

Quality Assurance Support of PM_{2.5} Chemical Speciation Network

Provided by ORIA-Montgomery

National Air and Radiation Environmental Laboratory (NAREL) ORIA-Montgomery



Specific QA Activities

- ▶ **PE Samples**
single-blind samples analyzed at different labs
- **Laboratory TSA**
on-site inspection and interviews with lab staff
- **Special Studies**
experimental investigations

Experimental Inter-comparison of Speciation Laboratories

- **Include Speciation Trends Network (STN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) Program**
- **Evaluate specific laboratory performance at those laboratories that routinely analyze PM_{2.5} chemical speciation samples**
- **PE samples were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL**

2008 Participating Laboratories

California Air Resources Board (CARB)	Sacramento, CA	Gravimetric mass IC analysis, Nylon® filters TOA carbon, IMPROVE_A method Elements by XRF (47-mm filters)
Desert Research Institute (DRI)	Reno, NV	Gravimetric mass IC analysis, Teflon® filters IC analysis, Nylon® filters TOA carbon, CSN method TOA carbon, IMPROVE_A method Elements by XRF (25- & 47-mm filters)
Oregon Dept. of Environmental Quality (ODEQ)	Portland, OR	Gravimetric mass IC analysis, Nylon® filters Elements by XRF (47-mm filters)
Research Triangle Institute (RTI)	Research Triangle Park, NC	Gravimetric mass IC analysis, Nylon® filters TOA carbon, CSN method TOA carbon, IMPROVE_A method Elements by XRF (25- & 47-mm filters)
South Coast Air Quality Management District (AQMD)	Diamond Bar, CA	Gravimetric mass IC analysis, Nylon® filters TOA carbon, IMPROVE_A method Elements by XRF (47-mm filters)
University of California / Davis (UCD)	Davis, CA	Gravimetric mass Elements by XRF (25- & 47-mm filters)
EPA's National Air and Radiation Environmental Laboratory (NAREL)	Montgomery, AL	Gravimetric mass IC analysis, Teflon® filters IC analysis, Nylon® filters TOA carbon, CSN method TOA carbon, IMPROVE_A method

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Speciation Air Samplers at NAREL



Speciation Air Samplers at NAREL



PE Samples Provided to Each Participating Lab

- ▶ Gravimetric Mass Analysis – ten filter samples and two metallic weights
- Ion Chromatography Analysis – six filter samples
- Carbon by Thermal Optical Analysis – six filter samples
- Elemental analysis by X-Ray Fluorescence – six filter samples

Gravimetric Mass Analysis

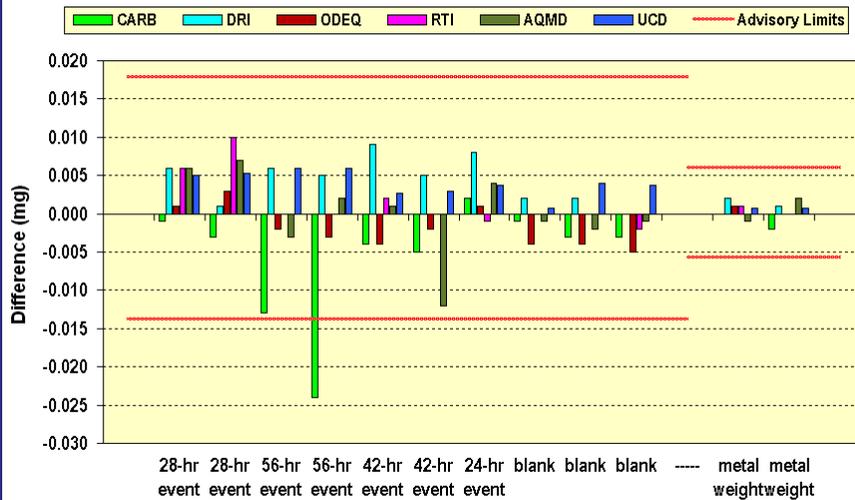
- A sample set of ten new filters and two metallic transfer weights were supplied by NAREL
- Samples placed into individual Petri slides and shipped by overnight mail to the receiving lab
- After tare measurements were completed at the receiving lab, the filters and metallic weights were returned to Montgomery
- Shortly after NAREL's tare measurements were complete, seven filters from each set were loaded with PM_{2.5} captured from the Montgomery air

Gravimetric Mass Analysis

- Forty-two filters were loaded during four separate collection events. A sufficient number of replicates were prepared during each event such that each lab could be provided with an almost identical set of loaded filters
- Following sample collection, the filters and the metallic weights were returned to the weighing chamber at NAREL and POST-weighed multiple times over the course of several days to demonstrate a stable final mass
- Finally, the filters and metallic weights were placed into small Igloo® coolers with ice substitute and shipped back to the participating labs for POST-weighing

PM2.5 Capture Comparisons – NAREL Value Minus Participating Lab Value

Negative value indicates a smaller capture determined by NAREL



Summary of Raw Data for Sample T08-12642

Date	Events and Comments	Filter Mass (mg)
01-Dec-08	Filter inspected at NAREL	145.605
03-Dec-08	Filter shipped to CARB by express mail	-----
09-Dec-08	Tare mass of record reported by CARB	145.600
11-Dec-08	Filter returned to NAREL	-----
15-Dec-08	Tare mass of record reported by NAREL	145.602
18-Dec-08	56-hour collection event started	-----
06-Jan-09	First POST-weighing at NAREL	145.781
13-Jan-09	POST-mass of record reported by NAREL	145.777
14-Jan-09	Filter shipped to CARB by express mail	-----
30-Jan-09	POST-mass of record reported by CARB	145.799
13-Mar-09	Filter returned to NAREL	-----
16-Mar-09	Extra POST-weighing performed at NAREL	145.789
07-Apr-09	Extra POST-weighing performed at NAREL	145.775

PT Samples Provided to Each Participating Lab

- Gravimetric Mass Analysis – ten filter samples and two metallic weights
- Ion Chromatography Analysis – six filter samples
- ▶ Carbon by Thermal Optical Analysis – six filter samples
- Elemental analysis by X-Ray Fluorescence – six filter samples

