

TECHNICAL MEMORANDUM



TO: Jim Homolya / OAQPS
FROM: Eric Boswell / NAREL
COPY: Mike Poore / CARB
Author: Jewell Smiley / NAREL
DATE: April 22, 2004
SUBJECT: CARB Laboratory Audit

Introduction

On March 2, 2004, 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.

This audit was performed by Steve Taylor and Jewell Smiley both of whom are physical scientists who normally work at EPA's National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. This TSA was a routine annual inspection of specific laboratory systems and operations at CARB that are required for the analysis of PM_{2.5} Speciation samples. The last TSA performed by NAREL was conducted in October of 2002 [see reference 1].

Summary of Audit Proceedings

After a brief meeting with some of the CARB staff and supervisors, the audit team visited specific areas of the laboratory to interview those technical staff who actually perform the analyses. At least one member of the CARB staff was always available to escort and assist the auditors. The following specific areas at the CARB facilities were visited and inspected.

- ✓ Sample Receiving and Handling Laboratory - George Dunstan, Arlene Bingaman
- ✓ Organic Carbon/Elemental Carbon (OC/EC) Laboratory - Peter Samra (not present to interview)
- ✓ Ion Chromatography (IC) Laboratory - George Dunstan
- ✓ Gravimetric Laboratory - Mike Humenny, Debbie Moreno-Thornsberry

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

- ✓ Michael Poore - Northern Laboratory Branch Chief
- ✓ Cliff Popejoy - Inorganics Laboratory Section Manager
- ✓ Samantha Scola - Air Pollution Specialist
- ✓ Dan Tackett - LIMS Specialist

CARB's Northern Laboratory Branch provides a large number of chemical analyses (600,000 results per year) using many different analytical methods. However, this TSA focused exclusively on the techniques listed above which are used to analyze PM_{2.5} filters collected at seven speciation sites and thirty mass sites. All seven of the speciation field sites use Met One SASS units for sample collection. CARB has been analyzing speciation samples since January of 2002.

Both of the auditors from NAREL were familiar with CARB's Quality Assurance Project Plan (QAPP) and pertinent SOPs. A few weeks before the TSA was scheduled, a set of single-blind Performance Evaluation (PE) samples were prepared at NAREL and submitted to CARB for analysis [see reference 2]. Most of the results from these PE samples were available to discuss with CARB staff during the audit.

The XRF laboratory was not inspected during this audit. The analyst who previously performed the XRF analysis has retired, and the instrument that he used has also been retired. CARB is in the process of purchasing a new XRF instrument, and after it is installed, a new analyst will be trained to perform the analysis. Meanwhile, the XRF filter samples that continue to arrive from the field are placed into storage to build a backlog. A set of PE filters from NAREL has also been placed into CARB's backlog. CARB will analyze the set of PE filters from NAREL as soon as the new XRF system has been installed and initial performance has been approved by the QA Manager and the Branch Chief.

Sample Receiving and Handling Laboratory

George Dunstan and Arlene Bingaman are immediately responsible for shipping clean filters to the field sites and receiving the loaded filters back at the lab. An SOP is available on the web that describes this critical process [see reference 3].

After a brief meeting with laboratory supervisors and some of the speciation analysts, both of the auditors were escorted to the sample receiving area to observe how samples were processed and handled in this area. 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. A summary of those results is presented in the following table.

