TECHNICAL MEMORANDUM

TO: Jim Homolya / OAQPS

FROM: Michael S. Clark / NAREL

COPY: Michael Miguel / CARB
Dennis Mikel / OAQPS
Mary Wisdom / NAREL
Dr. John Griggs / NAREL

DATE: February 26, 2003

SUBJECT: CARB Laboratory Audit

Introduction

On October 22-23, 2002, a Technical Systems Audit (TSA) was conducted at the Northern Laboratories Branch of the California Air Resources Board (CARB) facilities located in Sacramento, California. The TSA was conducted as part of the US EPA's quality assurance oversight for the $PM_{2.5}$ Speciation Network. CARB has elected to use their own laboratory facilities to analyze many of the speciation samples collected within the state rather than use other laboratories which are available to perform this function under a federal contract.

The US EPA audit team consisted of Michael Clark, Steve Taylor, and Jewell Smiley from the National Air and Radiation Environmental Laboratory (NAREL) and Jim Homolya from the Office of Air Quality Planning and Standards (OAQPS). This TSA was a first annual routine inspection of the CARB laboratory systems and operations.

Summary of Audit Proceedings

After a brief meeting with the CARB senior staff and supervisors, the audit team separated as necessary to complete specific assignments for the audit process. At least one member of the CARB staff was always available to escort and assist each auditor. The following specific areas at the CARB facilities were visited and inspected.

✓ Sample Receiving and Handling Laboratory - Mr. George Dunstan, Ms. Arlene Bingaman

✓ Organic Carbon/Elemental Carbon (OC/EC) Laboratory - Mr. Peter Samra

✓ X-ray Fluorescence (XRF) Laboratory - Dr. William Davis

✓ Ion Chromatography (IC) Laboratory - Mr. George Dunstan

✓ Gravimetric Laboratory - Mr. Mike Humenny, Ms. Debbie Moreno-Thornsberry

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

- ✓ Mr. Michael Poore - Northern Laboratory Branch Chief
- ✓ Mr. Russell Grace, Manager of Special Analysis Section
- ✓ Mr. Mike Miguel - Quality Assurance Manager
- ✓ Mr. Dan Tackett - LIMS Specialist

CARB has been analyzing speciation samples since January of 2002. Members of the audit team were familiar with CARB's Quality Assurance Project Plan (QAPP) and pertinent SOPs. A set of Performance Evaluation (PE) samples prepared at NAREL were submitted to CARB during the summer of 2002, and those PE results were discussed with CARB staff during the audit (see reference 1). Check lists were available to assist the auditors with the numerous questions directed to CARB staff.

Sample Receiving and Handling Laboratory

CARB's Northern Laboratory Branch produces a large volume of chemical analyses (600,000 results per year) using many different analytical methods. However, this TSA focused exclusively on the techniques used to analyze $PM_{2.5}$ filters collected at six speciation sites and thirty mass sites. All six of the speciation field sites were using Met One SASS units for sample collection. One of the SASS units was located on the roof of the laboratory building.

George Dunstan and Arlene Bingaman are immediately responsible for shipping filters to the field sites and receiving the loaded filters back at the lab. An SOP was available that describes this critical process.

- *Standard Operating Procedure for Filter and Canister Preparation for $PM_{2.5}$ Speciation Samples* [SOP MLD 062]

After a brief tour of the Northern Branch laboratories, all of the auditors were present in the sample receiving area to observe actual samples going through the shipping, receiving, and handling process. New clean filters are assembled into SASS canisters for shipment to the remote field sites. After the sampling event, the loaded filters are returned to the laboratory still mounted in the canister, but are cooled to approximately 4 °C for preservation during transit. Upon receipt at the laboratory, the canisters are removed from the shipping cooler, and the temperature is recorded. Each canister is disassembled, and the recovered filter is placed into a new container. The Nylon® filter is transferred to an extraction tube. The Teflon® and the quartz filters are transferred to petri slides to await analysis. Canisters and [filter holder] cassettes are expensive and must be cleaned for reuse. A dishwasher was used to clean these items. Field blanks were used to monitor for accidental contamination of the filter media. A request was made to query the Laboratory Information Management System (LIMS) for the field blank results. Those results were examined, and a summary of the blank results is presented in the following table.

