

Date: July 31, 2000

Subj: Performance Evaluation Samples for PM_{2.5} Chemical Speciation Network

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This report is a summary of the results of the performance evaluation samples sent to Research Triangle Institute (RTI) as part of the PM_{2.5} Chemical Speciation Quality Assurance Program. The performance evaluation samples were sent to RTI to evaluate their ability to perform total carbon, anion, and cation analyses on air filter samples collected by the PM_{2.5} Chemical Speciation Network. A separate report will be issued to discuss the results of the performance evaluation samples for elemental analyses.

The results of each type of analysis will be discussed individually in this report.

Total Carbon:

On September 20, 1999 EPA-NE sent standard solutions and filter samples to RTI for total carbon analyses. On October 21, 1999 results of the RTI analyses were sent to EPA-NE. An evaluation of those results and discussion are contained in a report from Dick Siscanaw, EPA-NE, which is included as an attachment to this report.

Anion and Cation:

On October 21, 1999, ten samples were sent to RTI by NAREL for analysis of anions and cations. The following table identifies the samples sent to RTI for analysis.

Sample ID	# of Ampules	Analysis	Concentration Range (mg/L)	Reporting Units	Sample Preparation
DI Water Blank	2	Anions*	NA	mg/L	None, ready to analyze
Standard #1 Mix #1	2	Anions*	0.2 -30	mg/L	None, ready to analyze
Standard #1 Mix #2	2	Anions*	0.2 -30	mg/L	None, ready to analyze
Standard #1 Mix #3	2	Anions*	0.2 -30	mg/L	None, ready to analyze
Standard #1 Mix #4	2	Anions*	0.2 -30	mg/L	None, ready to analyze
DI Water Blank	2	Cations**	NA	mg/L	None, ready to analyze
Standard #2 Mix #1	2	Cations**	0.2 -30	mg/L	None, ready to analyze
Standard #2 Mix #2	2	Cations**	0.2 -30	mg/L	None, ready to analyze
Standard #2 Mix #3	2	Cations**	0.2 -30	mg/L	None, ready to analyze
Standard #2 Mix #4	2	Cations**	0.2 -30	mg/L	None, ready to analyze

*Anions - nitrate, sulfate

**Cations - ammonium, sodium, potassium

Results of the RTI analyses were reported to Mary Wisdom on November 2, 1999. A summary table of the true value, acceptance limits, and reported value follows. As indicated in the RTI report of the analysis of the PE samples the cation samples were contaminated with approximately 1.7 mg/L of sodium. This was probably due to the glass ampules used to store the samples. If the 1.7 mg/L of sodium is subtracted from the reported value all sodium results are within the acceptance limits except for Standard #2 Mix #4.

A review of the RTI results also indicated a possible contamination of potassium in the PE samples of approximately 0.17 mg/L. If this value is subtracted from the Standard #2 Mix #4 potassium reported value the result is closer to the acceptance limits, but still high.

An evaluation of the results shows that RTI performance is acceptable, with 96 percent of the reported results within the acceptance limits. The results do indicate a possible problem analyzing cations (sodium and potassium) at low levels, and this will be investigated in future performance evaluation samples and audits.

