/EC Analyzer	Elemental Carbon	<0.2 µg/cm^2
			Organic Carbon	0.23 µg/cm^2
Q10-13562	25-mm quartz test filter #2	OC/EC Analyzer	Elemental Carbon	<0.2 µg/cm^2
			Organic Carbon	0.26 µg/cm^2
Q10-13563	47-mm quartz test filter #1	OC/EC Analyzer	Elemental Carbon	<0.2 µg/cm^2
			Organic Carbon	<0.2 µg/cm^2
Q10-13564	47-mm quartz test filter #2	OC/EC Analyzer	Elemental Carbon	<0.2 µg/cm^2
			Organic Carbon	0.31 µg/cm^2
T10-13567	Teflon® test filter #1	Balance	$PM_{2.5}$ Mass	2 µg/filter*****
T10-13568	Teflon® test filter #2	Balance	$PM_{2.5}$ Mass	5 µg/filter*****

**** 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 was determined by using the pre-mass value determined routinely 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 2009 through the second quarter of 2010.

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	4.4	-25	37	8.8	23	15	196
OC (TOR)	IMPROVE_A Method with URG 3000N samplers and 25-mm filters implemented in January of 2010	3.59	1.48	9.12	1.36	4.3	9.2	52
EC (TOR)		0.03	0.00	0.54	0.10	0.3	1.3	52
OC (TOT)		3.60	1.48	9.42	1.40	4.2	-----	52
EC (TOT)		0.02	0.00	0.27	0.06	0.2	-----	52
OC1		0.67	0.00	1.81	0.36	-----	-----	52
OC2		1.29	0.49	3.56	0.55	-----	-----	52
OC3		1.52	0.33	4.42	0.72	-----	-----	52
OC4		0.11	0.00	0.75	0.16	-----	-----	52
PyrolC (TOR)		0.00	0.00	0.12	0.02	0.9	1.4	52
PyrolC (TOT)		0.02	0.00	0.31	0.06	0.2	-----	52
OC (TOT)	CSN Method with R&P 2025 samplers and 47-mm filters discontinued in January of 2010	15.60	0.01	36.65	6.49	20.5	9.3	148
EC (TOT)		0.92	0.00	9.82	1.44	3.3	1.3	148
OC1		3.19	0.13	12.54	1.76	-----	-----	148
OC2		8.64	0.59	16.95	3.15	-----	-----	148
OC3		3.30	0.00	8.87	1.88	-----	-----	148
OC4		1.36	0.00	6.18	1.48	-----	-----	148
PyrolC (TOT)		-0.90	-9.82	0.04	1.41	3.2	1.4	148
Nitrate	IC	0.16	-0.03	2.10	0.23	0.65	0.28	196
Sulfate	IC	0.10	-0.04	0.47	0.10	1.21	0.30	196
Ammonium	IC	0.01	0.00	0.67	0.07	0.31	0.19	196
Potassium	IC	0.21	0.00	0.95	0.24	0.43	0.26	196
Sodium	IC	0.38	0.14	2.46	0.25	0.49	0.23	196
Aluminum	XRF	0.08	0.00	0.65	0.13	0.32	0.38	196
Antimony	XRF	0.02	0.00	0.14	0.03	0.17	0.22	196
Arsenic	XRF	0.00	0.00	0.01	0.00	0.01	0.02	196
Barium	XRF	0.03	0.00	0.47	0.07	0.17	0.23	196
Bromine	XRF	0.01	0.00	0.06	0.01	0.04	0.05	196
Cadmium	XRF	0.01	0.00	0.17	0.03	0.23	0.14	196
Calcium	XRF	0.04	0.00	0.29	0.06	0.23	0.09	196
Cerium	XRF	0.02	0.00	0.28	0.05	0.25	0.34	196
Cesium	XRF	0.00	0.00	0.10	0.01	0.13	0.17	196
Chlorine	XRF	0.02	0.00	0.56	0.05	0.14	0.05	196
Chromium	XRF	0.01	0.00	0.05	0.01	0.04	0.03	196
Cobalt	XRF	0.00	0.00	0.02	0.00	0.01	0.01	196
Copper	XRF	0.00	0.00	0.05	0.01	0.03	0.04	196