Table 1. Field Blank Results

Parameter	Instrument	Concentration (µg/filter) Average	Max.	Min.	Std. Dev.	LOD*	Number of Values
PM2.5 Mass	Balance	3.3	14.0	-8.0	6.0	1	26
Elemental Carbon	Carbon Anal.	0.0	0.0	0.0	0.0	9	12
Organic Carbon	Carbon Anal.	14.5	21.9	5.1	4.5	9	12
Ammonium	IC	0.138	0.280	0.090	0.042	0.5	26
Nitrate	IC	0.273	0.810	0.000	0.149	0.5	26
Potassium	IC	0.095	0.430	0.000	0.125	1	26
Sodium	IC	0.352	0.860	0.110	0.161	0.8	26
Sulfate	IC	0.047	0.220	0.000	0.081	2	26
Aluminum	XRF	0.009	0.050	-0.030	0.022	0.05	12
Antimony	XRF	-0.031	0.040	-0.170	0.063	0.1	12
Arsenic	XRF	-0.001	0.030	-0.020	0.018	0.02	12
Barium	XRF	0.061	0.500	-0.540	0.252	0.3	12
Bromine	XRF	-0.006	0.010	-0.020	0.011	0.01	12
Calcium	XRF	0.023	0.160	-0.040	0.060	0.2	12
Chlorine	XRF	-0.046	0.210	-0.300	0.162	0.07	12
Chromium	XRF	-0.002	0.010	-0.010	0.008	0.02	12
Cobalt	XRF	0.006	0.010	0.000	0.005	0.06	12
Copper	XRF	-0.004	0.040	-0.050	0.030	0.02	12
Iron	XRF	0.008	0.040	-0.030	0.022	0.02	12
Lead	XRF	-0.054	0.050	-0.170	0.070	0.05	12
Manganese	XRF	-0.002	0.010	-0.020	0.012	0.02	12
Mercury	XRF	0.017	0.060	-0.030	0.023	0.04	12
Molybdenum	XRF	-0.010	0.020	-0.040	0.020	0.03	12
Nickel	XRF	-0.002	0.010	-0.010	0.006	0.01	12
Phosphorus	XRF	-0.004	0.020	-0.030	0.016	0.02	12
Potassium	XRF	0.030	0.110	-0.050	0.053	0.1	12
Rubidium	XRF	-0.004	0.010	-0.010	0.007	0.02	12
Selenium	XRF	-0.004	0.020	-0.030	0.013	0.02	12
Silicon	XRF	0.008	0.050	-0.030	0.023	0.03	12
Strontium	XRF	0.004	0.020	-0.010	0.008	0.02	12
Sulfur	XRF	0.001	0.050	-0.030	0.019	0.02	12
Tin	XRF	-0.069	0.030	-0.200	0.074	0.09	12
Titanium	XRF	0.003	0.100	-0.160	0.078	0.04	12
Vanadium	XRF	0.003	0.040	-0.020	0.015	0.03	12
Yttrium	XRF	0.013	0.030	-0.020	0.013	0.02	12
Zinc	XRF	0.003	0.030	-0.010	0.011	0.01	12
Zirconium	XRF	0.013	0.030	-0.010	0.013	0.02	12

* LOD = Limit of Detection reported by CARB for recent PE study.

The field blanks summarized in Table 1 were from March, May, July, and September of 2002. It is important to notice that several negative values were reported for the XRF and gravimetric mass determinations which will influence the calculated average value. It is good to see that negative values are not being censored, since the variability of representative blanks, over time, is a good indicator of sensitivity.

Good laboratory practices were generally observed for preparing the fresh canisters to send to the field and for retrieving the loaded filters following sample collection. No deficiencies were noted for this area of laboratory operations.

Carbon Analysis Laboratory

The carbon analysis is normally performed by Peter Samra, and this part of the audit was conducted by Steve Taylor. The interview and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOP.

- *Standard Operating Procedure for the Organic and Elemental Carbon Analysis of Exposed Quartz Microfiber Filters* [SOP MLD 065]

Because of unresolved issues generated by the PE study, special attention was given to two specific data quality elements: (1) data comparability and (2) sensitivity. Some background is necessary to understand these issues.

EPA has established data quality objectives for the $PM_{2.5}$ Speciation Network, and it is critical that all participating laboratories produce analytical results that are comparable with the national contract laboratory, the Research Triangle Institute (RTI). The carbon analysis at RTI is based upon NIOSH method 5040 (see reference 2) which includes the determination of organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC) all of which are components of the total carbon (TC). RTI also reports an "OCX" fraction which may be useful for specific data manipulations. RTI and NAREL both use the carbon analyzer manufactured by Sunset Laboratories Inc.

The carbon analyzer used at CARB is a DRI Model 2001 manufactured by Atmoslytic Inc. Even though the DRI and the Sunset units are very similar, there are significant differences in both the hardware and the software. Both instruments require a punched segment of the filter to be manually inserted into a quartz oven. Once inside the oven, the filter segment is purged with pure helium and the temperature is increased in programmed stages. A laser aimed at the filter segment produces reflected light as well as light that is transmitted through the filter segment. The DRI instrument monitors both the transmitted and the reflected laser signals as the analysis proceeds. The Sunset instrument monitors only the transmitted laser signal. Many samples create optically dark char as the filter segment is heated in a pure helium atmosphere. The formation of char will cause the laser signal (both reflected and transmitted) to decrease. After a programmed amount of time (and temperature), the sample is allowed to cool briefly before the purge gas is switched from pure helium to an oxygen/helium mixture. More programmed heating stages are applied to the sample as the analysis continues. Near the end of the analysis, a methane spike is injected through the oven as an internal standard. All forms of carbon released from the sample are carried by the purge gas through a bed of MnO_2 to convert the carbon to CO_2. The CO_2 merges with a stream of hydrogen gas before it passes through a nickel catalyst to form methane. A Flame Ionizaton Detector (FID) located at the end of the sample train provides a signal for the methane equivalent of carbon released from the sample.

