# TECHNICAL MEMORANDUM

**TO:** Dennis Crumpler / OAQPS
**FROM:** Eric Boswell / NAREL
**COPY:** Dr. Raul Dominguez Jr. / AQMD
**AUTHOR:** Jewell Smiley / NAREL
**DATE:** February 6, 2013
**SUBJECT**: AQMD Laboratory Audit

## Introduction

On October 16, 2012, a Technical Systems Audit (TSA) was conducted at the South Coast Air Quality Management District (AQMD) Laboratory, located in Diamond Bar, CA. 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) of air monitoring stations. Most of the speciation samples that are collected from the CSN sites within the greater Los Angeles area are analyzed at the AQMD laboratory.

The audit was performed by two physical scientists from EPA: Steve Taylor and Jewell Smiley from the National Analytical Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. This TSA was a routine inspection of specific laboratory operations at AQMD and was the second on-site CSN audit performed by EPA. A report from the last TSA, conducted in 2009, is available on the web (reference 1).

## Summary of Audit Proceedings

Several days of planning and communication were necessary before the auditors actually traveled to AQMD. The auditors were provided copies of the laboratory Standard Operating Procedures (SOPs) and the Quality Assurance Project Plan to study before traveling. An agenda was prepared and distributed about two weeks in advance of the TSA.

The audit team arrived at AQMD early in the morning on October 16, and they were greeted by Dr. Raul Dominguez Jr. Raul works under the direction of the QA Manager and closely with the Laboratory Services & Source Testing Branch Manager to address QA issues and needs. After passing through security, the audit team was escorted to a conference room which was already occupied by several of the laboratory staff awaiting the audit briefing.

After introductions, the audit team gave a brief overview of the audit process. The agenda called for inspection of the following areas of the laboratory, and interviews were conducted with those analysts who actually perform the work.

- ✓ Sample Prep/Sample Receiving – Ms. Malou Cartwright
- ✓ Organic Carbon/Elemental Carbon (OC/EC) Analysis – Ms. Kelly Vanderkar
- ✓ Cations Analysis by Ion Chromatography (IC) – Ms. Judy Hwa
- ✓ Anions Analysis by IC – Mr. Dan Houghton
- ✓ Elements by X-ray Fluorescence (XRF) Analysis – Ms. Laura Saucedo
- ✓ Gravimetric Mass Analysis – Mr. Steve Taw

Several experimental activities were on the agenda which were discussed with AQMD 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. AQMD was one of several laboratories to participate in the annual inter-laboratory study which was sponsored by NAREL a few months earlier, and results from that study were discussed with AQMD staff during the audit.

At least one of the following AQMD managers and senior staff were present with the auditors for the entire audit and were able to participate in the interviews with technical staff.

- ✓ Mr. Rudy Eden – Manager, Laboratory Services & Source Testing Branch
- ✓ Mr. Solomon Teffera – Principal Air Quality Chemist
- ✓ Dr. Jason Low – Quality Assurance Manager
- ✓ Dr. Raul Dominguez – Senior Air Quality Chemist

### Sample Prep/Sample Receiving

At the time of this audit, AQMD was providing all of the field and laboratory support for eight Met One SASS units located at seven different monitoring sites within the district. Each SASS unit was supplied with eight filters for the 24-hour sampling event as shown in figure 1.