Parameter	Analysis Method	Concentration (µg/filter)						Number of Field Blanks
		Average	Min	Max	Std. Dev.	LQL*	MDL **	
Europium	XRF	0.09	0.00	0.80	0.16	0.51	0.64	196
Gallium	XRF	0.02	0.00	0.15	0.03	0.07	0.10	196
Gold	XRF	0.01	0.00	0.10	0.02	0.11	0.17	196
Hafnium	XRF	0.03	0.00	0.24	0.05	0.23	0.35	196
Indium	XRF	0.01	0.00	0.08	0.02	0.10	0.13	196
Iridium	XRF	0.01	0.00	0.08	0.02	0.08	0.12	196
Iron	XRF	0.06	0.00	0.42	0.07	0.22	0.10	196
Lanthanum	XRF	0.04	0.00	0.58	0.10	0.24	0.42	196
Lead	XRF	0.01	0.00	0.11	0.02	0.07	0.10	196
Magnesium	XRF	0.16	0.00	2.00	0.31	0.65	0.81	196
Manganese	XRF	0.01	0.00	0.07	0.02	0.06	0.07	196
Mercury	XRF	0.00	0.00	0.03	0.00	0.03	0.06	196
Molybdenum	XRF	0.00	0.00	0.06	0.01	0.05	0.08	196
Nickel	XRF	0.00	0.00	0.03	0.01	0.02	0.02	196
Niobium	XRF	0.00	0.00	0.05	0.01	0.06	0.08	196
Phosphorous	XRF	0.01	0.00	0.07	0.01	0.07	0.09	196
Potassium	XRF	0.02	0.00	0.10	0.02	0.09	0.07	196
Rubidium	XRF	0.00	0.00	0.04	0.01	0.03	0.03	196
Samarium	XRF	0.04	0.00	0.99	0.11	0.32	0.47	196
Scandium	XRF	0.03	0.00	0.33	0.07	0.07	0.10	196
Selenium	XRF	0.01	0.00	0.11	0.02	0.04	0.05	196
Silicon	XRF	0.06	0.00	0.50	0.08	0.24	0.23	196
Silver	XRF	0.01	0.00	0.12	0.02	0.11	0.14	196
Sodium	XRF	0.83	0.00	5.18	1.09	2.14	3.11	196
Strontium	XRF	0.01	0.00	0.05	0.01	0.05	0.06	196
Sulfur	XRF	0.01	0.00	0.15	0.02	0.35	0.21	196
Tantalum	XRF	0.02	0.00	0.34	0.05	0.19	0.27	196
Terbium	XRF	0.06	0.00	0.87	0.14	0.50	0.65	196
Tin	XRF	0.01	0.00	0.13	0.02	0.11	0.16	196
Titanium	XRF	0.01	0.00	0.09	0.02	0.04	0.05	196
Vanadium	XRF	0.00	0.00	0.02	0.00	0.01	0.01	196
Wolfram	XRF	0.03	0.00	0.24	0.06	0.28	0.42	196
Yttrium	XRF	0.00	0.00	0.05	0.01	0.03	0.03	196
Zinc	XRF	0.01	0.00	0.13	0.01	0.05	0.04	196
Zirconium	XRF	0.02	0.00	0.11	0.02	0.09	0.10	196

**** 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 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 Joel Langford 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 digital hydrometer/thermometer 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 #7 was placed near the balance, and EPA logger #8 was placed near the DRI logger. Figure 1 shows the comparison of the temperature and humidity measurements inside the weighing room as recorded by all three data loggers.