CARB does not report CC, nor does it calculate an OCX fraction. But these differences are not critical. According to the accumulated database, CC appears to be an insignificant component in most ambient air samples. Recent data have also raised doubt about the utility of OCX values.

A greater concern about the carbon analysis may be observed in the raw data thermograms. Replicate filters are frequently prepared at NAREL and used as PE samples. CARB's recent PE included replicate filters of Montgomery air and also blind spike solutions containing sucrose. When thermograms from NAREL and CARB were examined, a significant difference could be seen in the behavior of the laser signals in response to char. Figure 1 and Figure 2 are thermograms of replicate filters analyzed at NAREL and CARB respectively. The thermograms from both labs show evidence of char formation as indicated by a reduction in the initial laser signal. For the NAREL analysis, the char remains on the filter segment until the atmosphere is switched from pure helium to a helium/oxygen mixture. For the CARB analysis, however, most of the char is released from the filter before the bottled oxygen is introduced to the sample. This difference in char release was first observed for the PE samples split between CARB and NAREL (see reference 1). As stated earlier, the PE samples consisted of blind solutions of sucrose and replicate quartz filters loaded with $PM_{2.5}$ captured from the Montgomery air.

Figure 1

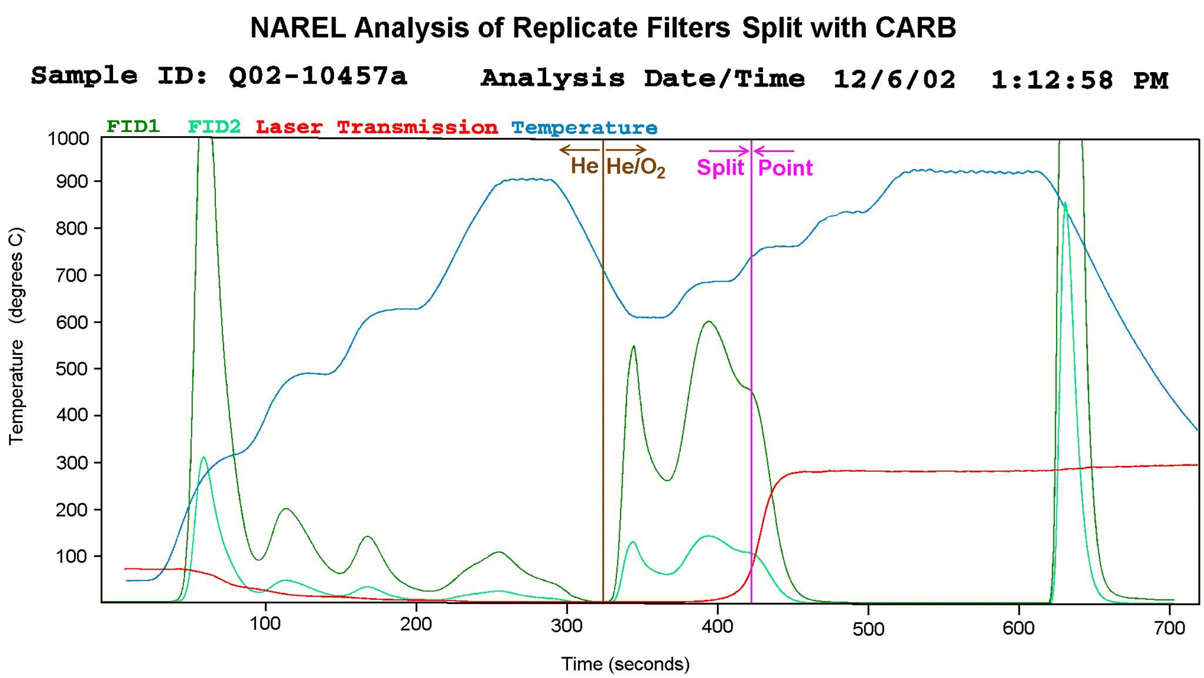