Table 1. Field Blank Results

Parameter	Instrument	Concentration ($\mu\text{g}/\text{filter}$)					Number of Values
		Average	Max.	Min.	Std. Dev.	LOD*	
PM2.5 Mass	Balance	2.3	21.0	-15.0	7.2	1	82
Elemental Carbon	Carbon Anal.	0.004	0.16	0.00	0.02	9	82
Organic Carbon	Carbon Anal.	13.4	26.2	5.1	4.5	9	82
Ammonium	IC	0.275	0.760	0.093	0.174	0.5	82
Nitrate	IC	0.432	1.440	0.000	0.305	0.5	82
Potassium	IC	0.072	0.428	0.000	0.093	1	82
Sodium	IC	0.632	1.595	0.105	0.318	0.8	82
Sulfate	IC	0.039	0.438	0.000	0.084	2	82
Aluminum	XRF	-0.001	0.102	-0.113	0.046	0.05	42
Antimony	XRF	-0.013	0.089	-0.171	0.051	0.1	42
Arsenic	XRF	-0.016	0.034	-0.054	0.019	0.02	42
Barium	XRF	-0.024	0.496	-0.536	0.176	0.3	42
Bromine	XRF	-0.006	0.015	-0.022	0.009	0.01	42
Calcium	XRF	0.032	0.487	-0.091	0.094	0.2	42
Chlorine	XRF	0.000	0.261	-0.303	0.149	0.07	42
Chromium	XRF	0.003	0.025	-0.014	0.011	0.02	42
Cobalt	XRF	0.006	0.014	-0.006	0.005	0.06	42
Copper	XRF	-0.011	0.037	-0.053	0.022	0.02	42
Iron	XRF	0.010	0.040	-0.034	0.015	0.02	42
Lead	XRF	-0.069	0.058	-0.175	0.061	0.05	42
Manganese	XRF	0.003	0.017	-0.020	0.010	0.02	42
Mercury	XRF	0.016	0.059	-0.027	0.019	0.04	42
Molybdenum	XRF	-0.006	0.036	-0.046	0.021	0.03	42
Nickel	XRF	0.000	0.008	-0.011	0.005	0.01	42
Phosphorus	XRF	-0.009	0.025	-0.057	0.017	0.02	42
Potassium	XRF	0.046	0.134	-0.060	0.046	0.1	42
Rubidium	XRF	-0.003	0.019	-0.023	0.010	0.02	42
Selenium	XRF	-0.006	0.021	-0.027	0.012	0.02	42
Silicon	XRF	0.001	0.086	-0.041	0.026	0.03	42
Strontium	XRF	0.005	0.024	-0.013	0.008	0.02	42
Sulfur	XRF	0.001	0.049	-0.029	0.017	0.02	42
Tin	XRF	-0.061	0.051	-0.204	0.063	0.09	42
Titanium	XRF	0.008	0.098	-0.155	0.475	0.04	42
Vanadium	XRF	0.005	0.039	-0.063	0.019	0.03	42
Yttrium	XRF	0.011	0.033	-0.018	0.011	0.02	42
Zinc	XRF	0.014	0.229	-0.013	0.044	0.01	42
Zirconium	XRF	0.011	0.041	-0.007	0.013	0.02	42

* LOD = Limit of Detection

The field blanks summarized in Table 1 were from the sampling period March 2002 to December 2003 except for XRF parameters which were from March 2002 to February 2003. 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.

It is critical that filter contamination must be consistently minimized during the routine handling of filter samples. A simple experiment was performed during the audit to measure the level of contamination that a filter may receive during canister assembly followed immediately by canister disassembly to retrieve the filter. Four sets of clean filters (four Teflon®, four Nylon®, and four quartz filters) were hand-carried from NAREL to the audit and were available for the experiment. Half of the filters (two sets) were assembled into “clean” canisters provided by CARB, and the remaining filters were treated as experimental control blanks since they were not removed from their containers during the TSA. Arlene Bingaman is normally responsible for canister assembly and filter retrieval. Therefore, Arlene performed the experiment while one of the auditors watched! All of the filters were carried back to NAREL for analysis and the results are presented in Table 2.