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Comparison of Temperature Protocols for Two TOA Methods

CSN Method TOT Analysis	IMPROVE_A Method TOR Analysis	Carrier Gas	Carbon Fraction*
heater off (90s)	heater off (90s)	He Purge	-----
310°C (60s)	140°C (150-580s)	He	OC1
480°C (60s)	280°C (150-580s)	He	OC2
615°C (60s)	480°C (150-580s)	He	OC3
900°C (90s)	580°C (150-580s)	He	OC4
heater off (40s)**	-----	He	
600°C (35s)	580°C (150-580s)	He/O ₂	EC1
675°C (45s)	740°C (150-580s)	He/O ₂	EC2
750°C (45s)	840°C (150-580s)	He/O ₂	EC3
825°C (45s)	-----	He/O ₂	
920°C (120s)	-----	He/O ₂	
heater off (110s)**	heater off (200s)**	He/O ₂ + IS	

* The Carbon fractions are not consistently defined among the different methods

** The "heater off" times are approximate and may have varied slightly among instruments during this study.

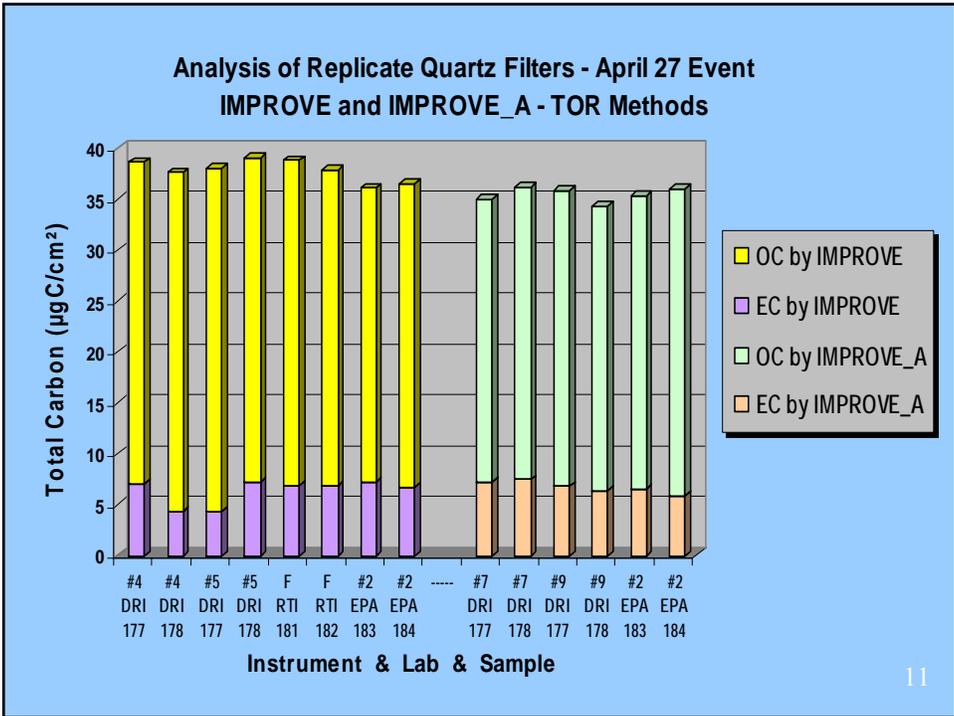
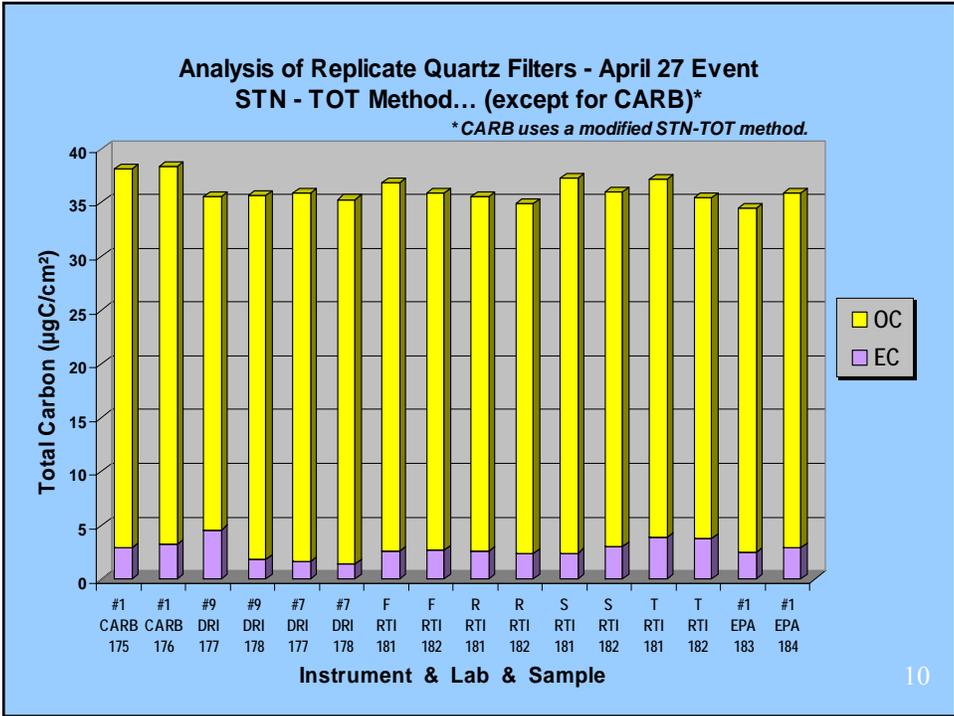
Sampling Schedule for TOA Carbon PE Filters 2008 Mega PE