Figure 1

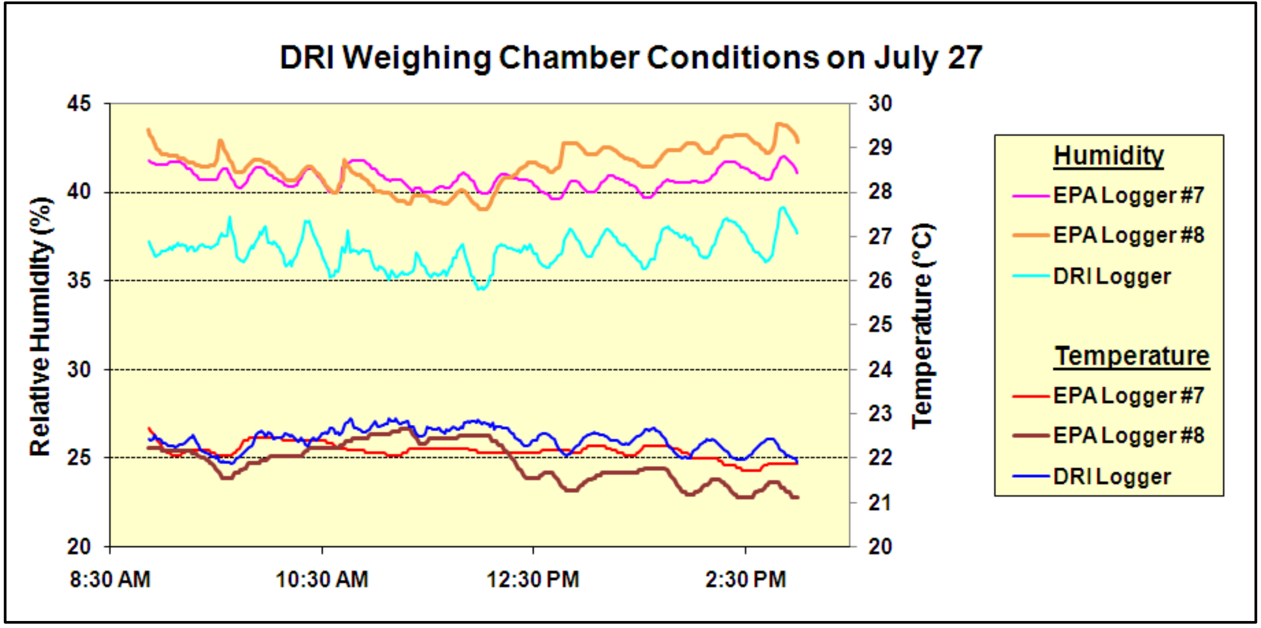

Figure 1 shows reasonably good agreement among the loggers for temperature, but a small bias was observed for humidity. During the period of simultaneous measurements, the average temperature recorded by EPA #7, EPA #8, and DRI logger was 22.2 °C, 21.9 °C, and 22.4 °C respectively. The average relative humidity (RH) recorded by EPA#7, EPA#8, and the DRI logger was 40.8%, 41.4% and 36.7% respectively. The EPA data loggers have an expected accuracy of ± 0.5 °C and ± 2% RH. Figure 1 shows us that the actual RH in the weighing room may be about 4% higher than the value indicated by DRI's logger.

The audit team was anxious to observe a weighing session that included filters and metallic weights brought to the scene from NAREL. 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 in NAREL’s weighing chamber, and then weighed to determine the conventional mass of each filter. 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.

Brenda and Joel were ready to start the gravimetric demonstration once the auditors arrived at the weighing lab. The filters and metallic weights had been place in a laminar flow hood with the petri slides open to facilitate sample equilibration. Joel started the weighing session using a Mettler Toledo XP6 microbalance. The session began with a zero check and a calibration check followed by the first filter sample. ^{210}Po was used to neutralize electrical static charge from each filter sample immediately before it was weighed. The session not only included the two filters and two metallic weights provided by NAREL, but also included two fully equilibrated filters provided by DRI 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 balance) and also expressed as true mass that includes a correction for the buoyant lifting force acting on an object weighed in air.

Table 3. Results from Gravimetric Demonstration

Sample ID	Sample Description	Conventional Mass (mg)			True Mass (mg)		
		NAREL	DRI	Difference	NAREL	DRI	Difference
MW10-13547	Metallic weight provided by NAREL	191.062	191.060	0.002	191.062	191.060	0.002
MW10-13548	Metallic weight provided by NAREL	96.353	96.351	0.002	96.353	96.351	0.002
T10-13549	Teflon® filter provided by NAREL	143.715	143.738	-0.023	143.867	143.864	0.003
T10-13550	Teflon® filter provided by NAREL	146.889	146.915	-0.026	147.044	147.044	0.000
T10-13551	Equilibrated Teflon® filter provided by DRI	146.406*	146.434	-0.028	146.559	146.562	-0.003
T10-13552	Equilibrated Teflon® filter provided by DRI	146.961*	146.982	-0.021	147.115	147.111	0.004
T10-13567	Teflon® filter removed from DRI stock	147.075*	147.098	-0.023	147.229	147.227	0.002
T10-13568	Teflon® filter removed from DRI stock	146.286*	146.306	-0.020	146.439	146.434	0.005