Table 2. Results from Canister Assembly & Filter Retrieval Experiment

Filter ID	Filter Description	Parameter	Instrument	Concentration (µg/filter)
TF04-11009	Teflon® test filter #1	PM2.5 Mass	Balance	1
TF04-11010	Teflon® test filter #2	PM2.5 Mass	Balance	0
TF04-11013	Teflon® control filter #1	PM2.5 Mass	Balance	-1
TF04-11014	Teflon® control filter #2	PM2.5 Mass	Balance	2
Q04-11023	Quartz test filter #1	Elemental Carbon	Carbon Anal.	not detected
Q04-11024	Quartz test filter #2	Elemental Carbon	Carbon Anal.	not detected
Q04-11027	Quartz control filter #1	Elemental Carbon	Carbon Anal.	not detected
Q04-11028	Quartz control filter #2	Elemental Carbon	Carbon Anal.	not detected
Q04-11023	Quartz test filter #1	Organic Carbon	Carbon Anal.	2.6
Q04-11024	Quartz test filter #2	Organic Carbon	Carbon Anal.	2.0
Q04-11027	Quartz control filter #1	Organic Carbon	Carbon Anal.	1.9
Q04-11028	Quartz control filter #2	Organic Carbon	Carbon Anal.	1.6
N04-11015	Nylon® test filter #1	Nitrate	IC	0.54
N04-11016	Nylon® test filter #2	Nitrate	IC	not detected
N04-11019	Nylon® control filter #1	Nitrate	IC	not detected
N04-11020	Nylon® control filter #2	Nitrate	IC	0.57
N04-11015	Nylon® test filter #1	Sulfate	IC	not detected
N04-11016	Nylon® test filter #2	Sulfate	IC	not detected
N04-11019	Nylon® control filter #1	Sulfate	IC	not detected
N04-11020	Nylon® control filter #2	Sulfate	IC	not detected

Table 2. Results from Canister Assembly & Filter Retrieval Experiment

Filter ID	Filter Description	Parameter	Instrument	Concentration (µg/filter)
N04-11015	Nylon® test filter #1	Ammonium	IC	not detected
N04-11016	Nylon® test filter #2	Ammonium	IC	not detected
N04-11019	Nylon® control filter #1	Ammonium	IC	not detected
N04-11020	Nylon® control filter #2	Ammonium	IC	not detected
N04-11015	Nylon® test filter #1	Potassium	IC	0.54
N04-11016	Nylon® test filter #2	Potassium	IC	not detected
N04-11019	Nylon® control filter #1	Potassium	IC	not detected
N04-11020	Nylon® control filter #2	Potassium	IC	not detected
N04-11015	Nylon® test filter #1	Sodium	IC	not detected
N04-11016	Nylon® test filter #2	Sodium	IC	not detected
N04-11019	Nylon® control filter #1	Sodium	IC	not detected
N04-11020	Nylon® control filter #2	Sodium	IC	not detected

Results from the canister assembly experiment in Table 2 may be compared to the field blank results presented in Table 1. It is important to remember, however, that filters for the canister assembly experiment were supplied by NAREL, and results will be influenced by activities such as pre-cleaning the quartz and Nylon® filters at NAREL.

CARB maintains a stock of ready-to-go filters, and during the audit, a request was made to remove two sets of these clean filters from their stock. These stock filters were carried back to NAREL for analysis, and the results are presented in Table 3.

Table 3. Results from Clean Filters Removed from CARB's Stock

Filter ID	Filter Description	Parameter	Instrument	Concentration (µg/filter)
TF04-11029	Teflon® test filter #1	PM2.5 Mass	Balance	-4
TF04-11030	Teflon® test filter #2	PM2.5 Mass	Balance	-3
Q04-11037	Quartz test filter #1	Elemental Carbon	Carbon Anal.	not detected
Q04-11038	Quartz test filter #2	Elemental Carbon	Carbon Anal.	not detected
Q04-11037	Quartz test filter #1	Organic Carbon	Carbon Anal.	1.4
Q04-11038	Quartz test filter #2	Organic Carbon	Carbon Anal.	1.9
N04-11033	Nylon® test filter #1	Nitrate	IC	not detected
N04-11034	Nylon® test filter #2	Nitrate	IC	not detected
N04-11033	Nylon® test filter #1	Sulfate	IC	not detected
N04-11034	Nylon® test filter #2	Sulfate	IC	not detected