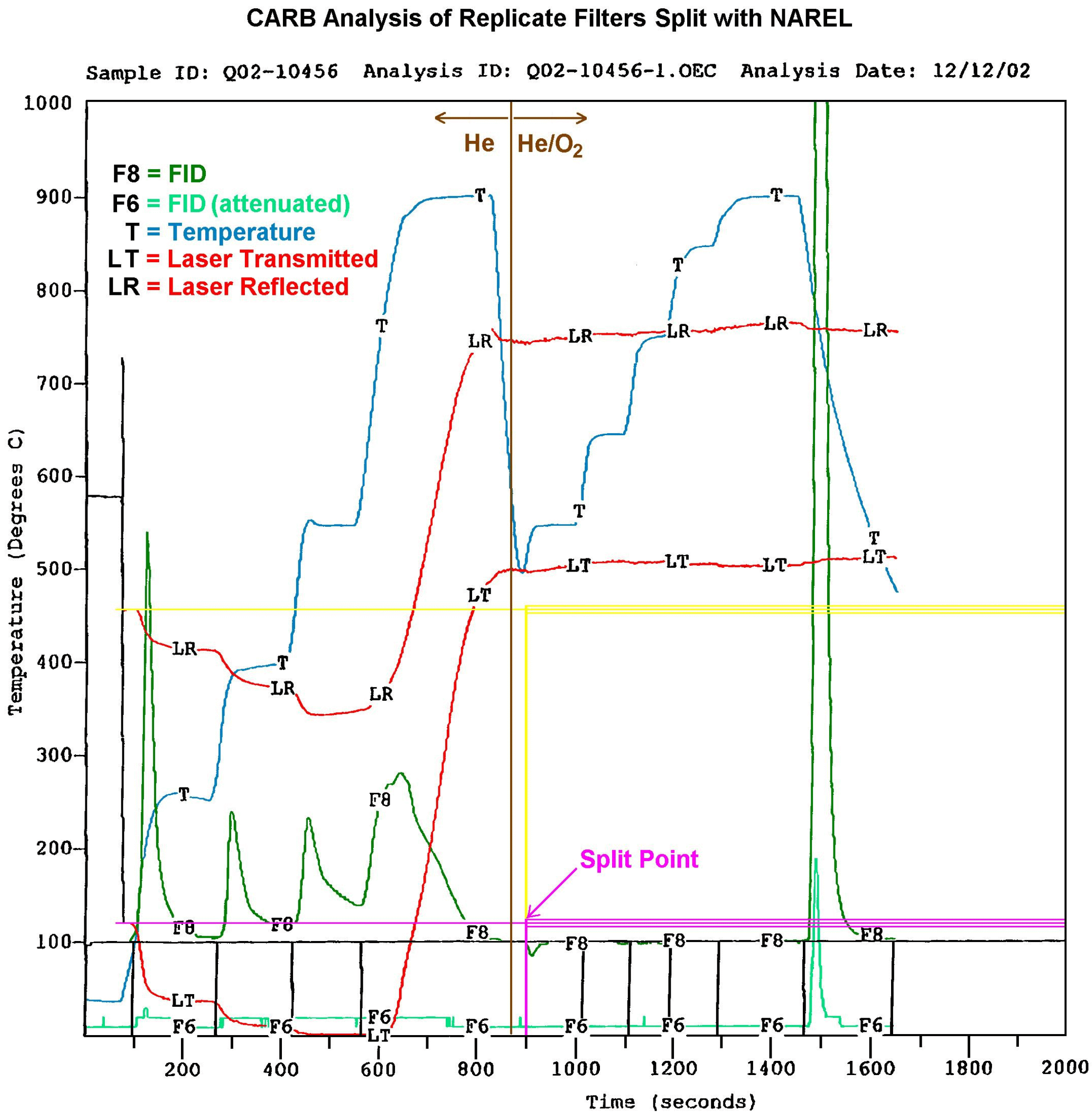


Figure 2



A special meeting was held at CARB during the TSA on the morning of October 23 to discuss the concerns about the carbon analysis. All of the stakeholders agreed that efforts were needed to better understand the difference(s) between NAREL's analysis and CARB's analysis. Mike Poore agreed to request assistance from DRI who sponsored a service contract for their instrument. The carbon analysis of routine field samples was suspended until remediation efforts could be made. The audit team volunteered to assist with any remediation efforts that might benefit from experiments conducted at NAREL.

Over the course of several days following the TSA, a list of possibilities was generated that might explain why the carbon analysis may be different at the two labs.

- Experiments performed at CARB suggest that their instrument may develop leaks at the higher temperatures, and the proposed leak would allow oxygen from the air to mix with the purge gas and cause the premature disappearance of char. The DRI software will not assign a split point before the program opens the helium/oxygen valve. The Sunset software will assign a split point before the helium/oxygen valve opens, if the laser signal supports that assignment.
- New scrubbers were added to remove potential contaminants from CARB's supply of bottled "pure" helium.
- Observations were made to check CARB's valve timing that controls the oven's purge gas.
- Different temperature profiles were tested at both labs.