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. 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/cm^3
ρ_x is the density of the sample

Although some of the samples were allowed only a few minutes to equilibrate, the corrected [true] mass values in table 3 shows good agreement between DRI and NAREL for all of the samples. 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 table 3 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 (MW10-13547 and MW10-13548) 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.

Good laboratory practices and good documentation were in place for the gravimetric weighing laboratory. The weighing experiments produced very good results. Only one small item needs attention. According to figure 1, the humidity sensor in the weighing lab needs to be recalibrated or replaced.

Ion Chromatography (IC) Laboratory

Mr. Edward Hackett is the wet chemistry lab supervisor, and he is responsible for the analysis of ions. The auditors were familiar with Ed'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. Ed 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.

Ed 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 Ed to analyze. He was advised to dilute each solution by a factor of ten before his analysis, and he should use his own pipets, 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 4. All of his results were excellent, except for lithium. The value reported for lithium was 16% higher than the expected value.

Table 4. Demonstration of Anion and Cation Analysis During the Audit

Sample_ID	Sample Description	Parameter	Expected Value (ppm)	DRI Result (ppm)
SS10-13553	Anion solution provided by NAREL	Fluoride	1.00	1.04
		Chloride	1.00	0.94
		Nitrite	1.00	not reported
		Nitrate	2.00	2.09
		Sulfate	2.00	2.09
SS10-13554	Cation solution provided by NAREL	Lithium	0.25	0.29
		Sodium	1.00	1.03
		Ammonium	2.00	2.08
		Potassium	1.00	1.02
		Magnesium	1.00	1.01
		Calcium	5.00	5.09

Ed was asked to give the auditors some of his calibration solutions so that they could be analyzed at NAREL. The results from NAREL's analysis are shown in table 5, and both calibration standards appear to be very accurate with one exception. According to NAREL's analysis, the lithium present in DRI's cation standard was 16% lower than the expected concentration.

Table 5. DRI Calibration Standards Analyzed at NAREL After the Audit

Sample_ID	Sample Description	Parameter	Expected Value (ppm)	NAREL Result (ppm)
SS10-13555	Anion standard provided by DRI	Fluoride	1.00	0.95
		Chloride	1.00	1.00
		Nitrate	1.00	0.97
		Sulfate	1.00	0.97
SS10-13556	Cation standard provided by DRI	Lithium	1.00	0.84
		Sodium	1.00	0.98
		Ammonium	1.00	1.08
		Potassium	1.00	0.96
		Magnesium	1.00	1.00
		Calcium	1.00	1.04

The experimental results indicate that one laboratory, either NAREL or DRI, has a faulty calibration for lithium. However, good agreement between labs was observed for all the other ions tested. It is worth stating that lithium is not normally reported to EPA as part of the speciation program. Lithium was present in the test solution provided by NAREL because the solution was purchased as a popular six-component cation standard. If accurate lithium results are needed for any of DRI's clients, further investigation should be initiated to better understand the experimental results from this audit.

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, the only possible problem observed for this area of laboratory operations was the questionable result for lithium.

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 eight 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 ±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 baseline correction. 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 Teflon® filter was brought to the audit and submitted to Steve during the initial audit briefing. He was told to analyze the filter as a demonstration of his analytical skills, but he was not given the history of the filter. In fact the filter had been analyzed previously at DRI and also at the Research Triangle Institute (RTI). RTI had served as a reference lab for a recent inter-laboratory comparison study (reference 16) with six XRF labs participating. Results from Steve's demonstration are presented in figure 2 along with results from the previous analysis at

DRI. The results for several elements are presented as a normalized stack bar graph. Only those elements with results greater than three times the reported uncertainty are shown in the graph.