Table 3. Results from Clean Filters Removed from CARB's Stock

Filter ID	Filter Description	Parameter	Instrument	Concentration (µg/filter)
N04-11033	Nylon® test filter #1	Ammonium	IC	not detected
N04-11034	Nylon® test filter #2	Ammonium	IC	not detected
N04-11033	Nylon® test filter #1	Potassium	IC	not detected
N04-11034	Nylon® test filter #2	Potassium	IC	not detected
N04-11033	Nylon® test filter #1	Sodium	IC	not detected
N04-11034	Nylon® test filter #2	Sodium	IC	not detected

The results in Table 3 show that the filters taken from CARB's stock were very clean. It should be explained that the PM_{2.5} mass concentration was determined by subtracting the tare mass determined at CARB from the final mass determined several days later at NAREL, and this procedure may be responsible for the negative concentrations shown for this parameter. XRF analysis was not performed for the Teflon® filters listed in Table 2 and Table 3.

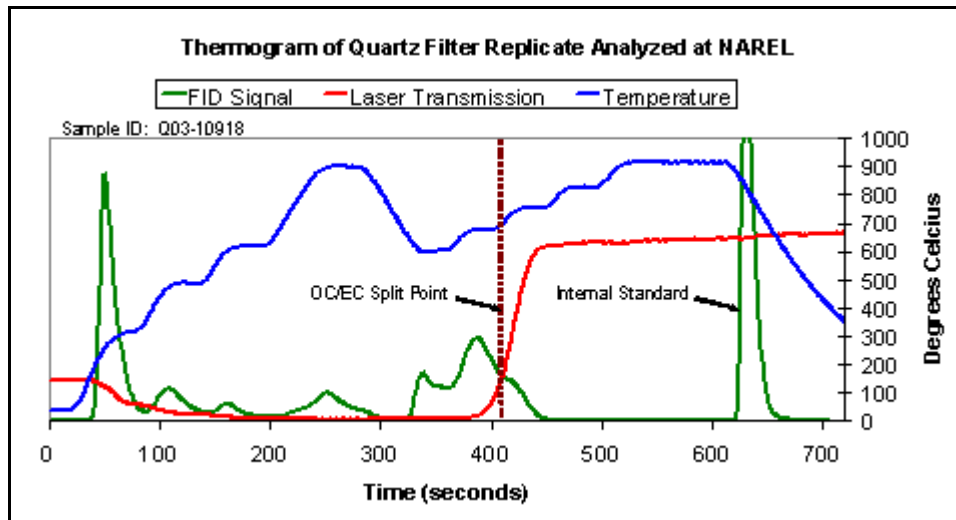
Good laboratory practices were generally observed for preparing the fresh canisters to send to the field and for retrieving the loaded filters following sample collection. No deficiencies were noted for this area of laboratory operations.

Carbon Analysis Laboratory

The carbon analysis is normally performed by Peter Samra using an SOP that is available for viewing on the web (see reference 4). Unfortunately, Peter was attending a remote training class during the audit, and he was not available for an interview. Nevertheless, a brief inspection of the carbon analysis laboratory was performed. Cliff Popejoy and Mike Poore were both present to answer questions about the carbon analysis and assist with the inspection of this laboratory.