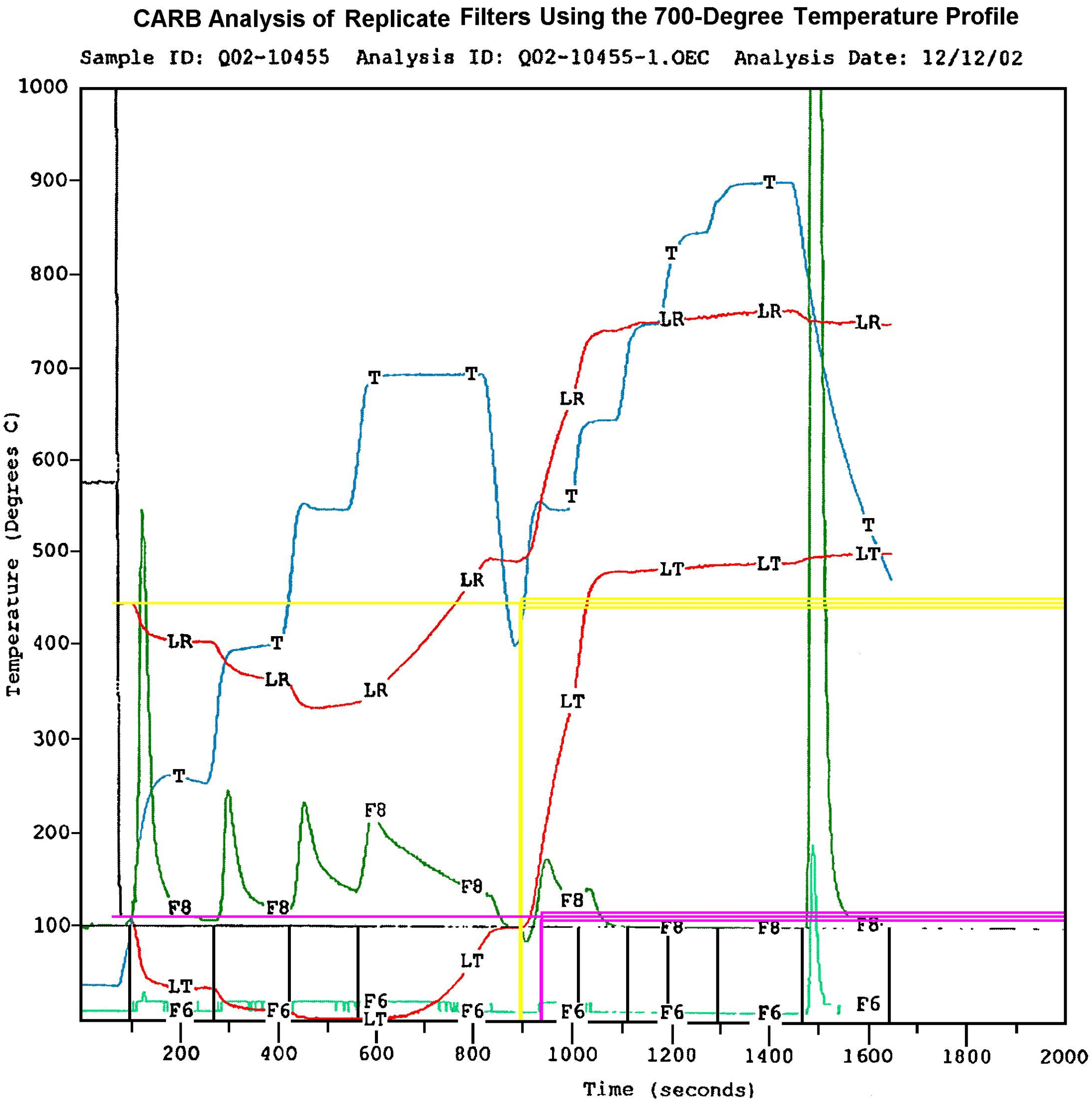
A new set of replicate filters, identified below as the November 27 sampling event, was prepared at NAREL following the TSA. The new replicate filters were split between CARB and NAREL to make them available for experiments and troubleshooting. Two of the replicates were analyzed at NAREL, and two of the replicates were analyzed at CARB using three different thermal profiles. The results from those analyses are presented in Table 2.

Table 2. Analysis of Replicate Filters - November 27 Sampling Event

		Concentration ($\mu g/cm^2$)			Max. Temperature in Pure Helium Atmosphere (°C)	Illustrated Reference
Laboratory	Filter ID	OC	EC	TC		
NAREL	Q02-10257	25.94	2.37	28.31	900	Figure 1
NAREL	Q02-10258	26.04	2.37	28.41	900	-----
CARB	Q02-10255	28.47	2.17	30.64	900	-----
CARB	Q02-10256	30.35	<0.8	30.35	900	Figure 2
CARB	Q02-10255	27.98	2.77	30.76	700	Figure 3
CARB	Q02-10256	27.64	2.44	30.08	700	-----
CARB	Q02-10255	27.77	2.93	30.70	600	Figure 4
CARB	Q02-10256	27.58	3.00	30.58	600	-----