Figure 2. Demonstration of XRF Analysis

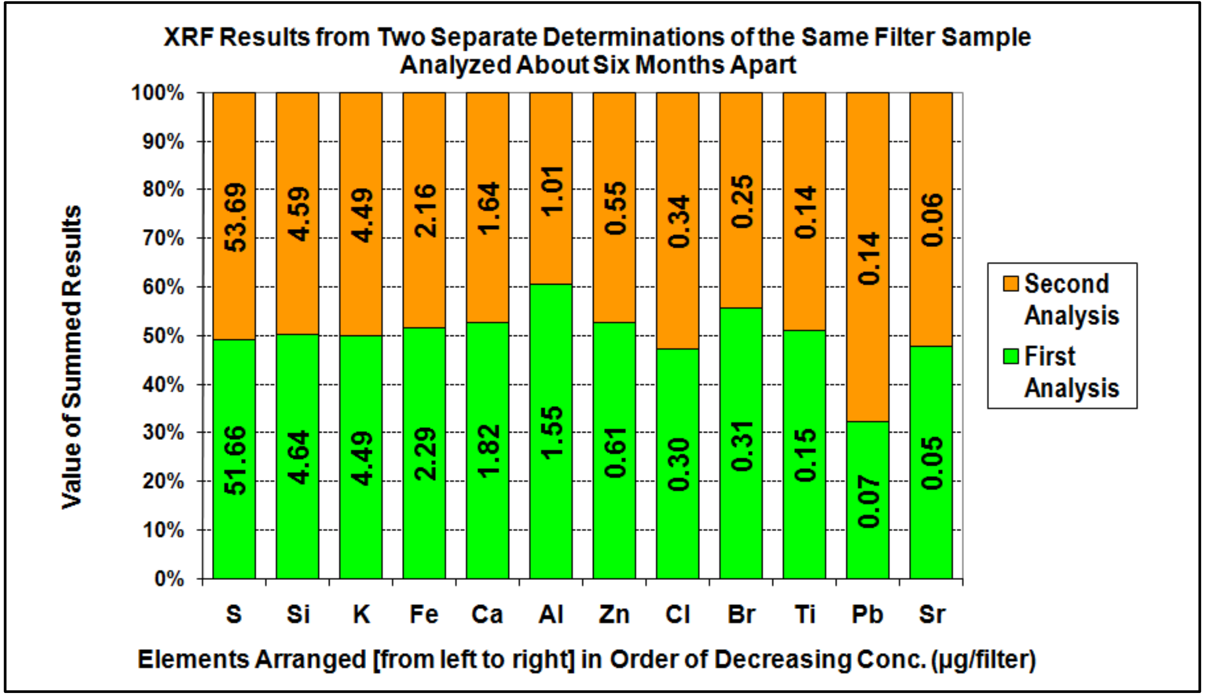

Figure 2 shows at a glance that the analysis performed on the day of the audit compares very well with the previous analysis for most elements. According to figure 2, lead (Pb) showed the worst performance (greatest percent difference) for the two determinations, but this observation is not surprising since the lead concentration was very low in the sample compared to the estimated MDL listed in table 6. Table 6 is a more comprehensive list of results that includes all of the elements reported. The data in table 6 also includes the uncertainty reported with each analysis and a current estimate of the MDL.

Table 6. 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	11.021	1.936	5.761	1.930	2.946
12	Mg	0.000	0.510	1.090	0.513	0.967
13	Al	1.549	0.108	1.009	0.106	0.456
14	Si	4.639	0.078	4.592	0.078	0.275
15	P	0.000	0.017	0.000	0.016	0.107
16	S	51.657	0.194	53.691	0.200	0.162
17	Cl	0.304	0.017	0.340	0.017	0.057
19	K	4.490	0.028	4.490	0.028	0.115
20	Ca	1.821	0.072	1.643	0.071	0.091
21	Sc	0.320	0.312	0.305	0.310	0.082
22	Ti	0.145	0.025	0.140	0.025	0.050
23	V	0.014	0.017	0.000	0.016	0.012

