



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards Research Triangle Park, NC 27711

MEMORANDUM

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SUBJECT: Interlaboratory Results of the 2024 Mega PE Speciation Event

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Background

The Mega Performance Evaluation (Mega PE) program is a supplemental study designed to evaluate the performance of laboratories routinely analyzing PM_{2.5} speciation samples as part of the PM_{2.5} Chemical Speciation Network (CSN) through the analysis of blind PE filter samples generated by EPA's Ambient Air Monitoring Group (AAMG). The 2024 Mega PE concluded in December 2024 with six laboratories participating: Research Triangle Institute (RTI), University of California, Davis (UCD), Desert Research Institute (DRI), California Air Resources Board (CARB), South Coast Air Quality Management District (SCAQMD), and Cook County Department of Environment and Sustainability (Cook Co; gravimetric only). All program activities were conducted by EPA staff, including flow checks, sample collection, maintenance of the sampling apparatus, and results comparison.

Sample Collection

Blind PE samples were prepared by AAMG at EPA's campus in Research Triangle Park, NC for four separate analyses: anion/cation analysis by ion chromatography (IC), carbon by thermal optical analysis (TOA), metals analysis by x-ray fluorescence (XRF), and total mass analysis by gravimetric weighing. For each analysis type, sets of colocated ambient air filter samples were collected over multiple sampling events to ensure sufficient particulates were collected to span the CSN's typical concentrations. Samples were collected in September/October 2024.

The system used for generating colocated sample filters was designed and fabricated at OAQPS in RTP and collects up to 32 colocated samples simultaneously while maintaining 5% precision between sample channels. Precision is verified through flowrate checks performed at each cyclone inlet before and after each sampling event. Photos of the sampling system are shown in Figures 1 and 2, below:

Figure 1. One of four sampling manifolds on the 32-cyclone collocated PE sampler at OAQPS in RTP, NC:



Figure 2. PE Sampling system consisting of 32 PM2.5 cyclones on four sampling manifolds and one dedicated pump (pump-box in the foreground):



Test laboratories were asked to adhere to CSN analytical procedures and received PE samples to assess the following analyses:

- Anion and Cation Analysis by Ion Chromatography (IC): three Nylon® filter samples, and three Nylon® filter blanks (all labs except UCD and Cook Co).
- Carbon by Thermal Optical Analysis (TOA): three quartz filter samples, and three quartz filter blanks (all labs except RTI and Cook Co).
- Elemental analysis by X-Ray Fluorescence (XRF): three 47mm Teflon® filter samples, and three 47mm Teflon® filter blanks (all labs except Cook Co).
- Total mass analysis by gravimetric weighing: three 47mm Teflon® filter samples, and three 47mm Teflon® filter blanks (all labs).

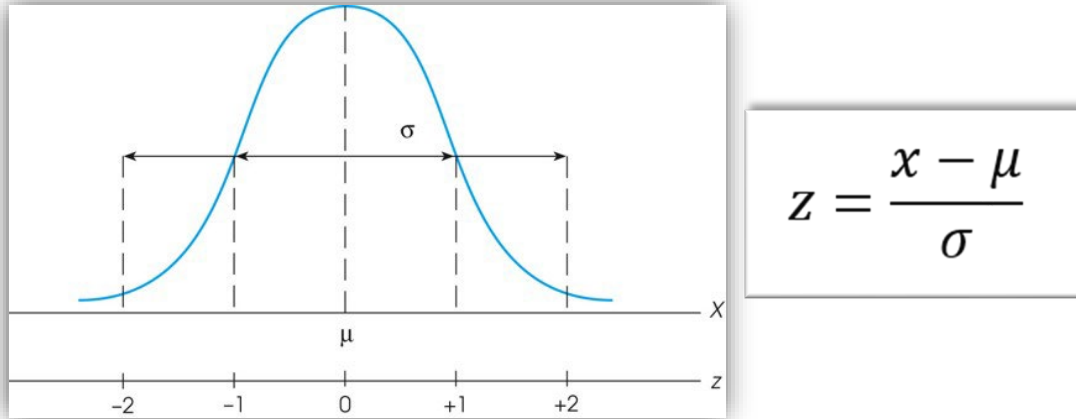
Data Analysis

OAQPS does not have its own speciation laboratories and is unable to serve as a referee lab for all analyses except for total mass by gravimetric weighing. Since lab results for IC, TOA, or XRF samples and blanks could not be evaluated against a reference value or referee lab result, AAMG evaluated each result through a comparison against the results of other participating labs. Raw values from results submitted as either “ND” (not detected) or “<DL” (less than the detection limit) were not included in the statistical analysis. Values labeled as “NR” (not reported) indicate that the test laboratory did not conduct an analysis for that parameter.