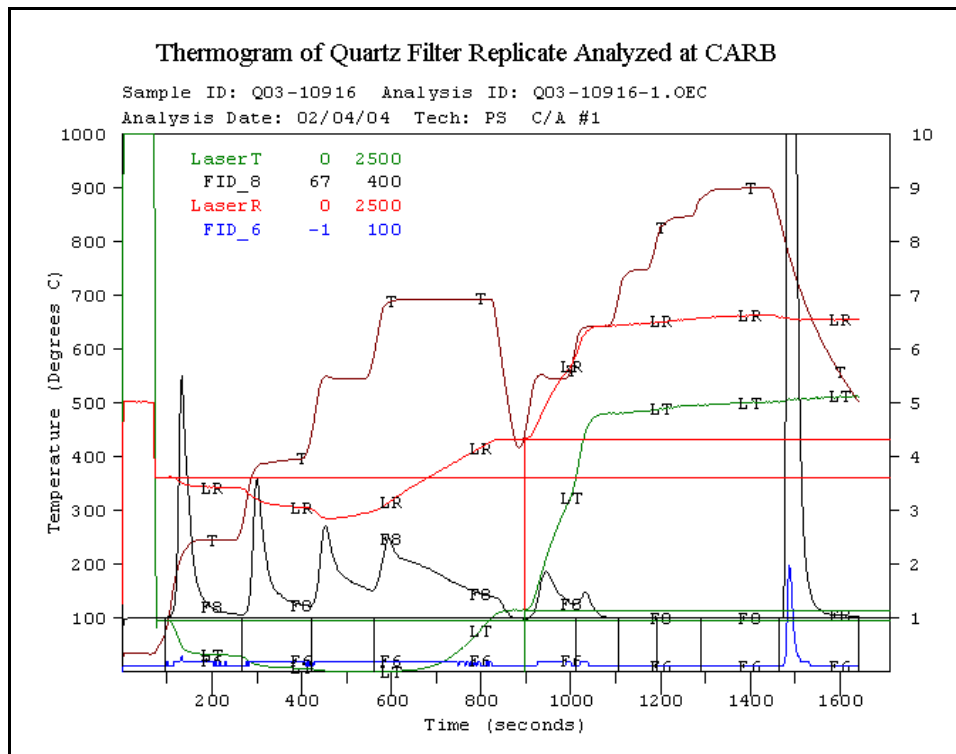
EPA has established data quality objectives for the PM_{2.5} Speciation Network, and it is critical that all participating laboratories produce analytical results that are comparable with the national contract laboratory, the Research Triangle Institute (RTI). The carbon analysis at RTI is virtually identical to the carbon analysis at NAREL. SOPs that describe the analysis at RTI and at NAREL are available for viewing on the web (see reference 5 and reference 6). RTI and NAREL both use the carbon analyzer manufactured by Sunset Laboratories Inc. The carbon analyzer used at CARB, however, 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

Figure 1



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 MnO₂ to convert the carbon to CO₂. The CO₂ merges with a stream of hydrogen gas before it passes through a nickel catalyst to form methane. A Flame Ionization Detector (FID) located at the end of the sample train provides a signal for the methane equivalent of carbon released from the sample. Typical recent thermograms from NAREL and from CARB are shown in Figure 1 and Figure 2 respectively.

Figure 2



The thermograms presented in Figure 1 and Figure 2 were created from the analysis of nearly identical filters analyzed at each laboratory. Replicate filters were prepared at NAREL and split with CARB during a recent PE study (see reference 2). Even though the thermograms look quite different, the calculated results were very similar.

As stated previously, the carbon analysis at CARB is different from the carbon analysis performed at NAREL in two important ways: the two labs operate different instrument hardware and also use different sample heating profiles during the analysis cycle. A custom heating profile was implemented at CARB in the fall of 2002 as a corrective action after NAREL's last TSA (see reference 1). The custom heating profile was adopted at that time to advance data comparability to a more desirable state. A few months after the custom heating profile was implemented, additional inter-laboratory comparisons were made in May of 2003 at which time CARB selected three field samples that were submitted to NAREL for re-analysis. The results from those split samples are presented here in Table 4. Table 4 includes results for the elemental carbon (EC) and the organic carbon (OC) the sum of which is the total carbon (TC) present on the filter.