**Figure 1. Filter Assembly for AQMD SASS Network Measurements**

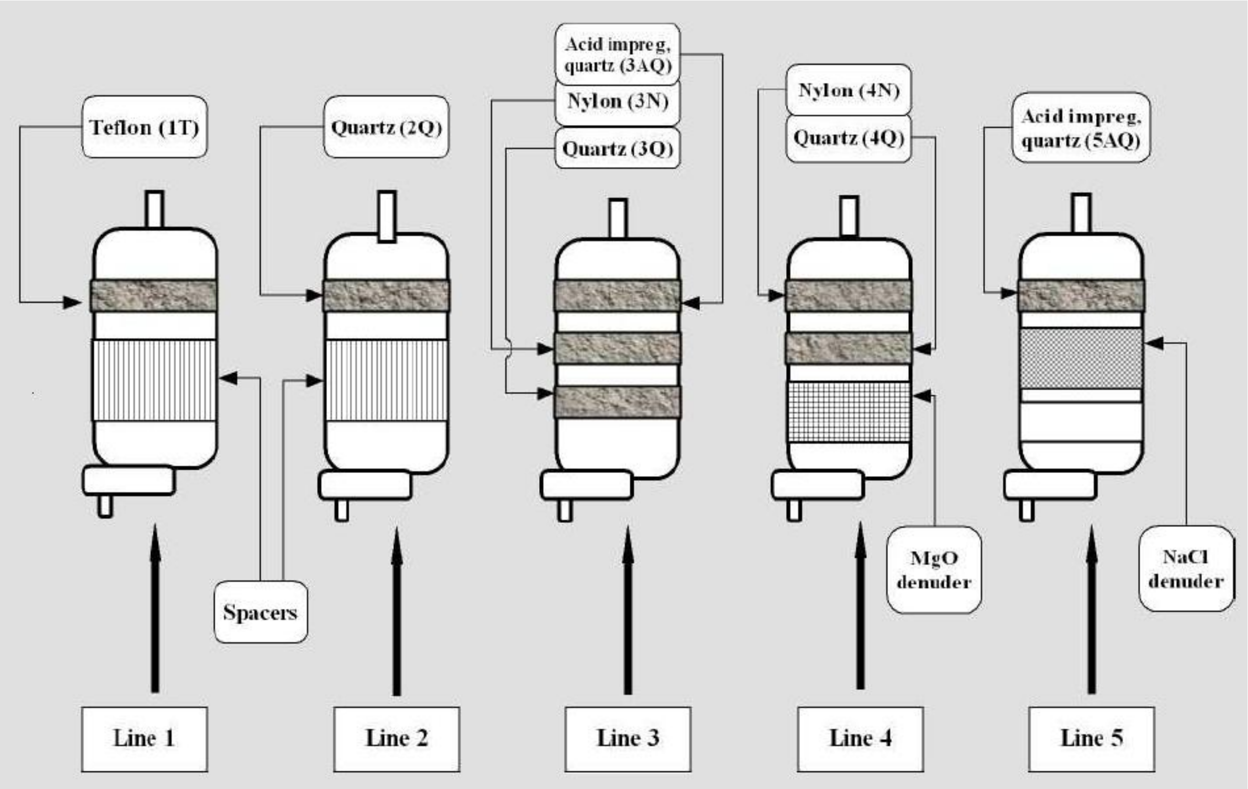
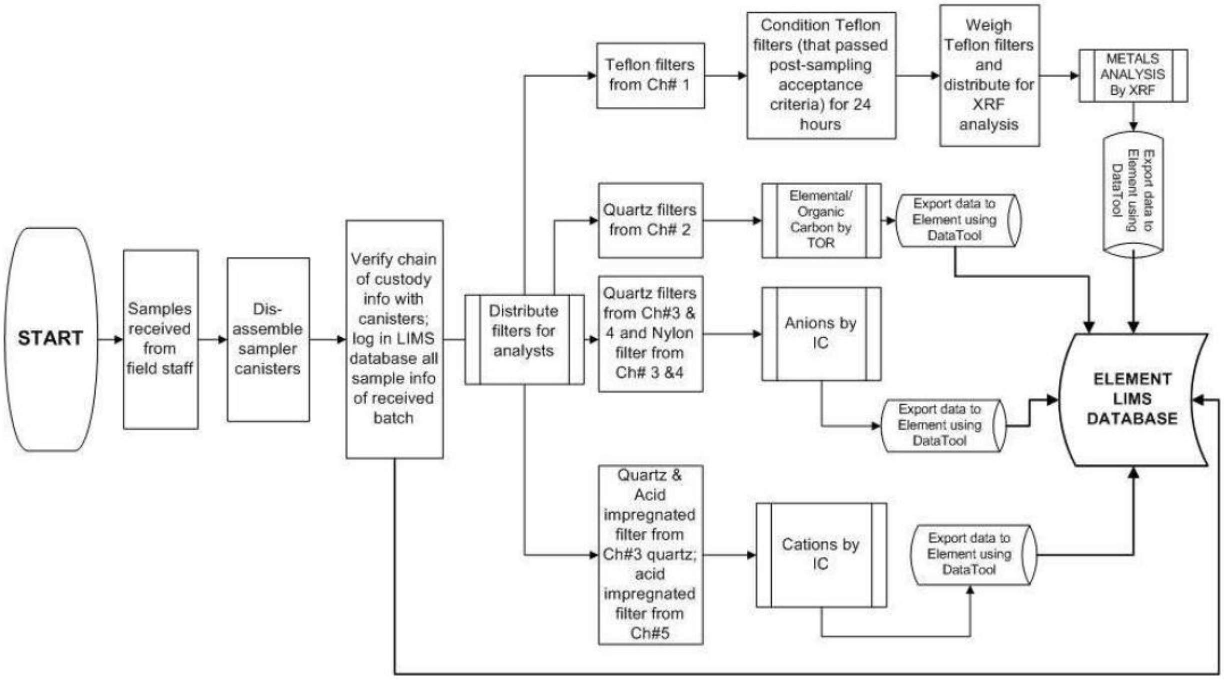


Figure 1 and figure 2 were taken from the Quality Assurance Project Plan (QAPP) which was still in draft status during the audit. Usually only three filters are used for CSN sampling. However, at the AQMD laboratory ions are determined from several different filters as shown in Figure 2.

**Figure 2. $PM_{2.5}$ Speciation Filter Analysis Flow Chart at AQMD**



Ms. Malou Cartwright was available to explain how fresh filters are prepared for transport to the field sites and how exposed filters are recovered. AQMD personnel are responsible for obtaining new filters, performing the filter acceptance testing, assembling fresh filters into the appropriate SASS canisters, and transporting the canisters to the field sites. Field activities were not discussed since the audit schedule did not include field operations. Malou explained that after each sampling event, the field service operator transports the canisters back to the laboratory after which a technician will disassemble the canisters to recover the exposed filters.

AQMD maintains a supply of unexposed filters that are ready for sampling. A request was made to remove a few filters from this supply. Two filters of each medium (Teflon®, Nylon®, and quartz) were randomly selected and carried to NAREL for analysis. Note that acid impregnated quartz filters were not taken for testing. Results from the analyses performed at NAREL are shown in table 1.