Filter ID	Filter Medium	Sample Start	Event Duration	Receiving Lab	Method(s)
Q08-12335	quartz	29-Aug-07	176-hour	CARB	IMPROVE_A
Q08-12336	quartz	29-Aug-07	176-hour	CARB	IMPROVE_A
Q08-12454	quartz	27-May-07	144-hour	CARB	IMPROVE_A
Q08-12455	quartz	27-May-07	144-hour	CARB	IMPROVE_A
Q08-12337	quartz	29-Aug-07	176-hour	DRI	IMPROVE_A and CSN
Q08-12338	quartz	29-Aug-07	176-hour	DRI	IMPROVE_A and CSN
Q08-12456	quartz	27-May-07	144-hour	DRI	IMPROVE_A and CSN
Q08-12457	quartz	27-May-07	144-hour	DRI	IMPROVE_A and CSN
Q08-12339	quartz	29-Aug-07	176-hour	RTI	IMPROVE_A and CSN
Q08-12340	quartz	29-Aug-07	176-hour	RTI	IMPROVE_A and CSN
Q08-12458	quartz	27-May-07	144-hour	RTI	IMPROVE_A and CSN
Q08-12459	quartz	27-May-07	144-hour	RTI	IMPROVE_A and CSN
Q08-12343	quartz	29-Aug-07	176-hour	AQMD	IMPROVE_A
Q08-12344	quartz	29-Aug-07	176-hour	AQMD	IMPROVE_A
Q08-12462	quartz	27-May-07	144-hour	AQMD	IMPROVE_A
Q08-12463	quartz	27-May-07	144-hour	AQMD	IMPROVE_A
Q08-12341	quartz	29-Aug-07	176-hour	NAREL	IMPROVE_A and CSN
Q08-12342	quartz	29-Aug-07	176-hour	NAREL	IMPROVE_A and CSN
Q08-12460	quartz	27-May-07	144-hour	NAREL	IMPROVE_A and CSN
Q08-12461	quartz	27-May-07	144-hour	NAREL	IMPROVE_A and CSN

2006 Mega PE

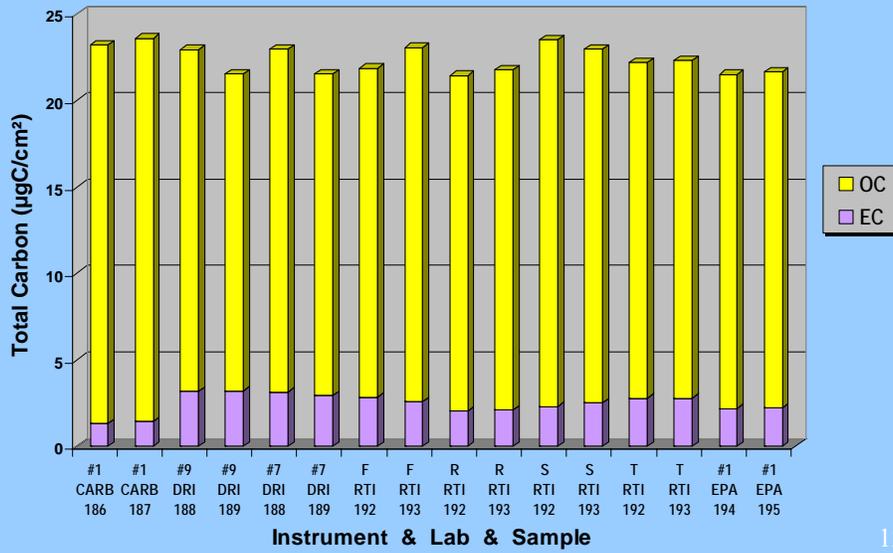
Sampling Schedule for TOA Carbon PE Filters

Filter ID	Filter Medium	Sample Start	Event Duration	Receiving Lab	TOA Method(s)
Q04-11175	quartz	27-Apr-04	287-hr	CARB	STN (modified)
Q04-11176	quartz	27-Apr-04	287-hr	CARB	STN (modified)
Q04-11186	quartz	16-Nov-04	192-hr	CARB	STN (modified)
Q04-11187	quartz	16-Nov-04	192-hr	CARB	STN (modified)
Q04-11177	quartz	27-Apr-04	287-hr	DRI	STN, IMPROVE, and IMPROVE_A
Q04-11178	quartz	27-Apr-04	287-hr	DRI	STN, IMPROVE, and IMPROVE_A
Q04-11188	quartz	16-Nov-04	192-hr	DRI	STN, IMPROVE, and IMPROVE_A
Q04-11189	quartz	16-Nov-04	192-hr	DRI	STN, IMPROVE, and IMPROVE_A
Q04-11181	quartz	27-Apr-04	287-hr	RTI	STN and IMPROVE
Q04-11182	quartz	27-Apr-04	287-hr	RTI	STN and IMPROVE
Q04-11192	quartz	16-Nov-04	192-hr	RTI	STN and IMPROVE
Q04-11193	quartz	16-Nov-04	192-hr	RTI	STN and IMPROVE
Q04-11183	quartz	27-Apr-04	287-hr	NAREL	STN, IMPROVE, and IMPROVE_A
Q04-11184	quartz	27-Apr-04	287-hr	NAREL	STN, IMPROVE, and IMPROVE_A
Q04-11194	quartz	16-Nov-04	192-hr	NAREL	STN, IMPROVE, and IMPROVE_A
Q04-11195	quartz	16-Nov-04	192-hr	NAREL	STN, IMPROVE, and IMPROVE_A