Value Scoring

Interlaboratory comparison was performed by calculating the average and standard deviation of the analytical results from each sampling event and analysis type, which were then used to calculate a z-score for each test laboratory result except for total mass (see Total Mass Results section for more detail). Z-scores were calculated using separate averages and standard deviations for each sample event and blank filter set. Each z-score indicates how many standard deviations (σ) an analytical result (x) lies from the mean (μ) of all laboratory results of that target compound/analysis and sampling event. The z-score can then be compared to a normal distribution curve to compare individual results to a “normal” population. The absolute value of z represents the distance between the raw score and the population mean in units of the standard deviation, as shown in Figure 3, below:

Figure 3. Relationship between z-score and standard deviation in a normal distribution:



Where:

- z is the z-score;
- x is the value of the individual analytical result;
- μ is the population mean across all laboratories for that analyte; and
- σ is the standard deviation of the population mean of that analyte.

Z-scores range from -3σ (falling to the far left of the normal distribution curve) to $+3\sigma$ (falling to the far right of the normal distribution curve). For this study:

- The analytical result is satisfactory when $ABS(z) < 2$ (95% of z-scores are expected to fall in this range for normally distributed data).
- The analytical result is considered questionable when $ABS(z)$ is between 2 to 3 (result should be investigated by the laboratory).
- The analytical result is unsatisfactory when $ABS(z) > 3$ (result should be investigated by the laboratory).

Cation/Anion Results

For cation and anion analysis by IC, filters were extracted and analyzed by each participating lab for the cations ammonium (NH_4^+), potassium (K^+), sodium (Na^+), and anions sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-). The z-score result from each filter's ion analysis, in addition to the average measurement for sample and blank filters, are included in Table 1. Note that Cl^- was not reported by CARB. No z-scores exceeded 2 for ions analyses.

Table 1. Cations and Anions by IC: Z-Score Results Per Filter

IC Z-score Results for 48-hour Samples							
Lab	Replicate	Ammonium	Chloride	Nitrate	Potassium	Sodium	Sulfate
CARB	1	ND	NR	0.00	1.04	1.31	1.20
DRI	1	ND	-1.01	1.38	-1.25	-1.05	-1.22
RTI	1	ND	0.99	-0.96	-0.30	-0.39	-0.15
SCAQMD	1	ND	0.02	-0.43	0.51	0.13	0.17