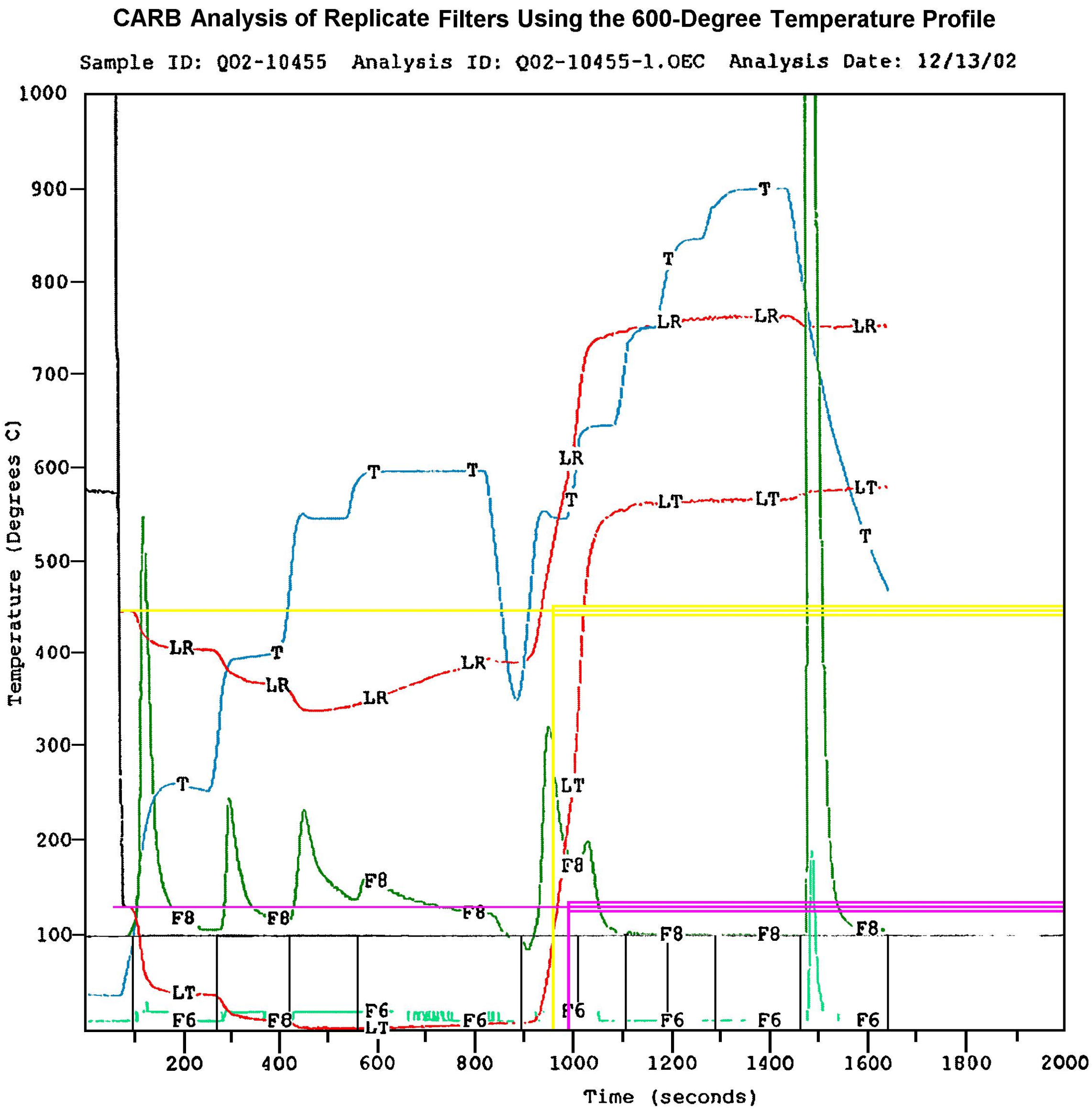
Different thermal profiles were tested to identify a set of instrument conditions that may be able to consistently produce comparable carbon data. CARB's analysis using the 900-degree profile shows inconsistent EC values. It has been assumed that leaks are responsible for the inconsistent values. Figure 1 and Figure 2 have been included in this report to illustrate the details of the frequently encountered problem. Experiments using the 700-degree profile and the 600-degree profile have shown a diminishing tendency to release char before the helium/oxygen valve opens. Figure 3 and Figure 4 illustrate the 700-degree and the 600-degree profiles respectively.

Figure 3



It has been suggested that temperatures above 550 °C, even within a pure helium atmosphere, may cause char to disappear from the filter segment. Figures 2, 3, and 4 support this statement. Thermograms of sucrose analyzed with the CARB instrument also support this statement. But the same materials analyzed at NAREL show insignificant release of char using a 900-degree profile.

Figure 4



The routine analysis of quartz filters has been restarted at CARB using the 700-degree thermal profile. Our experiments indicate that this remedy may produce carbon results that are most similar to the analysis at NAREL and RTI. As a followup, NAREL has volunteered to analyze a small number of samples that CARB chooses to split.