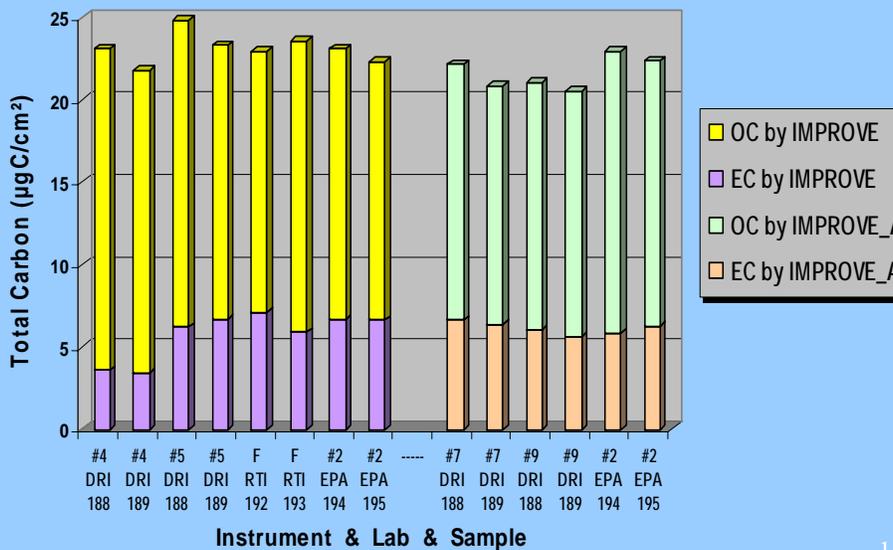


**Analysis of Replicate Quartz Filters - November 16 Event
STN - TOT Method... (except for CARB)***

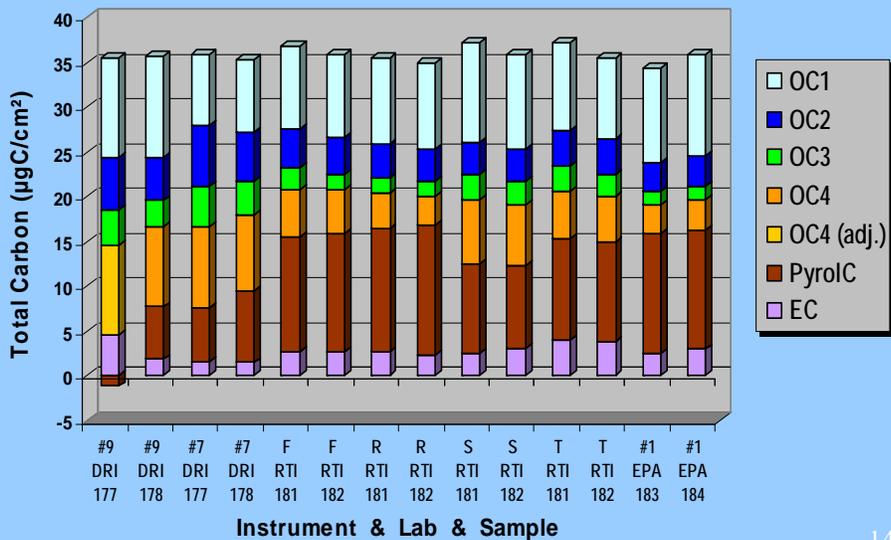
**CARB uses a modified STN-TOT method.*



**Analysis of Replicate Quartz Filters - November 16 Event
IMPROVE and IMPROVE_A - TOR Methods**

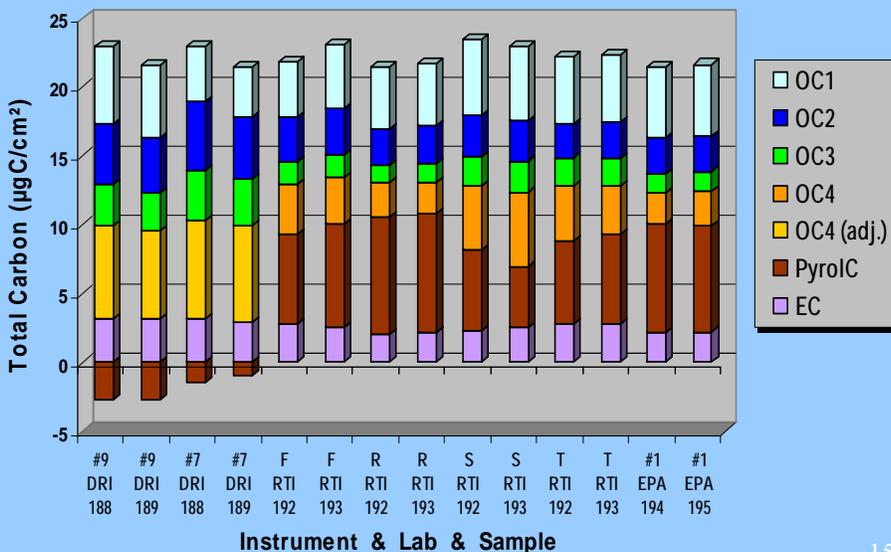