<i>Mean</i>	<i>ug/filter</i>	<i>N/A</i>	<i>1.98</i>	<i>2.88</i>	<i>0.61</i>	<i>2.20</i>	<i>4.29</i>
<i>Std Dev</i>	<i>ug/filter</i>	<i>N/A</i>	<i>0.14</i>	<i>0.56</i>	<i>0.34</i>	<i>0.62</i>	<i>0.45</i>
IC Z-score Results for 120-hour Samples							
Lab	Replicate	Ammonium	Chloride	Nitrate	Potassium	Sodium	Sulfate
CARB	1	1.40	NR	1.16	0.10	-0.10	1.37
CARB	2	-0.13	NR	0.08	0.25	0.59	1.14
DRI	1	0.43	0.59	1.24	-1.28	-0.45	-0.29
DRI	2	0.92	-0.43	-0.69	-1.52	-1.35	-1.54
RTI	1	-0.62	0.54	-0.05	0.49	0.49	-0.37
RTI	2	-0.35	-0.13	-0.66	0.21	0.05	-0.65
SCAQMD	1	-1.86	1.13	0.60	1.64	1.81	0.79
SCAQMD	2	0.21	-1.70	-1.68	0.10	-1.05	-0.43
<i>Mean</i>	<i>ug/filter</i>	<i>7.61</i>	<i>3.71</i>	<i>9.68</i>	<i>1.86</i>	<i>5.04</i>	<i>38.85</i>
<i>Std Dev</i>	<i>ug/filter</i>	<i>1.61</i>	<i>0.71</i>	<i>0.53</i>	<i>0.55</i>	<i>0.63</i>	<i>1.72</i>
IC Z-score Results for Blank Filters							
Lab	Replicate	Ammonium	Chloride	Nitrate	Potassium	Sodium	Sulfate
CARB	1	ND	NR	0.85	0.06	0.09	ND
CARB	2	ND	NR	-0.40	0.40	0.22	ND
CARB	3	ND	NR	-0.33	ND	-0.80	ND
DRI	1	ND	-0.78	N/A	ND	-1.09	ND
DRI	2	ND	-0.06	ND	-1.44	-0.40	-0.71
DRI	3	ND	-0.19	ND	-1.44	-0.54	0.71
RTI	1	ND	1.62	-0.93	1.12	1.77	ND
RTI	2	ND	-1.08	-0.80	-0.88	-1.04	ND
RTI	3	ND	1.44	-0.24	0.92	1.56	ND
SCAQMD	1	ND	0.20	ND	0.59	0.73	ND
SCAQMD	2	ND	-1.20	ND	ND	-1.07	ND
SCAQMD	3	ND	0.05	1.85	0.68	0.57	ND
<i>Mean</i>	<i>ug/filter</i>	<i>N/A</i>	<i>3.03</i>	<i>1.79</i>	<i>0.59</i>	<i>2.65</i>	<i>0.27</i>
<i>Std Dev</i>	<i>ug/filter</i>	<i>N/A</i>	<i>1.40</i>	<i>0.52</i>	<i>0.32</i>	<i>1.13</i>	<i>0.01</i>

Carbon Results

Carbon analysis by TOA was conducted by UCD, DRI, CARB, and SCAQMD for organic carbon (OC), elemental carbon (EC), and total carbon (TC) mass. The z-score result from each filter's TOA analysis, in addition to the average measurement for sample and blank filters, are included in Table 2. No z-scores exceeded 2 for carbon analysis.

Table 2. Carbon analysis by TOA: Values and Z-Score Results Per Filter

TOA Z-score Results for 24-hour Samples
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Lab	Replicate	Elemental Carbon	Organic Carbon	Total Carbon
CARB	1	ND	0.16	0.18
DRI	1	1.15	-1.13	-0.96
SCAQMD	1	-0.51	-0.30	-0.54
UCD	1	-0.64	1.27	1.32
<i>Mean:</i>	<i>ug/cm2</i>	<i>0.57</i>	<i>3.80</i>	<i>4.37</i>
<i>Std: Dev</i>	<i>ug/cm2</i>	<i>0.12</i>	<i>0.41</i>	<i>0.34</i>
TOA Z-score Results for 72-hour Samples				
Lab	Replicate	Elemental Carbon	Organic Carbon	Total Carbon
CARB	1	ND	0.85	0.53
CARB	2	ND	0.91	0.78
DRI	1	1.55	0.37	0.88
DRI	2	0.83	0.64	0.84
SCAQMD	1	-1.12	-1.79	-1.84
SCAQMD	2	-0.18	-1.27	-1.09
UCD	1	-0.69	0.00	-0.22
UCD	2	-0.40	0.29	0.12
<i>Mean:</i>	<i>ug/cm2</i>	<i>0.86</i>	<i>5.00</i>	<i>5.85</i>
<i>Std: Dev</i>	<i>ug/cm2</i>	<i>0.14</i>	<i>0.32</i>	<i>0.39</i>
TOA Z-score Results for Blank Filters				
Lab	Replicate	Elemental Carbon	Organic Carbon	Total Carbon
CARB	1	ND	1.49	1.49
CARB	2	ND	ND	ND
CARB	3	ND	ND	ND
DRI	1	ND	-0.64	-0.63
DRI	2	ND	-0.44	-0.45
DRI	3	ND	-0.41	-0.41
SCAQMD	1	ND	ND	ND
SCAQMD	2	ND	ND	ND
SCAQMD	3	ND	ND	ND
UCD	1	ND	ND	ND
UCD	2	ND	ND	ND
UCD	3	ND	ND	ND
<i>Mean:</i>	<i>ug/cm2</i>	<i>N/A</i>	<i>0.47</i>	<i>0.47</i>
<i>Std: Dev</i>	<i>ug/cm2</i>	<i>N/A</i>	<i>0.41</i>	<i>0.41</i>

Elemental Results

Elemental analysis by XRF was conducted by UCD, RTI, DRI, CARB, and SCAQMD for several elemental parameters. Ten parameters with high concentrations measured within CSN and with significant loadings during the Mega PE were selected to evaluate the interlaboratory comparison. The z-score

result from each filter's XRF analysis, in addition to the average measurement for sample and blank filters, are included in Table 3. As shown in red, two z-scores by UCD exceeded 2 for Ca and K. No z-scores exceeded 3 for elemental analysis.