**Table 1. Results from Clean Filters Removed from the Canister Assembly Area.**

| Filter ID | Filter Description | Parameter | Instrument | Concentration (µg/filter) |
|---|---|---|---|---|
| N12-14437 | Nylon® filter | Chloride | IC | 0.15 ± 0.08 |
| | | Nitrate | IC | 0.49 ± 0.53 |
| | | Sulfate | IC | not detected |
| | | Sodium | IC | 0.17 ± 0.08 |
| | | Ammonium | IC | -0.17 ± 0.05 |
| | | Potassium | IC | not detected |
| N12-14438 | Nylon® filter | Chloride | IC | 0.10 ± 0.08 |
| | | Nitrate | IC | 0.67 ± 0.53 |
| | | Sulfate | IC | not detected |

| Filter ID | Filter Description | Parameter | Instrument | Concentration (µg/filter) |
|---|---|---|---|---|
| | | Sodium | IC | not detected |
| | | Ammonium | IC | not detected |
| | | Potassium | IC | not detected |
| Q12-14435 | Quartz filter | Chloride | IC | not detected |
| | | Nitrate | IC | 0.30 ± 0.53 |
| | | Sulfate | IC | not detected |
| | | Sodium | IC | not detected |
| | | Ammonium | IC | 0.24 ± 0.05 |
| | | Potassium | IC | not detected |
| Q12-14436 | Quartz filter | Chloride | IC | 0.01 ± 0.08 |
| | | Nitrate | IC | 0.34 ± 0.53 |
| | | Sulfate | IC | not detected |
| | | Sodium | IC | 0.13 ± 0.08 |
| | | Ammonium | IC | 0.24 ± 0.05 |
| | | Potassium | IC | not detected |
| Q12-14433 | Quartz filter | OC | OC/EC Analyzer | 1.4 ± 2.3 |
| | | EC | OC/EC Analyzer | -1.5 ± 2.2 |
| Q12-14434 | Quartz filter | OC | OC/EC Analyzer | 1.7 ± 2.3 |
| | | EC | OC/EC Analyzer | -0.16 ± 2.3 |
| T12-14439 | Teflon® filter (serial number T2567529) | $PM_{2.5}$ Mass | Balance | -12 ± 5* |
| T12-14440 | Teflon® filter (serial number T2567530) | $PM_{2.5}$ Mass | Balance | -19 ± 5* |

***Pre-mass determined at AQMD and Post-Mass determined at NAREL**

No significant contamination was observed on the Nylon® and quartz filters listed in table 1 although somewhat troubling values are presented for the Teflon® filters. Please note that the gravimetric mass concentrations presented in table 1 were calculated by subtracting the tare mass determined by AQMD from the final mass determined several days later at NAREL. In an effort to better understand the weighing discrepancies between AQMD and NAREL, additional weighing measurements were performed at both labs as a follow-up to the audit. Results from the follow-up experiments will be presented later in the gravimetric mass analysis 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 used to evaluate the overall process for contamination. The field blanks are treated like other samples except that they are mounted on the sampler for only a few minutes. The audit team made a request to examine recent field blank results, and those results are summarized in table 2.

Table 2. Summary of Field Blank Results from 2011 and 2012

| Statistics | All Concentrations (µg/filter) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Grav. Mass | Carbon | | Anions | | | Cations | |
| | | OC | EC | Cl | $NO_3$ | $SO_4$ | Na | $NH_4$ |
| Average | 14 | 17 | 2 | 0.3 | 2.0 | 0.2 | 1.01 | 0.32 |
| Median | 13 | 16 | 0.2 | 0.3 | 1.9 | 0.2 | 0.96 | 0.00 |
| Std Dev | 10 | 8 | 4 | 0.1 | 0.9 | 0.2 | 0.50 | 0.67 |
| Minimum | -5 | 2 | 0 | 0.06 | 0.2 | 0.04 | 0.00 | 0.00 |
| Maximum | 50 | 38 | 17 | 0.8 | 5.8 | 2.1 | 2.13 | 2.40 |
| Count | 69 | 41 | 41 | 69 | 69 | 69 | 22 | 22 |
| | | | | | | | | |
| | Elements by X-Ray Fluorescence | | | | | | | |
| | Al | Si | S | K | Fe | Ni | Cu | Pb |
| Average | -0.024 | 0.031 | 0.002 | 0.009 | 0.015 | 0.009 | 0.016 | 0.005 |
| Median | -0.008 | 0.034 | 0.001 | 0.000 | 0.003 | 0.012 | 0.014 | 0.028 |
| Std Dev | 0.141 | 0.175 | 0.022 | 0.024 | 0.067 | 0.032 | 0.021 | 0.088 |
| Minimum | -0.604 | -0.502 | -0.035 | -0.028 | -0.066 | -0.071 | -0.023 | -0.210 |
| Maximum | 0.234 | 0.773 | 0.087 | 0.129 | 0.415 | 0.061 | 0.065 | 0.156 |
| Count | 65 | 65 | 65 | 65 | 65 | 65 | 65 | 65 |

## Organic Carbon/Elemental Carbon Analysis

Ms. Kelly Vanderkar was the new analyst responsible for performing the thermal-optical carbon analysis. Kelly had three carbon analyzers at her work station, and all three units were DRI model 2001 instruments. A new Sunset dual-mode carbon analyzer was also installed, and it was in the process of being evaluated. All of the instruments were set up to run the IMPROVE_A thermal profile. The auditors were familiar with the SOP for carbon analysis (reference 2). After the interview started, Kelly was joined by Mr. Taylor Neiman and Dr. Jerome Robles who were able to help with some of the questions from the auditors. Taylor was another analyst at the lab who was familiar with the analytical technique. Jerome was on-site as a contractor from DRI performing instrument maintenance.