The second issue of sensitivity was discussed during the TSA and requires a brief discussion in this report. The limit of detection (LOD) reported by CARB is 0.8 µg/cm^2. The detection limit reported by NAREL and RTI is approximately 0.2 µg/cm^2. Two factors may contribute to the difference in sensitivity. First and most important is the size of the punch used to produce the filter segment consumed during the analysis. The standard punch used at RTI and NAREL produces a filter segment that is 1.5 cm^2 in size. This is three times larger than the filter segment routinely analyzed with the DRI instrument. A second less important factor that may affect sensitivity is the time over which the FID signal must be integrated. Noise and drift which are present in the FID trace must be distinguished from the signal produced by the analyte. Longer data acquisition periods are generally more susceptible to signal drift, and also a given signal area will rise higher above the FID noise if that area is compressed into a shorter time interval. The thermograms show that CARB's data acquisition time is significantly longer than NAREL's analysis.

CARB has committed to experiments that may improve their sensitivity. An extra quartz filter will be collected and analyzed from some of the field sites. The extra filter will be loaded using a mask to reduce the area of the deposit zone. The plan is to create a "duplicate" sample which has a deposit zone three times smaller than "normal". If these special "duplicate" filters produce similar results, then masks will be implemented for all subsequent sampling events as a method to improve the overall analytical sensitivity. CARB has promised to share the results of their efforts.

Although much of this report has described concerns for the carbon analysis, let us not forget to say that good laboratory practices were generally in place. Furthermore, the immediate response and followup to the issues described in this report have demonstrated an appropriate level of concern for these findings.

X-Ray Fluorescence Analysis

The PM captured onto the surface of the Teflon® filter is not only weighed to determine its mass but is also analyzed to determine its elemental composition using the energy dispersive X-Ray Fluorescence (XRF) technique. The XRF analysis may not proceed before the gravimetric analysis has been completed. Fortunately the gravimetric lab is located very near the XRF lab.

Dr. William Davis is responsible for the XRF analysis. He was interviewed by Jewell Smiley during this part of the audit. The XRF analysis of the air filters is based upon EPA method IO-3.3 (see reference 3). At the time of this audit, the following SOP was listed on CARB's website, but the file was not available for download.

- *Determination of Elemental Concentrations in Ambient Air by Energy-Dispersive X-Ray Fluorescent Spectroscopy* [SOP MLD 034]

The XRF analysis is performed using an older Kevex instrument, and thirty elements are reported for the $PM_{2.5}$ filters. This is less than the forty-eight elements reported by RTI. There are numerous possible reasons why CARB does not expand its list of target elements. The instrument is old, and the cost to upgrade, modify, or replace it may be prohibitive. Significant effort (and therefore significant cost) may be required to modify the current analytical scheme so that extra elements may be determined with useful sensitivity. Many of the extra (heavier) elements reported by RTI are seldom detected in ambient air samples. Sodium and magnesium are very light elements not reported by CARB, and only modest detection limits can be achieved for these elements using the best instrument with an optimized analytical scheme. These facts are not presented to justify a thirty-element analysis, but are stated to acknowledge those obstacles that may hinder change.

Tin and lead were discussed during the interview. These two elements are seen in spectra as background, and Bill stated that they were present in new (blank) Teflon® filters. Negative analytical values such as those observed in Table 1 are the result of overcompensation for the background. New Teflon® filters that are supplied by EPA for the $PM_{2.5}$ program have been subjected to numerous XRF analyses to determine background before the filter lots are accepted for distribution. A summary of the most recent lot analysis was recently transmitted to CARB.

The only specific samples discussed were those from the recent PE study, and the details of those results are described in a separate report (see reference 1). The results from the PE study indicated good performance from the XRF laboratory for those elements reported.

Ion Chromatography (IC) Laboratory

The IC analyses are performed by George Dunstan. He was interviewed by Jewell Smiley for compliance to good laboratory practices, the QAPP, and the following SOPs.

- *Standard Operating Procedures for Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography* [SOP MLD 064]
- *Standard Operating Procedures for Filter and Canister Preparation for PM2.5 Speciation* Samples [SOP MLD 062]

The laboratory is equipped with an automated Dionex IC instrument. One channel is optimized for the analysis of anions and another channel is optimized for the analysis of cations. The lab also has access to equipment for cleaning and extracting Nylon® filters. Extractions are performed using an ultrasonic bath and a shaker table. Nanopure deionized water is the extraction solvent. 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 when the routine check samples indicate excessive calibration drift. Replicate injections of low level standards have been used to estimate sensitivity and low level precision. Duplicate injections of sample extracts have been used to evaluate mid-level precision. Blank spikes are extracted along with field samples to evaluate method accuracy. Statistically derived limits have been developed over the lifetime of the IC program and are used to control the analytical system.

The only specific samples discussed were those from the recent PE study, and the details of those results are described in a separate report (see reference 1). The results from the PE study indicated good performance from the IC laboratory.