Table 3. Elemental analysis by XRF: Z-Score Results Per Filter

XRF Z-score Results for 24-hr Samples											
Filter Lab	Replicate	Aluminum	Calcium	Iron	Lead	Potassium	Silicon	Sodium	Sulfur	Titanium	Zinc
CARB	1	0.51	-0.43	-0.79	ND	0.17	0.07	NR	0.62	ND	1.04
DRI	1	-1.16	1.76	-0.80	ND	-1.19	-1.69	-0.39	1.28	-0.71	-0.77
RTI	1	-0.98	-0.64	1.53	-0.71	-0.45	0.14	0.41	-0.83	0.71	-1.31
SCAQMD	1	0.62	-0.17	-0.42	ND	-0.05	0.61	-1.16	-1.13	ND	0.34
UCD	1	1.02	-0.52	0.48	0.71	1.53	0.87	1.15	0.06	ND	0.69
<i>Mean</i>	<i>ug/cm2</i>	<i>0.05</i>	<i>0.02</i>	<i>0.04</i>	<i>0.01</i>	<i>0.04</i>	<i>0.05</i>	<i>0.09</i>	<i>0.30</i>	<i>0.00</i>	<i>0.01</i>
<i>Std Dev</i>	<i>ug/cm2</i>	<i>0.04</i>	<i>0.00</i>	<i>0.01</i>	<i>0.01</i>	<i>0.01</i>	<i>0.02</i>	<i>0.04</i>	<i>0.03</i>	<i>0.00</i>	<i>0.00</i>
XRF Z-score Results for 120-hr Samples											
Filter Lab	Replicate	Aluminum	Calcium	Iron	Lead	Potassium	Silicon	Sodium	Sulfur	Titanium	Zinc
CARB	1	0.74	-0.02	-1.01	-0.56	-0.64	-0.30	NR	-0.07	0.19	-0.45
CARB	2	0.47	-0.44	0.50	-0.48	-0.47	-0.55	NR	0.29	0.06	0.62
DRI	1	-1.46	-0.68	0.15	ND	-0.58	-1.56	-0.34	1.56	-0.52	1.39
DRI	2	-1.45	-0.46	-1.92	ND	-0.52	-1.43	-0.65	1.42	-1.40	-0.18
RTI	1	-0.78	1.09	-0.70	ND	-0.04	0.08	1.19	-0.82	-0.82	-1.58
RTI	2	-0.63	0.58	0.61	ND	1.31	0.53	1.59	-0.38	1.24	-1.58
SCAQMD	1	0.18	-0.01	-0.13	ND	-1.25	0.92	-0.89	-1.45	ND	0.99
SCAQMD	2	0.91	1.19	0.10	ND	-0.02	1.38	-0.33	-1.14	ND	0.12
UCD	1	1.25	-2.11	0.81	1.46	0.10	-0.12	0.58	0.10	1.24	-0.01
UCD	2	0.76	0.87	1.58	0.57	2.12	1.04	-1.14	0.51	ND	0.67
<i>Mean</i>	<i>ug/cm2</i>	<i>0.08</i>	<i>0.07</i>	<i>0.09</i>	<i>0.01</i>	<i>0.14</i>	<i>0.12</i>	<i>0.60</i>	<i>1.14</i>	<i>0.01</i>	<i>0.01</i>
<i>Std Dev</i>	<i>ug/cm2</i>	<i>0.04</i>	<i>0.01</i>	<i>0.01</i>	<i>0.00</i>	<i>0.01</i>	<i>0.03</i>	<i>0.14</i>	<i>0.11</i>	<i>0.00</i>	<i>0.00</i>
XRF Z-score Results for Blank Filters											
Filter Lab	Replicate	Aluminum	Calcium	Iron	Lead	Potassium	Silicon	Sodium	Sulfur	Titanium	Zinc
CARB	1	ND	ND	ND	N/A	ND	ND	NR	ND	ND	ND
CARB	2	ND	ND	ND	N/A	-1.13	ND	NR	ND	ND	ND
CARB	3	ND	ND	ND	N/A	ND	ND	NR	ND	ND	ND
DRI	1	-1.47	ND	ND	N/A	ND	ND	ND	ND	ND	ND
DRI	2	ND	ND	ND	N/A	ND	ND	ND	ND	ND	ND
DRI	3	ND	ND	ND	N/A	ND	ND	ND	ND	ND	ND
RTI	1	ND	ND	ND	N/A	ND	ND	ND	ND	ND	ND