Table 4. Results from Split Quartz Filter Samples

Filter ID	Filter Description	Sample Collection Date	Parameter	CARB Analysis (µg/filter)	NAREL Analysis (µg/filter)	RPD*
PFS00424	Portola-Nevada St	04Jan03	EC	30	42	32%
PFS00424	re-analysis	04Jan03	EC	30	38	24%
PFS00430	Portola-Nevada St	09Jan03	EC	15	25	47%
PFS00443	Calexico-Ethyl St	17Jan03	EC	13	31	85%
PFS00424	Portola-Nevada St	04Jan03	OC	364	305	-17%
PFS00424	re-analysis	04Jan03	OC	364	294	-21%
PFS00430	Portola-Nevada St	09Jan03	OC	269	216	-22%
PFS00443	Calexico-Ethyl St	17Jan03	OC	133	96	-32%
PFS00424	Portola-Nevada St	04Jan03	TC	395	347	-13%
PFS00424	re-analysis	04Jan03	TC	395	333	-17%
PFS00430	Portola-Nevada St	09Jan03	TC	285	241	-17%
PFS00443	Calexico-Ethyl St	17Jan03	TC	145	127	-13%

$$* RPD = 2 \times (NAREL \text{ result} - CARB \text{ result}) \div (NAREL \text{ result} + CARB \text{ result})$$

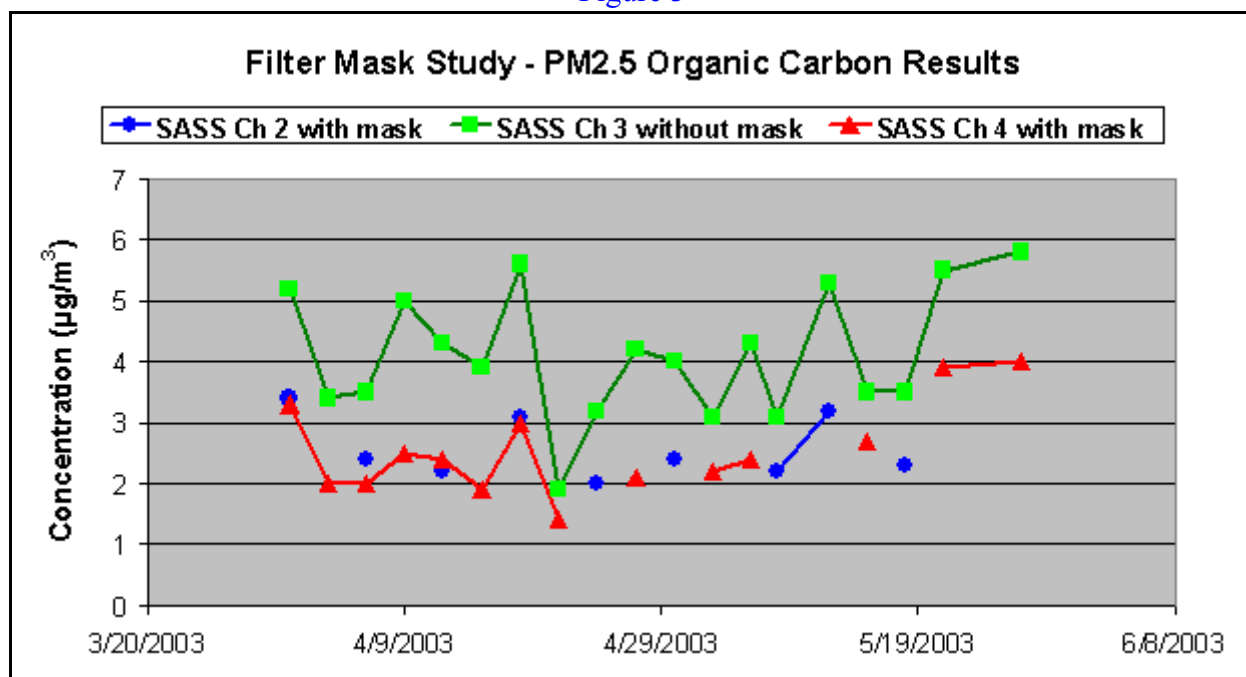
Table 4 also includes the Relative Percent Difference (RPD) between the results determined at both laboratories. One of the filters was identified as PFS00424, and this filter was analyzed twice at each lab to give some indication of the precision within the same lab. It is possible to re-analyze a filter sample because each analysis consumes only a measured aliquant punched from the original filter. At first glance, the RPD values seem quite large. The OC and TC values from NAREL were consistently lower than the values determined at CARB. There is one possible explanation for this bias that should be considered. CARB's measurements were made in January, but NAREL's measurements were not performed until four months later in May. It is possible that some of the OC escaped from the filter material before NAREL performed its analysis.