During the briefing at the beginning of the audit, Kelly 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.

Kelly had already started her analysis of the audit samples when the auditors arrived at her workstation. The auditors were able to review the raw data produced by her analysis and discuss her results which are presented in table 3 along with spike levels and results from independent analyses performed at NAREL.

### Table 3. Demonstration of Carbon Analysis

| Sample ID | Sample Description | Carbon Fraction | Spike Level (µgC/cm$^2$) | AQMD Result (µgC/cm$^2$) | NAREL Pre-Audit Result (µgC/cm$^2$) | NAREL Post-Audit Result (µgC/cm$^2$) |
|---|---|---|---|---|---|---|
| Q12-14429 | Blank Quartz | OC | 0.00 | 0.27 | 0.09 ± 0.2 | 0.10 ± 0.2 |
| | | EC | 0.00 | 0.00 | -0.26 ± 0.2 | -0.11 ± 0.2 |
| Q12-14430 | Spiked Quartz | OC | 40.0 | 38.7 | 38.4 ± 2.1 | 40.2 ± 2.2 |
| | | EC | 0.00 | 1.6 | 0.50 ± 0.2 | 0.46 ± 0.2 |

Notice that table 3 includes NAREL results which were determined before the audit and also after the audit. The small increase in OC may have been due to accidental contamination which is commonly associated with filter transport and handling. Table 3 shows good agreement between labs. The most significant discrepancy can be seen in the EC values determined for sample Q12-14430. 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 4.

### Table 4. Trip Blanks and Calibration Standard Analyzed at NAREL

| Sample ID | Sample Description | Carbon Fraction | Spike Level (µgC/cm$^2$) | NAREL Post-Audit Result (µgC/cm$^2$) |
|---|---|---|---|---|
| Q12-14433 | Quartz Travel Blank #1 | OC | 0.00 | -0.04 ± 0.2 |
| | | EC | 0.00 | -0.14 ± 0.2 |
| Q12-14433 | Quartz Travel Blank #2 | OC | 0.00 | 0.15 ± 0.2 |
| | | EC | 0.00 | -0.04 ± 0.2 |
| SS12-14431 | KHP solution provided by AQMD | OC | 36.1 | 36.2 ± 2.0 |
| | | EC | 0.00 | -0.02 ± 0.2 |

Table 4 also contains results from a potassium hydrogen phthalate (KHP) solution. Kelly 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 KHP solution was very accurate.

## Analysis of Cations by Ion Chromatography (IC)

Ms. Judy Hwa was the analyst responsible for the analysis of cations, and the auditors were familiar with her SOP document (reference 3). Her workstation was equipped with a Metrohm IC instrument running IC Net 2.3 SR3 software. Cation results were calculated using external standards, and at least three levels of analyte were routinely analyzed to establish the instrument response curve. A second source standard was used to verify the calibration. Independent calibration checks were analyzed at the beginning of the analytical sequence and again after every tenth sample during the sequence. Samples were injected using a 40-µL loop. Duplicate injections were routinely performed for every sample. This practice is remarkable since the auditors have not observed this high frequency of duplicate injections at other labs. The auditors examined the most recent calibration curves at Judy's instrument and were pleased to see a linear response curve for ammonium. The auditors have not seen a linear response curve for ammonium at any other lab.

Judy was also given the opportunity to demonstrate her ability to analyze an unknown solution during the audit. She was given the unknown solution (sample SS12-14426) during the initial briefing, and she was also advised to dilute it by a factor of ten before her analysis using her own pipets, containers, and the local reagent water to perform the dilution. Her results were excellent, and they are presented in table 5.

**Table 5. Demonstration of Cation Analysis**

| Sample_ID | Sample Description | Parameter | Expected Value (ppm) | AQMD Result (ppm) |
|---|---|---|---|---|
| SS12-14426 | Cation solution provided by NAREL | Lithium | 0.25 | not reported |
| | | Sodium | 1.00 | 1.02 |
| | | Ammonium | 2.00 | 1.97 |
| | | Potassium | 2.00 | 1.96 |
| | | Magnesium | 1.00 | not reported |
| | | Calcium | 5.00 | not reported |

Judy provided the auditors with some of her calibration solution so that it could be analyzed at NAREL. The results from NAREL's analysis are shown in table 6.