Analysis of Replicate Quartz Filters - April 27 Event STN - TOT Method

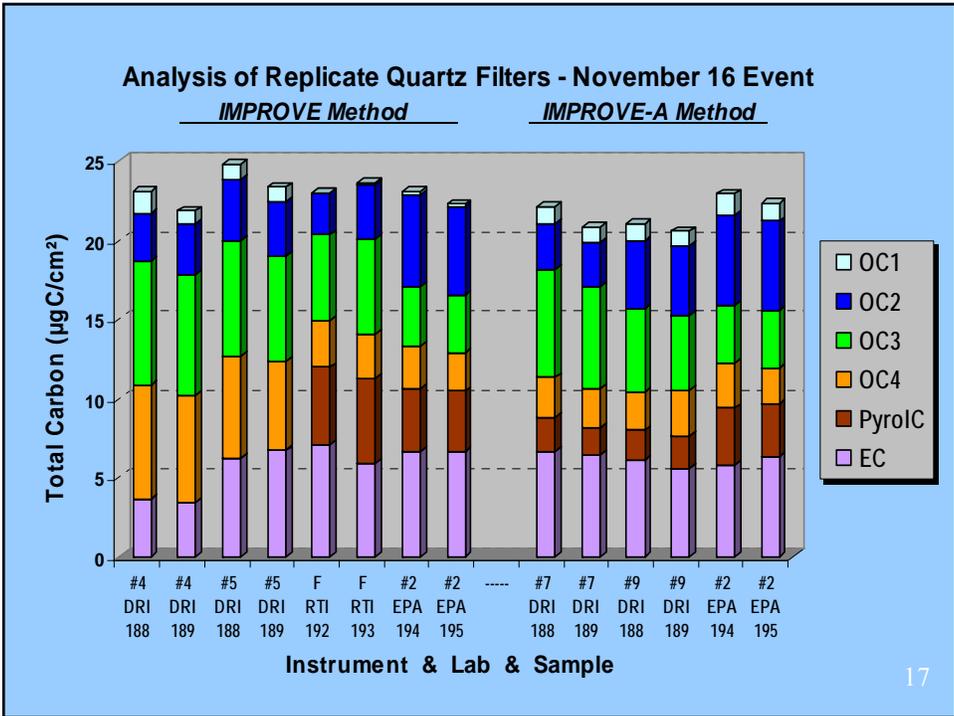
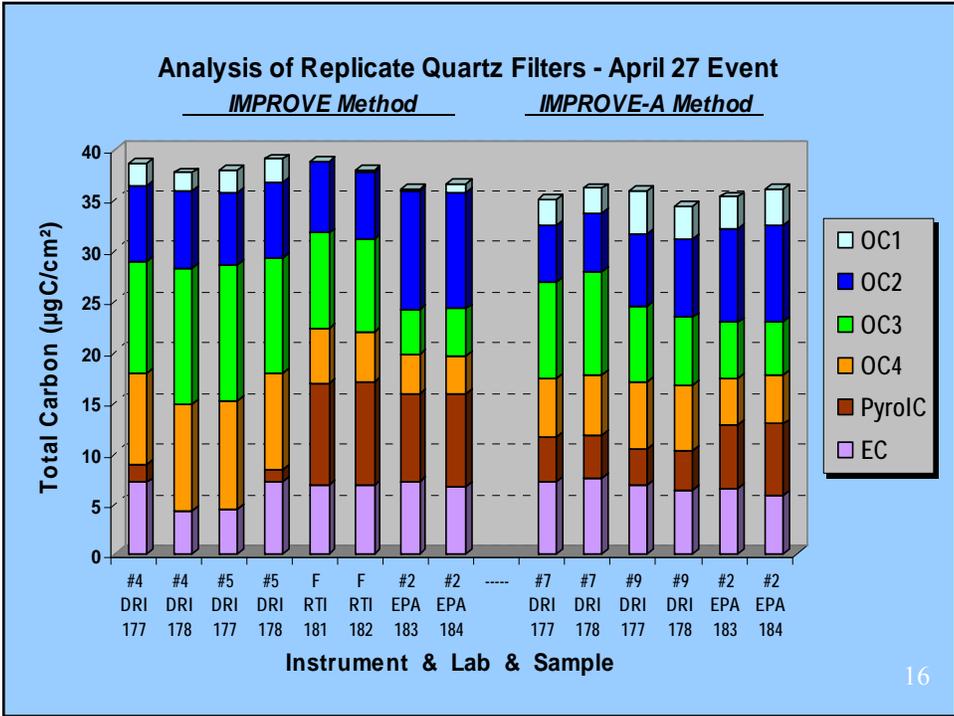


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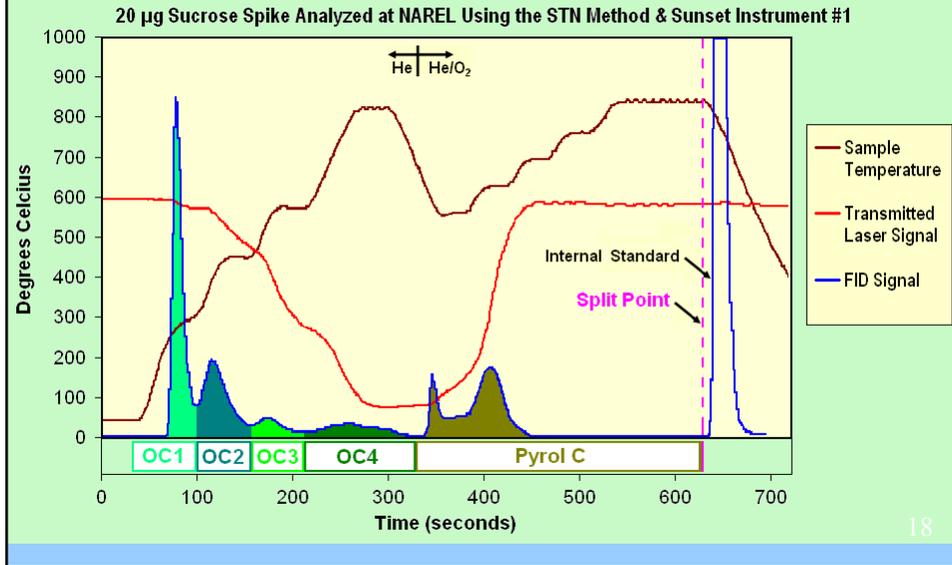
Analysis of Replicate Quartz Filters - November 16 Event STN - TOT Method



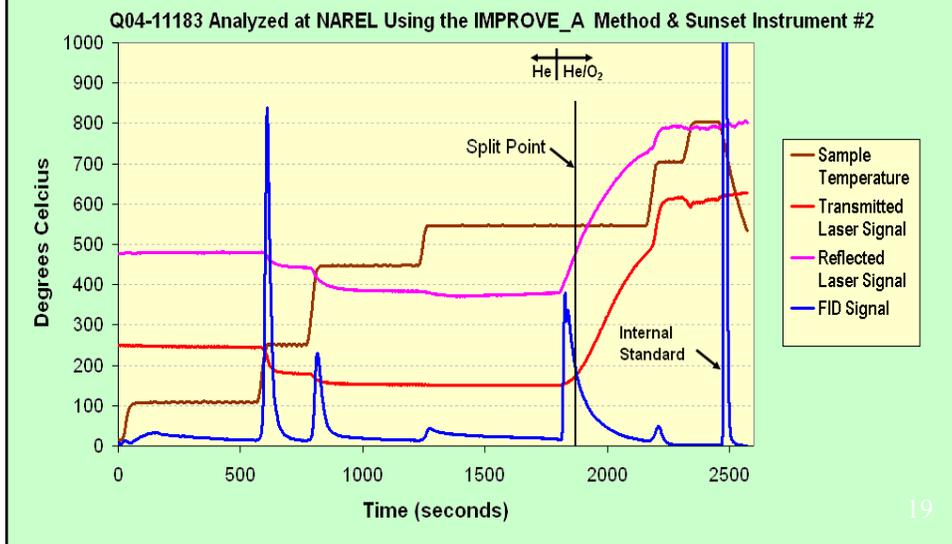
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Example Thermogram