RTI	2	ND	ND	ND	N/A	ND	ND	ND	ND	ND	ND
RTI	3	ND	ND	ND	N/A	ND	ND	ND	ND	ND	ND
SCAQMD	1	ND	1.60	ND	N/A	-0.87	-0.55	ND	ND	ND	-0.27
SCAQMD	2	ND	0.51	1.48	N/A	ND	ND	ND	ND	ND	ND
SCAQMD	3	ND	0.33	ND	N/A	ND	ND	ND	ND	ND	-0.84
UCD	1	0.39	-0.71	-0.32	-1.00	1.10	0.43	N/A*	-0.58	ND	ND
UCD	2	0.32	-1.02	-0.67	1.00	0.02	-1.06	ND	1.15	ND	ND
UCD	3	0.76	-0.71	-0.49	0.00	0.88	1.18	ND	-0.58	ND	1.11
Mean	ug/cm2	0.06	0.01	0.02	0.01	0.01	0.02	0.12	0.01	NA	0.00
Std Dev	ug/cm2	0.03	0.00	0.01	0.01	0.00	0.01	NA	0.00	0.00	0.00

Total Mass Results

Total mass analysis by gravimetric weighing was conducted by UCD, RTI, DRI, SCAQMD, and Cook Co for samples and blanks. Z-scores for total mass were not used since measurements from test labs can be directly compared to measurements observed by OAQPS, and evaluation criteria from EPA's PM2.5 gravimetric round robin program were instead used to evaluate test lab performance for total mass (e.g. value is generally acceptable if difference <0.020mg). As shown in red, two filters for DRI had a measurement difference >0.020mg (see Discussion section for detail). CARB was unable to participate in the Mega PE evaluation for total mass due to filter masses exceeding the laboratory microbalance's calibration range.

Table 4. Total Mass by Gravimetric Weighing: Z-Score Results Per Filter

Metal Weights				
Lab	Filter Number	OAQPS Mass	Lab Mass	Difference
CARB	1	349.996	NR	NR
CookCo	1	300.003	300.004	0.001
DRI	1	299.996	299.992	-0.004
RTI	1	400.008	400.003	-0.005
SCAQMD	1	350.011	350.007	-0.004
UCD	1	299.999	299.992	-0.007
Mean	ug			-0.004
Std Dev	ug			0.003
Sample Filters				
CARB	1	141.131	NR	NR
CARB	2	368.246	NR	NR
CARB	3	386.104	NR	NR
CookCo	1	375.670	375.671	0.001
CookCo	2	363.362	363.384	0.022
CookCo	3	360.477	360.467	-0.010
DRI	1	141.019	141.036	0.017
DRI	2	141.470	141.493	0.023

DRI	3	140.054	140.074	0.020
RTI	1	141.646	141.636	-0.010
RTI	2	141.245	141.237	-0.009
RTI	3	140.625	140.615	-0.010
SCAQMD	1	141.233	141.235	0.002
SCAQMD	2	140.054	140.056	0.002
SCAQMD	3	139.469	139.471	0.002
UCD	1	142.534	142.527	-0.007
UCD	2	142.777	142.763	-0.014
UCD	3	142.158	142.149	-0.009
Mean	ug			0.001
Std Dev	ug			0.013
Blank Filters				
CARB	1	380.899	NR	NR
CARB	2	383.094	NR	NR
CARB	3	376.524	NR	NR
CookCo	1	380.329	380.326	-0.003
CookCo	2	373.670	373.667	-0.004
CookCo	3	380.657	380.648	-0.009
DRI	1	375.523	375.535	0.012
DRI	2	379.442	375.417	-4.025
DRI	3	375.406	379.456	4.050
RTI	1	376.281	376.263	-0.018
RTI	2	376.541	376.524	-0.017
RTI	3	379.374	379.356	-0.018
SCAQMD	1	377.700	377.698	-0.002
SCAQMD	2	380.102	380.098	-0.004
SCAQMD	3	381.862	381.858	-0.004
UCD	1	377.485	377.461	-0.024
UCD	2	391.814	391.790	-0.024
UCD	3	379.583	379.560	-0.023
Mean	ug			-0.007
Std Dev	ug			1.526