The largest RPD's in Table 4 were observed for the EC results. How significant is this information, and how alarmed should one be? First consider the size of the EC values, because they are small and very near the uncertainty of measurement. For example, CARB has estimated its Limit of Detection (LOD) at 9.4 $\mu\text{g}/\text{filter}$ which is not very different from the EC values shown in Table 4. Larger RPD's should be expected when the measurements are near the LOD.

In July of 2003, RTI was awarded a new contract to continue providing laboratory services for the $\text{PM}_{2.5}$ Speciation Network. The new contract required a few additional parameters to be calculated and reported for the carbon analysis. The new contract required RTI to report four OC fractions and pyrolytic carbon (OC1, OC2, OC3, OC4, and Pyro1C). The first four OC fractions are based upon the heating profile that the instrument is required to use. As a consequence of using a custom heating profile, CARB will not be able to report meaningful OC fractions.

How does the LOD at CARB compare to the LOD at NAREL? This was an issue from the last TSA at CARB (see reference 1). One factor that affects the LOD is the size of the filter segment that is actually placed into the instrument and consumed during the analysis. CARB uses a punch device to remove a 0.5 cm^2 segment from the filter for the analysis while NAREL normally analyzes a 1.5 cm^2 segment. This difference in sample size alone will account for a three-fold difference in LOD. CARB's instrument will not accept a larger filter segment to improve their LOD, so CARB volunteered to conduct a study investigating the use of filter masks. The study was designed to collect an extra quartz filter at the field site, and the extra quartz filter would have a filter mask installed to concentrate the captured $\text{PM}_{2.5}$ onto a smaller area of the filter. If this study demonstrated equivalent results from the masked and unmasked filters, CARB was willing to implement a mask at all of their sites to improve their LOD. Results from the study are presented in Figure 3. All of the results shown in Figure 3 were derived from collection events at a single California site.

Figure 3



The filter mask study was discontinued after about eight weeks of sample collection because virtually all of the data points showed a significant bias toward lower OC concentration in the ambient air when a mask was used to collect the sample. It was assumed that the increased face velocity generated by the mask was responsible for the observed bias.

Ion Chromatography (IC) Laboratory

The IC analyses are performed by George Dunstan, and an SOP is available on the web that describes the IC analysis at CARB [see reference 7]. 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 2). 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 and Debbie Moreno-Thornsberry are responsible for the gravimetric analysis following an SOP that is available for viewing on the web (see reference 8). Mike Humenny was interviewed during the audit.

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 5.

Table 5

Metallic weight ID	NAREL Value (mg)	CARB Value (mg)
MW04-11021	190.521	190.518
MW04-11022	94.834	94.835

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

Other Staff Interviews

Mike Poore and Cliff Popejoy should be given much of the credit for making this TSA go smoothly. At least one of them was available every time the auditors needed information or assistance. They were both present when the XRF analysis was discussed. We talked about how long NAREL should wait before releasing a report for the recent PE study since XRF results may not be available for several weeks. We all agreed that a separate report for the XRF results might be best, so that PE results from the other analytical areas could be reported right away.