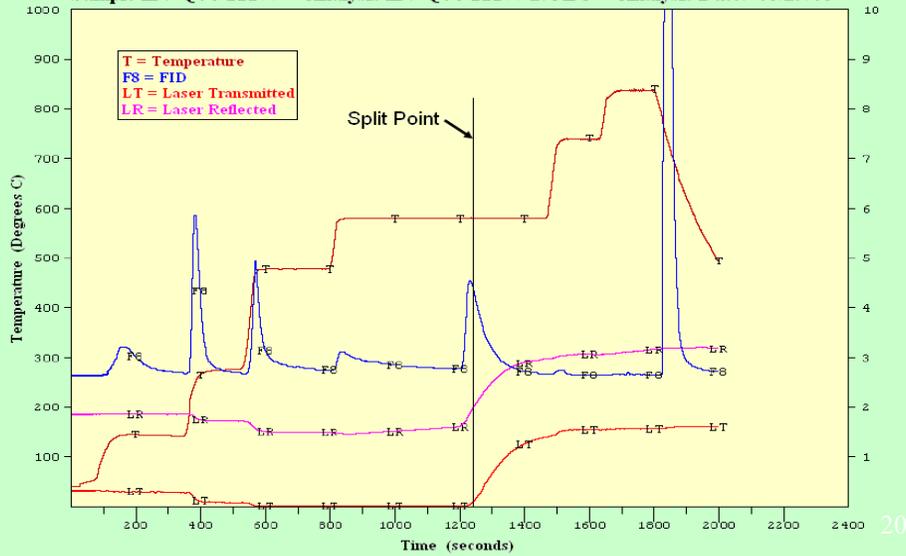


Analysis of Replicate Quartz Filter – April 27 Event



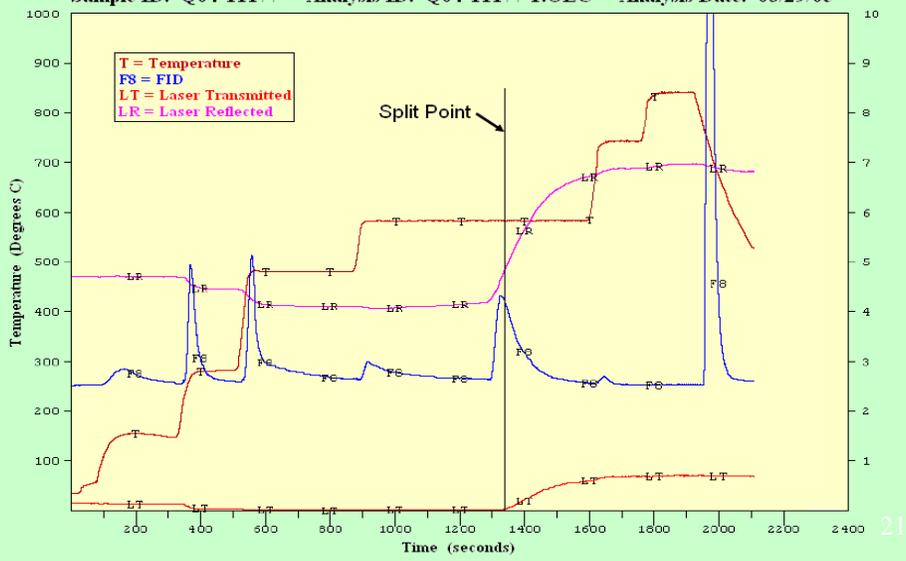
Analysis of Replicate Quartz Filter – April 27 Event

Carbon Analysis at DRI Using the IMPROVE A Method & DRI/Model 2001 Instrument #9
Sample ID: Q04-11177 Analysis ID: Q04-11177-2.OEC Analysis Date: 03/29/05



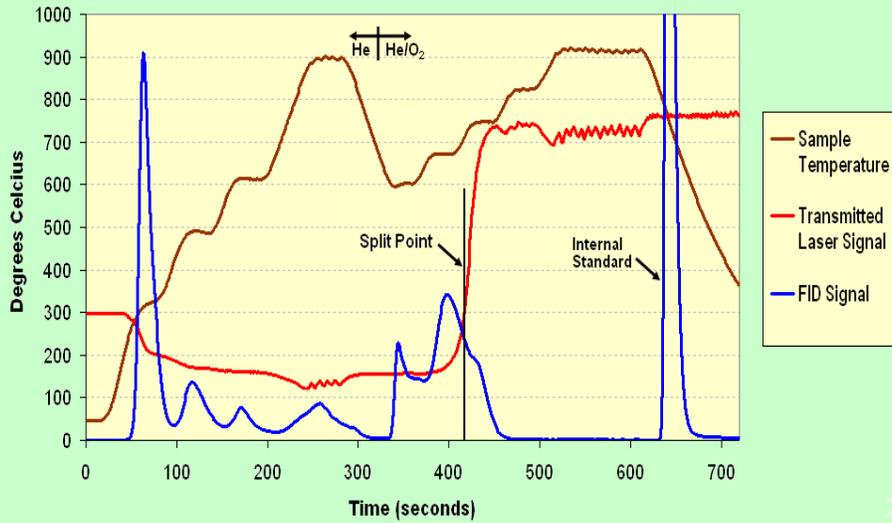
Analysis of Replicate Quartz Filter – April 27 Event

Carbon Analysis at DRI Using the IMPROVE A Method & DRI/Model 2001 Instrument #7
Sample ID: Q04-11177 Analysis ID: Q04-11177-1.OEC Analysis Date: 03/29/05