**Table 6. AQMD Calibration Standard Analyzed at NAREL**

| Sample_ID | Sample Description | Parameter | Expected Value (ppm) | NAREL Result (ppm) |
|---|---|---|---|---|
| SS12-14428 | Cation solution provided by AQMD | Sodium | 2.00 | 2.02 |
| | | Ammonium | 2.00 | 2.06 |
| | | Potassium | 2.00 | 2.03 |
| | | Magnesium | 2.00 | 2.03 |
| | | Calcium | 2.00 | 1.91 |

### Analysis of Anions by Ion Chromatography (IC)

Mr. Paul Williamson was the analyst normally responsible for the analysis of anions, but he was not present for this audit. Fortunately, Mr. Dan Houghton was available and fully qualified to stand in for Paul during the audit. The workstation was equipped with a Dionex IC instrument running Chromeleon software. Anion results were calculated using external standards, and multiple levels of analyte were routinely analyzed to establish instrument response curves. Independent calibration checks were analyzed at the beginning of the analytical sequence and again after every tenth sample during the sequence. At the instrument it was noticed again that duplicate injections were performed for every sample.

Dan was given the opportunity to demonstrate his ability to analyze an unknown solution during the audit. The auditors had brought a calibration standard with them for Dan to analyze. He was advised to dilute it 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 solution (sample SS12-14425) during the initial briefing so there was plenty of time to perform his analysis. His results are presented in table 7, and they were very good, especially considering his temporary "stand in" status.

**Table 7. Demonstration of Anion Analysis**

| Sample_ID | Sample Description | Parameter | Expected Value (ppm) | AQMD Result (ppm) |
|---|---|---|---|---|
| SS12-14425 | Anion solution provided by NAREL | Fluoride | 0.00 | not reported |
| | | Chloride | 1.00 | 0.95 |
| | | Nitrite | 1.00 | not reported |
| | | Nitrate | 2.00 | 1.80 |
| | | Sulfate | 3.00 | 2.87 |

Dan was asked to give the auditors some of his calibration solution so that it could be analyzed at NAREL. According to NAREL's analysis shown in table 8, the anion solution provided by Dan was very accurate.

**Table 8. AQMD Calibration Standard Analyzed at NAREL**

| Sample_ID | Sample Description | Parameter | Expected Value (ppm) | NAREL Result (ppm) |
|---|---|---|---|---|
| SS12-14427 | Anion solution provided by AQMD | Chloride | 1.00 | 1.05 |
| | | Nitrate | 5.00 | 5.16 |
| | | Sulfate | 4.00 | 4.02 |

## X-Ray Fluorescence (XRF) Analysis

Teflon® filters returned from the field sites are first analyzed for the gravimetric mass of $PM_{2.5}$ captured by the filter. After the gravimetric analysis is complete, the filter is then submitted for XRF analysis using AQMD's SOP (reference 4) to determine the elements present on the filter. Ms. Laura Saucedo was the analyst responsible for the XRF analysis. Her workstation was equipped with a PANalytical Epsilon 5 instrument running version 2.0C software.

A single Teflon® filter was brought to the audit and submitted to Laura during the initial audit briefing. She was told to analyze the filter as a demonstration of her analytical skills, but she was not given the history of the filter. In fact the filter had been analyzed previously at AQMD and also at the Research Triangle Institute (RTI). RTI had served as a reference lab for a recent inter-laboratory comparison study with six XRF labs participating.

Results from Laura's demonstration are presented in figure 3 along with results from the previous analysis at AQMD. The results for several elements are presented as a normalized stack bar graph. Only those elements with results significantly above the method detection limit (MDL) are shown in the graph.