Discussion

The results in the questionable z-score range for elemental analyses do not track with any sampler inlet/position and cannot be explained by variation in filter loading. Flow checks conducted before and after each sample event confirming uniform airflow across each inlet (see Appendix).

Total mass results revealed two filters from DRI which had significant differences between OAQPS' and DRI's measurement. Upon investigation, DRI shared a photocopy of the original laboratory notes

confirming that these two values were inadvertently “swapped” when preparing to share Mega PE results with EPA.

Findings from this Mega PE will be used by EPA in assessing irregular or questionable results from laboratories participating in CSN and in validating the performance of the sampling apparatus in subsequent evaluations.

Appendix: OAQPS flow-rate verifications for XRF, IC, and Carbon samples used in the 2024 Mega PE.

Filter ID	Filter Media	Start Sample Flow (Lpm)	End Sample Flow (Lpm)	Analysis Type	Lab Assign
N5	Nylon-48hr	6.78	6.59	IC	CARB
N18	Nylon-120hr	6.86	7.00	IC	CARB
N21	Nylon-120hr	6.68	6.80	IC	CARB
Q4	Quartz-24hr	6.89	6.98	TOA	CARB
Q14	Quartz-72hr	6.66	6.64	TOA	CARB
Q15	Quartz-72hr	6.77	6.75	TOA	CARB
12345713	Teflon-24hr	6.72	6.69	XRF	CARB
12345699	Teflon-120hr	6.71	6.70	XRF	CARB
12345698	Teflon-120hr	6.74	6.76	XRF	CARB
N2	Nylon-48hr	6.60	6.40	IC	DRI
N13	Nylon-120hr	6.89	6.98	IC	DRI
N14	Nylon-120hr	6.91	6.99	IC	DRI
Q2	Quartz-24hr	6.49	6.57	TOA	DRI
Q10	Quartz-72hr	6.81	6.81	TOA	DRI
Q11	Quartz-72hr	6.88	6.88	TOA	DRI
12345715	Teflon-24hr	6.85	6.75	XRF	DRI
12345705	Teflon-120hr	6.92	6.93	XRF	DRI
12345704	Teflon-120hr	6.76	6.76	XRF	DRI
N1	Nylon-48hr	6.72	6.52	IC	RTI
N10	Nylon-120hr	6.89	6.92	IC	RTI
N11	Nylon-120hr	6.75	6.81	IC	RTI
12345716	Teflon-24hr	6.50	6.43	XRF	RTI
12345708	Teflon-120hr	6.45	6.45	XRF	RTI
12345706	Teflon-120hr	6.66	6.64	XRF	RTI
N4	Nylon-48hr	6.80	6.61	IC	SCAQMD
N16	Nylon-120hr	6.86	6.93	IC	SCAQMD
N17	Nylon-120hr	6.67	6.78	IC	SCAQMD
Q3	Quartz-24hr	6.67	6.76	TOA	SCAQMD
Q12	Quartz-72hr	6.59	6.60	TOA	SCAQMD
Q13	Quartz-72hr	6.73	6.74	TOA	SCAQMD
12345714	Teflon-24hr	6.82	6.74	XRF	SCAQMD
12345701	Teflon-120hr	6.72	6.74	XRF	SCAQMD
12345700	Teflon-120hr	6.69	6.71	XRF	SCAQMD

Q1	Quartz-24hr	6.80	6.89	TOA	UCD
Q7	Quartz-72hr	6.78	6.87	TOA	UCD
Q8	Quartz-72hr	6.90	6.99	TOA	UCD
12345718	Teflon-24hr	6.73	6.65	XRF	UCD
12345710	Teflon-120hr	6.74	6.66	XRF	UCD
12345709	Teflon-120hr	6.63	6.60	XRF	UCD