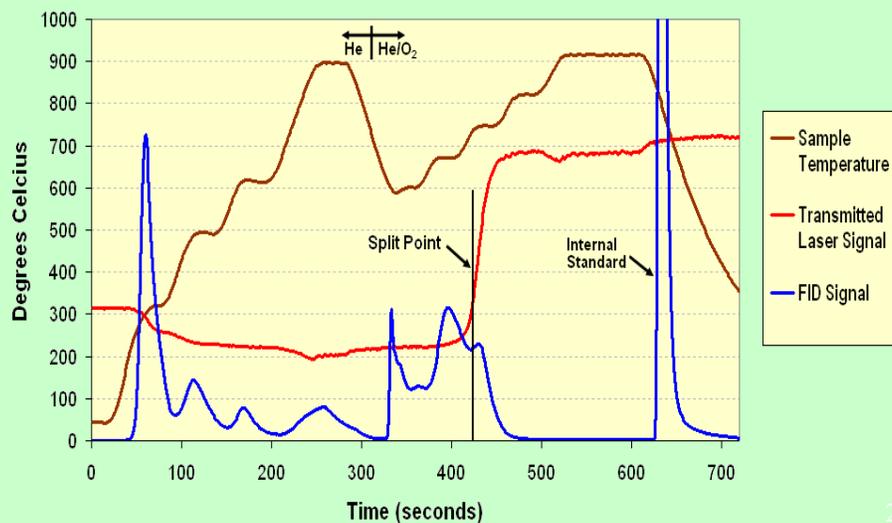
Analysis of Replicate Quartz Filter – April 27 Event

Q04-11183 Analyzed at NAREL Using the STN Method & Sunset Instrument #1



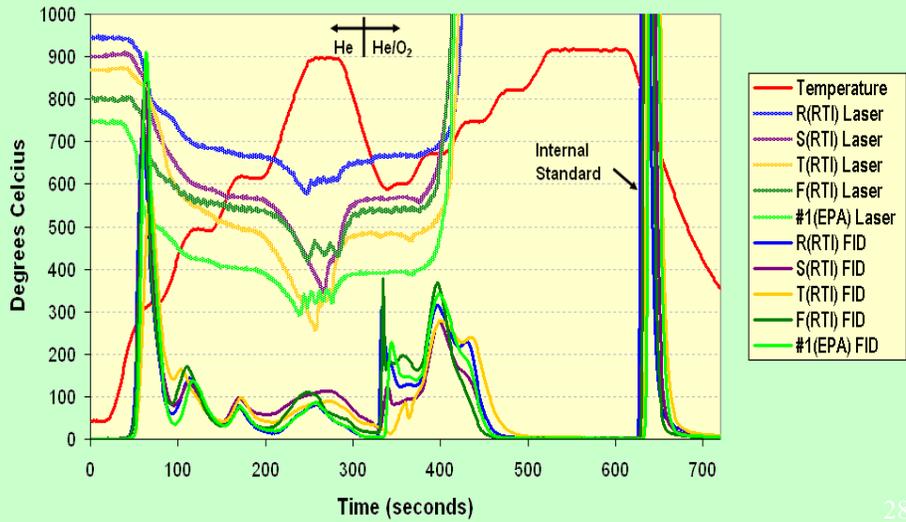
Analysis of Replicate Quartz Filter – April 27 Event

Q04-11182 Analyzed at RTI Using the STN Method & Sunset Instrument R



Analysis of Replicate Quartz Filter – April 27 Event

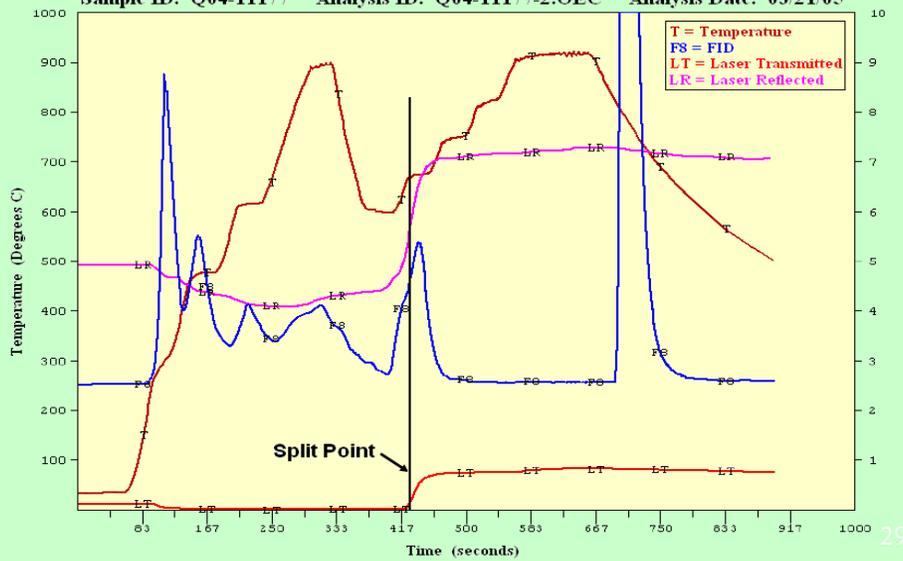
One Sample Analyzed on Five Sunset Instruments



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Analysis of Replicate Quartz Filter – April 27 Event