**Figure 3. Demonstration of XRF Analysis**

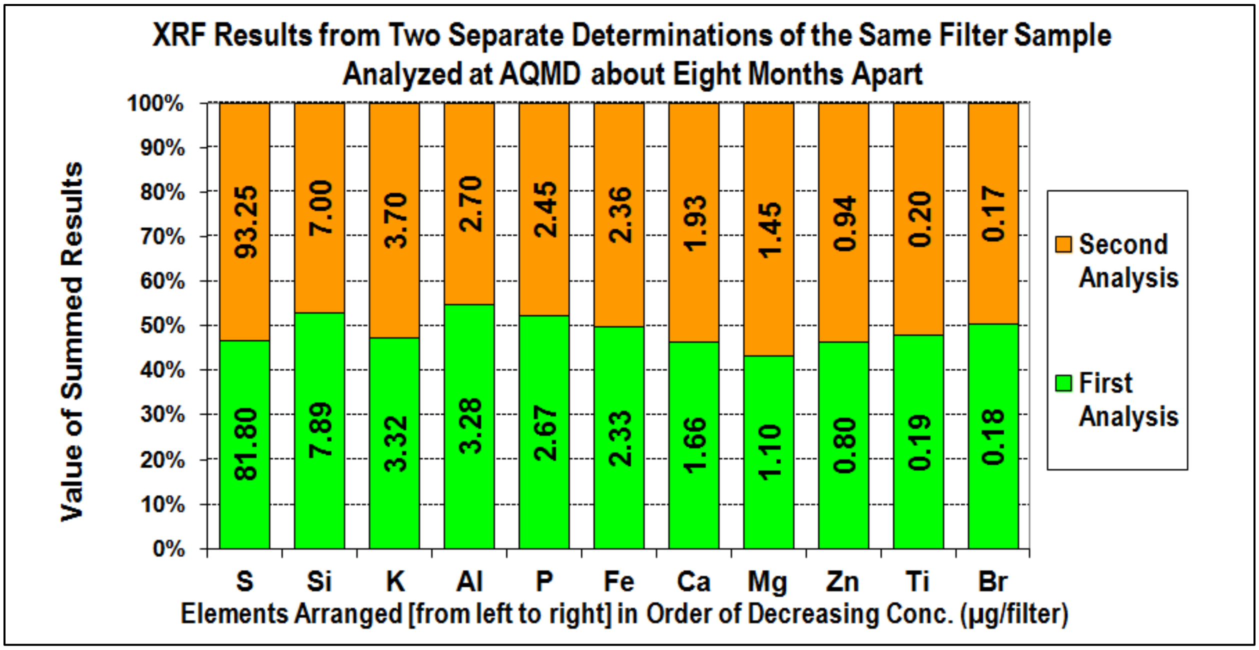


Figure 3 shows at a glance that the analysis performed on the day of the audit compares very well with the previous analysis. Table 9 is a more comprehensive list of results that includes all of the elements reported. The data in table 9 also includes the relative percent difference between the two analyses and also includes the estimated MDL for each reported element.

**Table 9. XRF Results from Demonstration Filter**

| Z | Element | All Concentrations (µg/filter) | | | |
|---|---|---|---|---|---|
| | | First Analysis | Second Analysis | Relative Difference | MDL |
| 12 | Mg | 1.10 | 1.45 | 28% | 0.316 |
| 13 | Al | 3.28 | 2.70 | -19% | 0.225 |
| 14 | Si | 7.89 | 7.00 | -12% | 0.132 |
| 15 | P | 2.67 | 2.45 | -8% | 0.034 |
| 16 | S | 81.8 | 93.2 | 13% | 0.037 |
| 17 | Cl | not detected | 0.09 | ----- | 0.014 |
| 19 | K | 3.32 | 3.70 | 11% | 0.036 |
| 20 | Ca | 1.66 | 1.93 | 15% | 0.044 |
| 21 | Sc | not detected | not detected | ----- | 0.294 |
| 22 | Ti | 0.187 | 0.204 | 9% | 0.041 |
| 23 | V | not detected | 0.006 | ----- | 0.008 |
| 24 | Cr | not detected | 0.036 | ----- | 0.020 |

| Z | Element | All Concentrations (µg/filter) | | | |
|---|---|---|---|---|---|
| | | First Analysis | Second Analysis | Relative Difference | MDL |
| 25 | Mn | not detected | 0.162 | ----- | 0.097 |
| 26 | Fe | 2.33 | 2.36 | 1% | 0.084 |
| 27 | Co | not detected | not detected | ----- | 0.028 |
| 28 | Ni | not detected | 0.036 | ----- | 0.020 |
| 29 | Cu | 0.058 | not detected | ----- | 0.050 |
| 30 | Zn | 0.804 | 0.936 | 15% | 0.039 |
| 31 | Ga | not detected | not detected | ----- | 0.036 |
| 32 | Ge | not detected | 0.090 | ----- | 0.092 |
| 33 | As | not detected | 0.048 | ----- | 0.032 |
| 34 | Se | not detected | not detected | ----- | 0.144 |
| 35 | Br | 0.176 | 0.174 | -1% | 0.030 |
| 37 | Rb | not detected | not detected | ----- | 0.060 |
| 38 | Sr | not detected | not detected | ----- | 0.068 |
| 39 | Y | not detected | not detected | ----- | 0.058 |
| 41 | Nb | not detected | 0.078 | ----- | 0.057 |
| 42 | Mo | not detected | not detected | ----- | 0.042 |
| 46 | Pd | not detected | 0.102 | ----- | 0.102 |
| 47 | Ag | not detected | not detected | ----- | 0.110 |
| 48 | Cd | not detected | not detected | ----- | 0.148 |
| 49 | In | not detected | not detected | ----- | 0.196 |
| 50 | Sn | not detected | not detected | ----- | 0.165 |
| 51 | Sb | not detected | not detected | ----- | 0.298 |
| 55 | Cs | not detected | not detected | ----- | 0.425 |
| 56 | Ba | not detected | not detected | ----- | 0.347 |
| 57 | La | not detected | not detected | ----- | 1.419 |
| 62 | Sm | not detected | not detected | ----- | 0.905 |
| 78 | Pt | not detected | not detected | ----- | 0.156 |
| 79 | Au | not detected | not detected | ----- | 0.186 |
| 82 | Pb | not detected | 0.210 | ----- | 0.118 |
| 83 | Bi | not detected | 0.024 | ----- | 0.024 |
| 92 | U | not detected | not detected | ----- | 0.129 |

## Gravimetric Mass Analysis

AQMD has a spacious weighing chamber which was set up for determining the filter-based gravimetric mass of particulate matter (PM) captured from ambient air. The auditors were familiar with the gravimetric SOP for weighing air filters (reference 5). The procedures are consistent with EPA guidance (reference 6).

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 was 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 was used to equilibrate filters before they are weighed. Criteria for temperature and humidity control were 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. AQMD uses a digital hydrometer/thermometer to monitor and record the weighing room humidity and temperature.

Dickson temperature/humidity data loggers were brought from NAREL to independently measure conditions inside AQMD'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 #8 was placed near the AQMD logger, and EPA logger #10 was placed in the sample equilibration area of the chamber. Figure 1 shows the comparison of the temperature and humidity measurements inside the weighing room as recorded by all three data loggers.