The field blanks summarized in Table 1 show respectably low levels of ion contamination. Therefore the overall process used to clean new Nylon® filters, assemble canisters, retrieve, and extract the Nylon® filters offers an attractive baseline for IC measurements at CARB.

Gravimetric Laboratory

Mike Humenny is responsible for the gravimetric analysis, and Debbie Moreno-Thornsberry was training so that she also will be able to perform the analysis. This part of the audit was conducted by Steve Taylor. The interview and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOP.

- *Standard Operating Procedure for the Determination of $PM_{2.5}$ Mass in Ambient Air by Gravimetric Analysis* [SOP MLD 055]

The actual weighing area was a dedicated room with controlled temperature, humidity, and dust. Chamber blanks which are left open inside the room are routinely analyzed to monitor dust. A Dickson data logger was brought to the TSA and placed near one of CARB's two devices used to measure temperature and humidity inside the weighing room. Good agreement was observed between the local devices and the Dickson device.

The microbalance used to weigh the $PM_{2.5}$ Teflon® filters was a Sartorius MC5. Although excellent gravimetric mass results were reported for CARB's recent PE samples (see reference 1), two metallic mass units were brought to the interview so that direct observations could be made as they were weighed. Results are presented in Table 3.

Table 3

Metallic weight	NAREL Value (mg)	CARB Value (mg)
Mass unit 1	100.001	100.001
Mass unit 2	200.002	200.001

No deficiencies for the gravimetric lab were noted. Overall good laboratory practices were observed during this TSA.

Other Staff Interviews

Michael Poore, Russell Grace, and Mike Miguel were interviewed by Michael Clark, and Jim Homolya. The following topics were discussed.

1. Facility and Equipment
    a. Facility, Equipment, and Support Services
    b. Security
    c. Health and Safety
    d. Waste Management
2. Organizational Structure and Management Policies
    a. Personnel

    b. Job Descriptions and Qualifications
    c. Training Program and Training Records
3. Quality Assurance
    a. Standard Operating Procedures
    b. Performance Evaluation Results and Corrective Action Responses
    c. Previous Audit Reports and Responses
    d. Quality Reports to Management
    e. Quality Control Records and Oversight
    f. Review Process for QAPP's
    g. Review Process for Client Data Packages
4. Procurement
    a. Materials and Equipment
    b. Services
5. Document Control
    a. Controlled Document Production
    b. Document Distribution and Tracking
    c. Revisions to Control Documents
    d. Retrieval and Disposal of Outdated Documents
6. Computer Management and Software Control
    a. Personnel and Training
    b. Facilities and Equipment
    c. Procedures
    d. Security
    e. Data Entry
    f. Records and Archives

Dan Tackett was briefly interviewed by Jewell Smiley and Steve Taylor. Dan was able to demonstrate some of the LIMS capabilities. Dan provided the information regarding field blanks which is summarized in Table 1 of this report.

Conclusions

Observations have been made by the audit team to determine CARB's compliance with good laboratory practices, the QAPP, and SOPs. Special attention was given to areas of concern established by recent PE samples. This audit produced the following findings, recommendations, and comments.

1. Significant differences were observed in the raw data thermograms of samples split with NAREL. CARB thermograms frequently show symptoms of an air leak. After considerable experimentation which followed this TSA, CARB has adopted a new 700-degree thermal profile for the instrument. This action seems to be the best practical option which will produce data that agrees with the carbon analysis at RTI.

   Recommendation. CARB should select a small number of filters from some of the sites and split them with NAREL to further evaluate any inter-laboratory differences.

2. The LOD currently reported by CARB for the carbon analysis is 0.8 $\mu g/cm^2$, and the detection limit reported by RTI and NAREL is approximately 0.2 $\mu g/cm^2$. An extra quartz filter will be loaded at some of the field sites using a mask to reduce the deposit area by a factor of 3. The ambient air concentration determined from the masked filter will be compared to the concentration determined from the "unmasked duplicate". If the comparison is favorable, the mask will be utilized for all quartz filters to improve CARB's sensitivity.

   Recommendation. NAREL would be very interested to see the results of this investigation using the quartz filter mask. For example, what will be the effect of changing the face velocity? How will the new field blanks look based upon µg/filter? This would be good information to share.

References

1. EPA/NAREL. September 12, 2002. Technical Memorandum: Performance Evaluation - CARB Laboratories. U.S. Environmental Protection Agency. [currently available at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/carb2002.pdf]

2. NIOSH. 1999. Method 5040, Issue 3, Elemental Carbon (Diesel Particulate), NIOSH Manual of Analytical Methods, Fourth Edition. National Institute for Occupational Safety & Health, Cincinnati, OH.

3. EPA. 1999. Method IO-3.3, Determination of Elements Captured on Filter Material and Analyzed by X-Ray Fluorescence (XRF) Spectroscopy. U.S. Environmental Protection Agency.