Sample ID	Analyte	True Value	Acceptance Limits	Reported Value	Within Acceptance Limits Y/N	Ratio TV/RV
DI Water Blank	Nitrate as N	0.00	NA	0.00	NA	NA
DI Water Blank	Sulfate	0.00	NA	0.023	NA	NA
Standard #1 Mix #1	Nitrate as N	19.0	16.9 - 21.1	19.3	Y	0.984
Standard #1 Mix #1	Sulfate	23.0	19.8 - 26.2	23.229	Y	0.990
Standard #1 Mix #2	Nitrate as N	11.4	10.1 -12.7	11.584	Y	0.984
Standard #1 Mix #2	Sulfate	13.8	11.9 -15.7	14.267	Y	0.967
Standard #1 Mix #3	Nitrate as N	4.56	4.06 -5.06	4.676	Y	0.975
Standard #1 Mix #3	Sulfate	5.52	4.75 - 6.29	5.700	Y	0.968
Standard #1 Mix #4	Nitrate as N	0.228	0.203 - 0.253	0.231	Y	0.987
DI Water Blank	Ammonium	0.0	NA	0.00	NA	NA
DI Water Blank	Sodium	0.0	NA	1.730	NA	NA
DI Water Blank	Potassium	0.0	NA	0.172	NA	NA
Standard #2 Mix #1	Ammonium	21.0	17.85 - 24.1	21.029	Y	0.999
Standard #2 Mix #1	Sodium	18.0	15.3 - 20.7	19.529 (17.8)*	Y *	0.922 (1.011)
Standard #2 Mix #1	Potassium	24.0	20.4 -27.6	25.722	Y	0.933
Standard #2 Mix #2	Ammonium	12.6	10.7 - 14.5	12.030	Y	1.047
Standard #2 Mix #2	Sodium	10.8	9.18 - 12.4	12.425 (10.7)*	Y *	0.869 (1.009)
Standard #2 Mix #2	Potassium	14.4	12.2 - 16.6	15.420	Y	0.934
Standard #2 Mix #3	Ammonium	5.04	4.28 - 5.80	4.695	Y	1.073
Standard #2 Mix #3	Sodium	4.32	3.67 - 4.97	6.032 (4.332)*	Y *	0.716 (0.998)
Standard #2 Mix #3	Potassium	5.76	4.90 - 6.62	6.326	Y	0.911
Standard #2 Mix #4	Ammonium	0.252	0.214 - 0.290	0.221	Y	1.140
Standard #2 Mix #4	Sodium	0.216	0.184 - 0.248	1.785 (0.085)*	N *	0.121 (2.541)
Standard #2 Mix #4	Potassium	0.288	0.245 - 0.331	0.514 (0.344) **	N **	0.560 (0.837)

* As indicated in the RTI report of the analysis of the PE samples the cation samples were contaminated with approximately 1.7 mg/L of sodium. This was probably due to the glass ampules used to store the samples. If the 1.7 mg/L of sodium is subtracted from the reported value all sodium results are within the acceptance limits except for Standard #2 Mix #4.

** A review of the RTI results also indicated a possible contamination of potassium in the PE samples of approximately 0.17 mg/L. If this value is subtracted from the Standard #2 Mix #4 potassium reported value the result is closer to the acceptance limits, but still high.

To: Mary Wisdom, Quality Assurance Officer, NAREL
 From: Rob Maxfield and Dick Siscanaw, EPA, Lexington, MA
 Subject: Evaluation of Research Triangle Institute's (RTI) Initial Demonstration of Performance Evaluation Samples for PM2.5 Carbon Analyses
 Date: 11/27/99
 File: rtim.ltr

This report summarizes the results of a laboratory performance evaluation study performed in support of the PM2.5 speciation program. The EPA New England, Regional Laboratory (EPA) conducted this study to evaluate the proficiency of the PM2.5 contract laboratory, Research Triangle Institute (RTI), for analysis of carbon on air particulates samples.

Approach:

On September 20, 1999, twenty one performance evaluation samples were shipped to RTI to evaluate their ability to meet the method performance criteria for the analyses of organic, elemental and total carbon. Three types of samples and reference materials were provided to access various aspects of the analytical method performance. The following table details the sample type, number, purpose and criteria used in this evaluation.

Type	Purpose	Initial Acceptance Criteria
Blanks	Evaluate sample shipment, handling, and storage	Total carbon less than 1 ug/cm ²
Standard Solutions —Sucrose —Potassium hydrogen phthalate (KHP)	Evaluate the instrument's linearity, calibration and precision	—Within 5 %D of the true value —Within 10% RPD for duplicates
Split Filters — Collected by RTP — Collected by NIST	Evaluate the OC, EC and total carbon (TC) analysis of real world air particulate samples relative to reference lab average values	— For concentrations greater than 10 ug/cm ² , within 15 % RPD of average value. — For concentrations between 5 - 10 ug/cm ² , within 20 % RPD of average value. — For concentrations less than 5 ug/cm ² , within 1 ug/cm ² of average value.