**Figure 4. Temperature and Humidity Measurements**

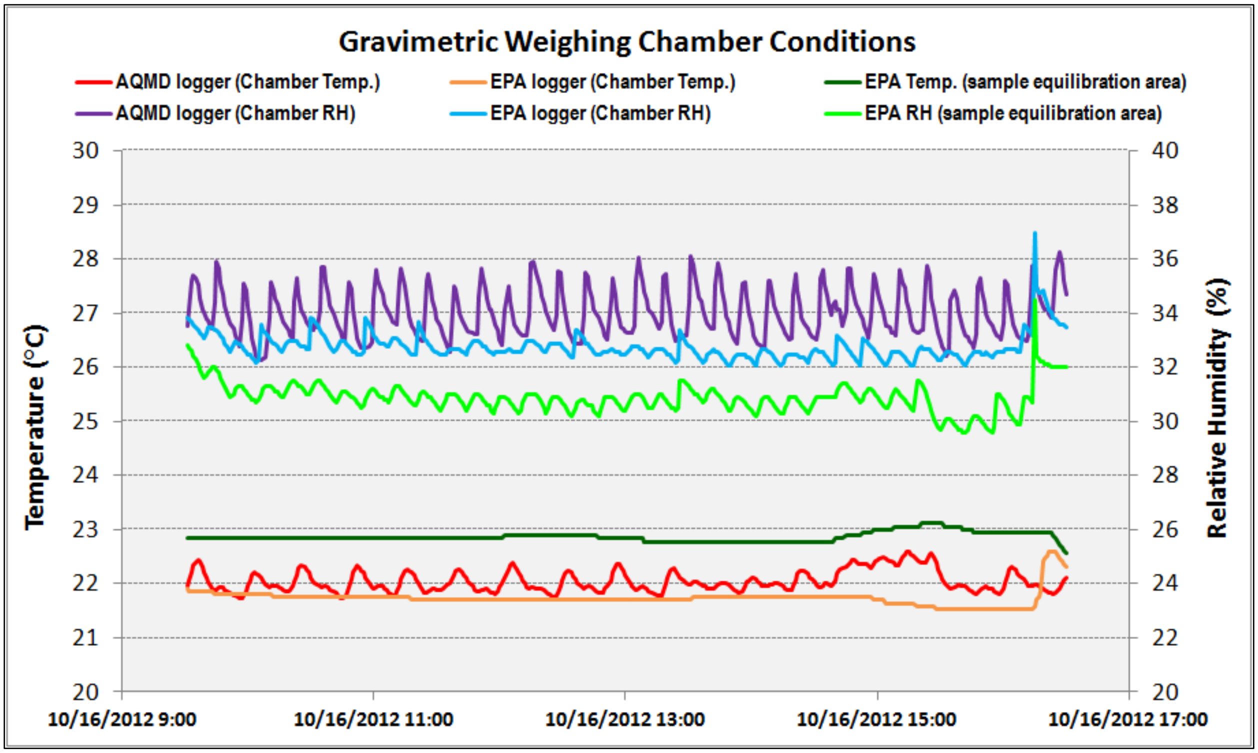


Figure 4 is a visual comparison of the data collected by the collocated devices. Figure 4 shows good steady control of the chamber temperature and humidity even when five people were inside the chamber during the audit. The two EPA loggers were calibrated to read the same temperature and the same relative humidity when they are placed together. Knowing this, it is possible to separate the two EPA loggers and look for gradients inside the chamber.

The auditors had planned to observe a small weighing demonstration during the audit. In preparation for the event, two Teflon® filters were inspected at NAREL, equilibrated in NAREL's weighing chamber, and then weighed at NAREL to determine the 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 audit where they were used to demonstrate AQMD’s weighing procedures in the gravimetric lab.

Mr. Steve Taw was the laboratory technician on duty when the audit team entered the weighing chamber. Steve was ready to start the demonstration once the auditors arrived at the weighing lab. The filters and metallic weights had been placed in the weighing chamber about five hours earlier to stabilize. Steve started the weighing session using one of the two Sartorius MC5 microbalances to perform the weighing. The session began with a zero check and a calibration check followed by the first test sample. Polonium-210 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 AQMD and two filters randomly selected by the auditors from AQMD's stock of filters. Table 10 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 10. Demonstration of Gravimetric Mass Analysis**

| Sample ID | Sample Description | Conventional Mass (mg) | | | True Mass (mg) | | |
|---|---|---|---|---|---|---|---|
| | | AQMD | NAREL | Difference | AQMD | NAREL | Difference |
| MW12-14419 | Metallic weight provided by NAREL | 478.384 | 478.384 | 0.000 | 478.384 | 478.384 | 0.000 |
| MW12-14420 | Metallic weight provided by NAREL | 91.559 | 91.558 | -0.001 | 91.558 | 91.559 | -0.001 |
| T12-14421 | Teflon® filter provided by NAREL | 394.421 | 394.403 | -0.018 | 394.533 | 394.548 | -0.015 |
| T12-14422 | Teflon® filter provided by NAREL | 390.854 | 390.847 | -0.007 | 390.976 | 390.980 | -0.004 |
| T12-14423 | Equilibrated Teflon® filter provided by AQMD | 366.774 | 366.738* | -0.036 | 366.858 | 366.892 | -0.033 |
| T12-14424 | Equilibrated Teflon® filter provided by AQMD | 371.970 | 371.959* | -0.011 | 372.081 | 372.089 | -0.008 |
| T12-14439 | Teflon® filter taken from AQMD stock | 365.454 | 365.439* | -0.015 | 365.559 | 365.571 | -0.012 |
| T12-14440 | Teflon® filter taken from AQMD stock | 368.257 | 368.235* | -0.022 | 368.356 | 368.375 | -0.019 |

***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 10 were taken directly from the balance display. Table 10 also shows the true mass of each sample which was calculated using the following equation (reference 7 and 8).