Dan Tackett and Samantha Scola were helpful to provide the auditors with historical data that were requested during the audit. Dan provided the summary information regarding field blanks which was presented in Table 1 of this report. Samantha was able to provide the auditors with an eight-page listing of the EC values reported for seven California field sites during 2003. This specific information was requested to check the pattern and frequency for detecting EC since the last audit period. At one site, twelve of the sixty-one EC values (18%) were above 0.5 $\mu\text{g}/\text{m}^3$ which is CARB's LOD. Prior to implementing the custom heating profile for the carbon analysis, hardly any EC was detected at the field sites.

Conclusions

Special attention was given to areas of concern established by recent PE samples and followup from the last routine TSA. This audit produced the following findings, recommendations, and comments.

1. Suspicious [unexplained] differences are still observed in the raw data thermograms of samples split with NAREL. The CARB thermograms frequently will contain laser signals that might be interpreted as an air leak. Experiments that were performed after the last TSA, however, failed to confirm an air leak. Nevertheless, a custom heating profile was adopted for CARB's instrument which limits the maximum sample temperature to 700 °C during the "non-oxidizing" portion of the thermogram. Based upon the results from a limited number of samples split with NAREL, CARB's OC/EC results have improved since the custom heating profile was implemented.

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

2. A special study was conducted by CARB to investigate the use of filter masks to lower the LOD. Results from this study have shown that a filter mask introduces a significant bias into the analysis, and so filter masks have not been adopted for use at the field sites.

Comment. CARB has made good effort to look for a reasonable way to improve their LOD.

References

1. EPA/NAREL. February 26, 2003. Technical Memorandum: CARB Laboratory Audit. U.S. Environmental Protection Agency. [currently available on the web] <http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/carbrept.pdf>
2. EPA/NAREL. March 25, 2004. Technical Memorandum: Performance Evaluation - CARB Laboratories. U.S. Environmental Protection Agency. [currently available on the web] http://www.epa.gov/narel/reports/carb_pe_report_2004.pdf
3. CARB. June 20, 2002. *Standard Operating Procedure for Filter and Canister Preparation for PM_{2.5} Speciation Samples*, SOP MLD062, Northern Laboratory Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency. [currently available on the web] http://www.arb.ca.gov/aaqm/sop/MLD062_fin.pdf
4. CARB. August 1, 2002. *Standard Operating Procedure for Organic and Elemental Carbon Analysis of Exposed Quartz Microfiber Filters*, SOP MLD065, Northern Laboratory Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency. [currently available on the web] http://www.arb.ca.gov/aaqm/sop/MLD065_fin.pdf
5. RTI. August 15, 2003. *Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical Transmittance Carbon Analyzer*, Environmental & Industrial Sciences Division, Research Triangle Institute, Research triangle Park, NC. [currently available on the web] <http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/ocecsop.pdf>
6. NAREL. November 1, 2002. *Standard Operating Procedure, Carbon Analysis for the PM_{2.5} Chemical Speciation QA Program*, National Air and Radiation Environmental Laboratory, U.S. Environmental Protection Agency, Montgomery, AL. [currently available on the web] http://www.epa.gov/narel/sops/sop_pm2.5_carbon.pdf
7. CARB. June 18, 2002. *Standard Operating Procedure for the Analysis of Anions and Cations in PM_{2.5} Speciation Samples by Ion Chromatography*, SOP MLD064, Northern Laboratory Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency. [currently available on the web] http://www.arb.ca.gov/aaqm/sop/MLD064_fin.pdf
8. CARB. July 30, 2002. *Standard Operating Procedure for the Determination of PM_{2.5} Mass in Ambient Air by Gravimetric Analysis*, SOP MLD055, Northern Laboratory Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency. [currently available on the web] http://www.arb.ca.gov/aaqm/sop/MLD055_fin.pdf