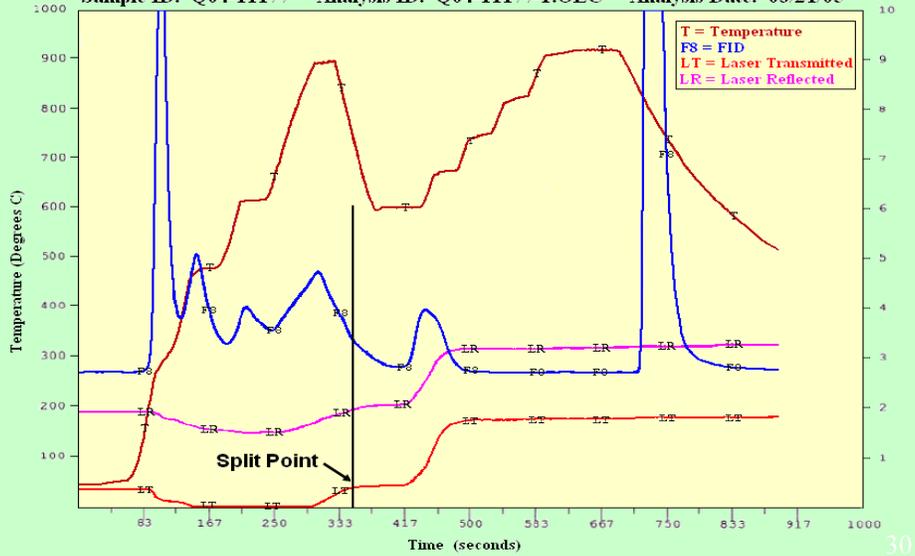
Carbon Analysis at DRI Using the STN Method & DRI/Model 2001 Instrument #7
 Sample ID: Q04-11177 Analysis ID: Q04-11177-2.OEC Analysis Date: 03/21/05



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Analysis of Replicate Quartz Filter – April 27 Event

Carbon Analysis at DRI Using the STN Method & DRI Model 2001 Instrument #9
Sample ID: Q04-11177 Analysis ID: Q04-11177-1.OEC Analysis Date: 03/21/05

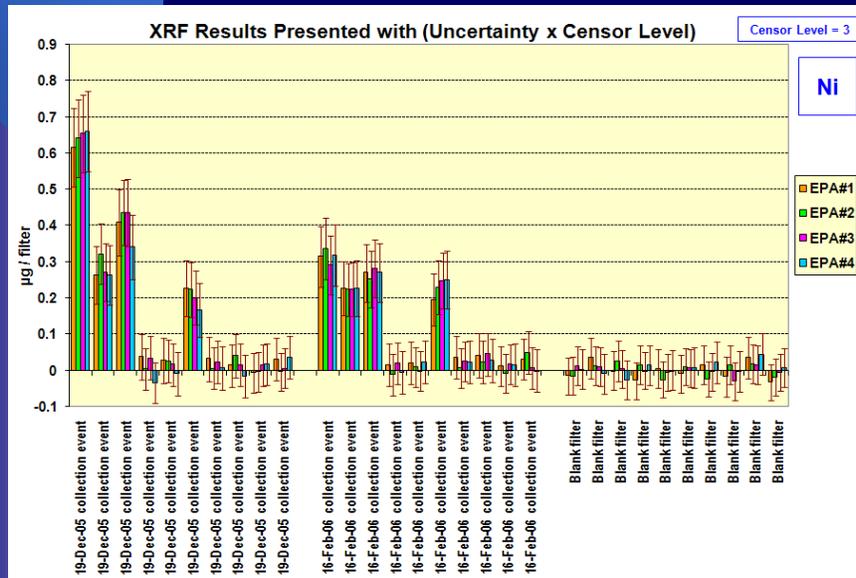


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Problem with Cyclone Corrosion



Multiple Determinations of Nickel by EPA Lab



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Specific QA Activities

- PE Samples
single-blind samples analyzed at different labs
- ▶ Laboratory TSA
on-site inspection and interviews with lab staff
- Special Studies
experimental investigations

DRI & UC Davis in May 2007

DRI

- This TSA was the second inspection of DRI's Environmental Analysis Facility conducted as part of the EPA required quality assurance oversight of the PM2.5 Chemical Speciation Network and the IMPROVE Network.
- Observations made by the audit team on this inspection again found the DRI Laboratory to be a modern facility with state of the art instrumentation, good documentation, and well qualified staff. DRI meets or exceeds compliance with good laboratory practices, the TCEQ QAPP and SOPs.
- The auditors as well as DRI staff found one area of concern during the audit regarding the gravimetric laboratory. The gravimetric performance demonstration produced mixed results for filters and metallic samples, indicating a possible balance stability problem.

DRI & UC Davis in May 2007

UCD

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

1. Many of the QA documents are not current and need to be updated. Recommendation: The Air Quality Group at CNL should work with the IMPROVE Steering Committee to set priorities and establish a schedule for updating the QA documents.

2. Currently blank filters are weighed more than once to generate precision data, but loaded filters are not routinely weighed more than once. This audit has demonstrated that large swings in humidity occur inside the weighing room which could affect loaded filters more than blank filters.

Recommendation: A small percentage of loaded filters should be weighed more than once to generate new precision data. The repeat measurement should not be made immediately but it should not be delayed for more than a few hours. NAREL has observed loaded filters to gradually lose mass over time possibly due to the vapor pressure of the captured semi-volatile components of the PM.

CARB & ODEQ in Sep 2008

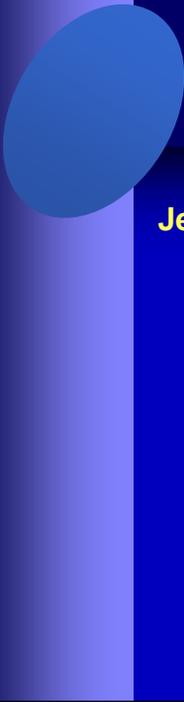
CARB

This audit was preceded by single-blind PE samples which were submitted to all of the labs that were inspected. Results from all of the PE samples were discussed with the analysts and supervisors involved. Some of the supporting raw data were examined during the audit, and some raw data were carried back to NAREL for examination as part of the audit follow-up. The auditors are pleased to report that no significant technical problems were found during the audit.

CARB & ODEQ in Sep 2008

ODEQ

Results of NAREL's most recent PE study that included the ODEQ laboratory as well as other CSN laboratories were available for discussion with ODEQ staff during the audit. The results indicated overall good performance from the ODEQ lab. Several experimental activities conducted during the TSA also gave additional objective evidence that good quality control and good laboratory practices are being followed at the ODEQ laboratory.



Recognition

**Jewell Smiley, Steve Taylor, R. L. Hines
NAREL, Montgomery**