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

where

| | |
|---|---|
| $m_x$ | is the true mass of the sample |
| $m_c$ | is the conventional mass indicated by the balance display |
| $\rho_{air}$ | is the air density |
| $\rho_{std}$ | is the density of the balance calibration standard, 8 g/cm$^3$ |
| $\rho_x$ | is the density of the sample |

The true mass values were calculated because AQMD's location is approximately 700 feet above sea level compared to NAREL's location at 300 feet above sea level. At higher elevation the air density may be smaller 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. The "true mass" shown in table 10 is the balance reading corrected to account for a measurable difference in the buoyant lifting force at two locations, NAREL and AQMD. Since the density of the metallic samples (MW12-14419 and MW12-14420) 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 used during this TSA to compare the filter mass determined at NAREL with the filter mass determined at AQMD, 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.

Table 10 shows excellent agreement between AQMD and NAREL results for the two metallic weights. However, the agreement was not very good for some of the Teflon® filters. Some of the samples were allowed only a few hours to equilibrate, but this is not likely the reason for poor agreement between labs. A decision was made following the audit to mail the test filters back to AQMD for additional measurements. The conventional mass results from the follow-up measurements are presented in table 11 along with the original audit values, and the follow-up values showed much better agreement with NAREL's values.

**Table 11. Demonstration of Gravimetric Mass Analysis**

| Sample ID | Sample Description | Conventional Mass (mg) | | | | |
|---|---|---|---|---|---|---|
| | | AQMD Audit Values | AQMD Follow-up Values | NAREL Values | Original Lab Difference | Follow-up Lab Difference |
| T12-14421 | Teflon® filter provided by NAREL | 394.421 | 394.409 | 394.403 | -0.018 | -0.006 |
| T12-14422 | Teflon® filter provided by NAREL | 390.854 | 390.853 | 390.847 | -0.007 | -0.006 |
| T12-14423 | Equilibrated Teflon® filter provided by AQMD | 366.774 | 366.740 | 366.738 | -0.036 | -0.002 |
| T12-14424 | Equilibrated Teflon® filter provided by AQMD | 371.970 | 371.959 | 371.959 | -0.011 | 0.000 |
| T12-14439 | Teflon® filter taken from AQMD stock | 365.454 | 365.444 | 365.439 | -0.015 | -0.005 |
| T12-14440 | Teflon® filter taken from AQMD stock | 368.257 | 368.236 | 368.235 | -0.022 | -0.001 |

It is unclear what may have caused the larger disparity between labs for the original test measurements. It is possible that failure to completely neutralize the electrical static may have biased the measurements toward high values. Other explanations are possible. The auditors noticed that each filter was placed on a polonium-210 strip for several seconds to eliminate static charge. Placing a polonium strip on both sides of the filter, like shown in figure 5, might improve a static problem. Some labs have even built a small confined-space box with multiple polonium-210 strips and use it to remove static charge from the filter.

**Figure 5**

## Conclusions

This TSA has produced the following findings, recommendations, and comments.

1. Many of the QA documents were not available for the last TSA, but documentation was much improved for this audit. More SOPs were in place and seem to accurately reflect the work being done with one noted exception. The SOP for thermal-optical carbon analysis (reference 2) describes temperature calibration being performed using Tempilaq liquids. This procedure should not be performed using a fully assembled and functioning instrument. Section 5 of the SOP should be modified to clarify this point.

   Note: A new version of the SOP has already been drafted and is currently being reviewed for final approval.

2. False-positive elemental carbon (EC) was observed during the last audit but was greatly improved for this audit.

3. Results reported to EPA's annual inter-laboratory studies have consistently shown elevated total carbon (TC) values compared to the other participating labs. The sucrose test sample analyzed during this TSA produced an excellent TC result. Furthermore, the daily calibration check solution was analyzed at NAREL and found to be very accurate. The findings from this audit were not able to offer a reason for the elevated TC results.

4. XRF uncertainties have not yet been reported for the most recent inter-laboratory study. All XRF labs that participate in this annual study are encouraged to develop a method for estimating and reporting a standard (one-sigma) uncertainty for every element including those that are below detection in the sample. Unfortunately EPA is not able to suggest a single method that works well for all XRF labs.

   Note: AQMD has initiated discussions with another XRF lab at the University of California in Davis. Both labs have similar XRF systems, and both labs are actively pursuing a new method for estimating the uncertainty.

5. Test samples that included metallic weights and Teflon® filters were weighed during this audit, and some of the initial filter results showed poor agreement with the expected values determined at NAREL.

   Note: Following the audit, AQMD staff worked with NAREL to better understand the problem, and much better agreement with the expected values was achieved for all of the test filters.

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

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