Z	Element	First Analysis (µg/filter)		Second Analysis (µg/filter)		MDL (µg/filter)
		Sample Conc.	Uncertainty	Sample Conc.	Uncertainty	
24	Cr	0.064	0.017	0.030	0.016	0.033
25	Mn	0.078	0.051	0.162	0.052	0.089
26	Fe	2.291	0.021	2.162	0.020	0.079
27	Co	0.000	0.017	0.000	0.016	0.022
28	Ni	0.018	0.048	0.017	0.048	0.030
29	Cu	0.098	0.060	0.086	0.059	0.044
30	Zn	0.607	0.018	0.548	0.017	0.034
31	Ga	0.000	0.081	0.000	0.080	0.124
33	As	0.000	0.017	0.066	0.016	0.013
34	Se	0.006	0.017	0.000	0.016	0.038
35	Br	0.313	0.017	0.251	0.017	0.066
37	Rb	0.000	0.017	0.000	0.016	0.034
38	Sr	0.052	0.017	0.057	0.016	0.082
39	Y	0.016	0.017	0.013	0.016	0.046
40	Zr	0.070	0.028	0.027	0.028	0.116
41	Nb	0.000	0.023	0.000	0.023	0.100
42	Mo	0.000	0.035	0.027	0.035	0.106
46	Pd	0.000	0.040	0.000	0.039	-----
47	Ag	0.000	0.038	0.000	0.038	0.166
48	Cd	0.071	0.049	0.021	0.048	0.160
49	In	0.000	0.051	0.000	0.051	0.164
50	Sn	0.079	0.051	0.049	0.051	0.206
51	Sb	0.000	0.081	0.000	0.080	-----
55	Cs	0.000	0.166	0.000	0.164	0.314
56	Ba	0.000	0.192	0.000	0.195	0.404
57	La	0.000	0.244	0.214	0.235	0.666
58	Ce	0.000	0.226	0.000	0.233	0.541
62	Sm	0.000	0.400	0.000	0.412	0.786
63	Eu	0.000	0.571	0.000	0.582	0.997
65	Tb	0.000	0.439	0.000	0.456	1.082
72	Hf	0.135	0.127	0.000	0.122	0.372
73	Ta	0.000	0.066	0.000	0.066	0.315
74	W	0.000	0.192	0.000	0.189	0.433
77	Ir	0.002	0.030	0.000	0.030	0.145
79	Au	0.000	0.030	0.000	0.030	0.195
80	Hg	0.000	0.017	0.000	0.016	0.061
81	Th	0.016	0.020	0.000	0.020	-----
82	Pb	0.065	0.018	0.138	0.019	0.123
92	U	0.000	0.027	0.000	0.026	-----

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. Teresa Bohannan and Dr. Jerome Robles 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. If results from the test filters confirm that the OC concentration is less than 1.5 $\mu g/cm^2$ and the EC is less than 0.5 $\mu g/cm^2$, then the batch is accepted and may be assigned to a project.

The laboratory has eleven DRI Model 2001 instruments that are needed to handle the large volume of work. 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). Until recently, DRI supplied 47-mm filters to TCEQ for speciation sampling, and those filters required analysis using the CSN method (reference 19). However, changes have been implemented at the TCEQ sites. New URG 3000N samplers have been installed at the speciation sites, and on January 1, 2010, TCEQ switched to the IMPROVE_A method of analysis. Currently, almost all of the routine samples received at the laboratory are 25-mm filters with a request for analysis using the IMPROVE_A method. For the past few years, EPA has been encouraging the states and other monitoring organizations to move toward IMPROVE-like sampling using quartz filters and filter analysis using the IMPROVE_A method.

Instruments are calibrated at least twice per year using four different sources of carbon: methane gas, carbon dioxide gas, sucrose, and potassium hydrogen phthalate. A calibration check using NIST traceable 5% methane in helium is performed daily. 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.

During the briefing at the beginning of the audit, Dana had been given two blind samples with a request to analyze them at her earliest convenience. The samples had been prepared at NAREL and brought to the audit. One sample was prepared from a thermally cleaned quartz fiber filter from which several circular 0.5 cm^2 subsamples were removed using a punch tool and 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 $µg/cm^2$) of carbon from a sucrose solution that was allowed to air dry in a separate labeled Petri-dish. Except for the labels, the two samples were visibly indistinguishable.

By the time the auditors arrived at the carbon analysis lab, results were available for the demonstration samples. The auditors were able to review the raw data and discuss the details of the analysis. The results from DRI's analysis are presented in table 7 along with spike levels and results from the independent analyses performed at NAREL.

Table 7. Demonstration of Carbon Analysis

Sample ID	Sample Description	Carbon Fraction	Spike Level ($µg/cm^2$)	DRI Result ($µg/cm^2$)	NAREL Result ($µg/cm^2$)
Q10-13557	Blank Quartz	OC	0.00	0.20 ± 0.27	0.25 ± 0.21
		EC	0.00	0.00 ± 0.06	0.01 ± 0.20
Q10-13558	Spiked Quartz	OC	40.0	37.58 ± 3.05	39.21 ± 2.16
		EC	0.00	0.75 ± 0.06	0.51 ± 0.23

Table 7 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.

Travel blanks were brought to the audit and were not opened before they were carried back to NAREL for analysis. Experience has shown that travel blanks can be very useful for those audits that include demonstration blanks. The results from two quartz travel blanks are shown in table 8.

Table 8. Trip Blanks and Calibration Standard Analyzed at NAREL

Sample ID	Sample Description	Carbon Fraction	Spike Level ($µg/cm^2$)	NAREL Post-Audit Result ($µg/cm^2$)
Q10-13573	Quartz Travel Blank #1	OC	0.00	0.07 ± 0.20
		EC	0.00	0.01 ± 0.20
Q10-13574	Quartz Travel Blank #2	OC	0.00	0.02 ± 0.20
		EC	0.00	0.01 ± 0.20
SS10-13559	Sucrose solution provided by DRI	OC	18.77	17.51 ± 1.08
		EC	0.00	0.10 ± 0.20

Table 8 also contains results from a sucrose solution provided by DRI. Dana was asked to give the auditors some of her calibration solution so that it could be analyzed at NAREL. According to NAREL's analysis, the sucrose solution was very accurate.

During the interviews in the carbon laboratory, the auditors were able to observe DRI 2001 instruments in operation. The auditors were quite impressed with the new software that provided a graphical interface with all the instruments at a single workstation.

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 third 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 being followed.

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.

This audit produced two small findings that were discussed earlier in this report.

1. Humidity values recorded by EPA data loggers inside the weighing lab were significantly higher than values recorded by the DRI logger (see figure 1).

   In response to this finding, DRI took several actions. They replaced their RH monitor (rather than recalibrate it) and conducted an assessment of T and RH variation within their weighing room using five different NIST-traceable T and RH loggers, including the two used by EPA in the audit. The assessment indicated that when the sensors were in close proximity, the mean temperature was 21.06 ± 0.21 °C with a maximum difference of 0.49 °C; while for RH, the mean was 35.82 ± 0.34 %RH with a maximum difference of 0.46 %RH. However, the outcome changed when the EAF sensor was kept in its normal location and the other sensors were situated in different locations around the weighing room, including having the two EPA loggers in roughly their audit positions. In that case, the maximum RH difference was roughly 4 %RH between the logger located under the cabinets on the conduit next to the wall and the logger near the weighing chamber. The 4 %RH is also the peak to peak difference in the periodic sinusoidal variation of RH in the weighing room over time. However, the mean difference between the EAF probe and the logger near the weighing chamber was only about 0.2 %RH. Results with other locations for the probe indicated that inhomogeneities in both temperature and RH could be found within the weighing room depending on height, whether near a hood or not, or distance from the walls. However, the location of the EAF sensor produces results that are in good agreement with those near the weighing chamber.

2. The analytical results presented in tables 4 and 5 indicate a faulty lithium calibration at DRI or possibly at NAREL. Since lithium is not reported to EPA as part of the speciation program, this observation may be academic.

   In response to this finding, DRI followed up by checking with the manufacturer of the supposedly certified standard that they used. They found that the standard was in error for lithium only. The manufacturer has made and sent to DRI a newly created batch of a new certified standard which is now correct for lithium. DRI has confirmed that the new standard is correct for lithium.

The audit team appreciates the professionalism they observed as well as the warm hospitality they experienced during this audit.

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