Split samples were placed in Gelman petri dishes, wrapped with aluminum foil, and sealed in a zip lock bag. Standard solution samples were sealed in glass vials with Teflon screw caps. All samples were shipped by overnight courier to RTI in a Styrofoam cooler containing blue ice.

Five reference laboratories provided comparison data for this study.

National Institute for Occupational Safety and Health (NIOSH),
Cincinnati, OH;
Desert Research Institute (DRI), Reno, NV,
Sunset Laboratories, RTP, NC
Environmental Protection Agency, Lexington, MA.

The RTI data was returned to the EPA for evaluation on October 21, 1999, well within the contract required 30 day turn around.

II **Discussion:**

Initial acceptance criteria are proposed as starting point for evaluating PM_{2.5} carbon data. The criteria were developed based on the best available information from RTI's QAPP, method SOPs from the Sunset and DRI laboratories, discussions with various carbon analysis "experts", and region 1 internal QC tables. Due to the variable composition of PM 2.5 particles across the country and the expected range of filter loading from different types of sites these initial acceptance criteria may not be appropriate for the actual PM_{2.5} program. It is anticipated that experience will dictate more appropriate operational data acceptance criteria which may be stricter or looser than those used for this preliminary study. These criteria will therefore be updated periodically by NAREL as outlined in the program QAPP.

Study data provided in the attached table are reported in units of ug/cm², rather than ug/m³ to simplify the data evaluation. It is anticipated that future round robins studies may be expressed in ug/m³, and evaluation criteria would then be converted to this unit. Lastly, three of the laboratories ran internal duplicates as internal quality control, only the average values have been reported in the attached evaluation table.

The EPA trip blank was a 1.5 cm² quartz filter punch that was pre-cleaned in the EPA total carbon analyzer, immediately analyzed and then sealed in a Gelman petri dish. This trip blank was used to evaluate any handling contamination that might have occurred during transport or analysis. Two additional blank quartz filters were provided by NIST. Both filters had total carbon values greater than the 1 ug/cm² criteria established by EPA for blank filters. Therefore RTI data for these "blanks" was evaluated against the criteria established for split samples.

Instrument calibration(accuracy) and linearity was checked with several primary sucrose and potassium hydrogen phthalate solutions. Two sets of duplicate solutions were used to evaluate analysis precision. A high standard was used to evaluate the attenuated FID2 signal and the instrument's methanator. This high sucrose standard failed the 5% D criteria for both EPA and RTI. As a result this data has been omitted from the evaluation. Both laboratory values were within the 15% D, criteria stated in the RTI QAPP. It is anticipated that actual values for real samples would never approach the concentration of this high standard, though understanding method variability at this level is important to the evaluation. Five levels were used within a typical sample range. The formula used to measure the accuracy is listed below.

$$\%D = \frac{\text{observed value} - \text{true value}}{\text{true value}} * 100$$

Actual filter samples collected by NIST and RTP were split and portions were analyzed by RTI and the reference laboratories. Since there is no true value for these samples, average observed results from the reference laboratories were used for evaluation of RTI data.

The RTP samples were collected by Chuck Lewis at Fort Cornelia's airport in Nashville, TN. All of the samples were collected over an 11.5 hour period on 90 mm quartz filters (sampling data is provided below).

Sample Number	StartDate/Time	Flow Rate (L/min)
NAS99A-MSP-10	21 June 1999 0800	300
NAS99A-MSP-29	02 July 1999 1900	300
NAS99A-MSP-30	03 July 1999 0700	300
NASA99A-URG-1Q-16	02 July 1999 1900	100
NASA99A-URG-1Q-17	03-July 1999 0700	100

NIST samples consisted of five filters artificially loaded with SRM 1649a urban dust. The loadings are listed in the table below. Even with a 1 cm² punch it was difficult to obtain 4 uniform samples because of the small size of the filter and variability in the deposit. For samples, SCG00164 and ACG00661, only 3 good punches were obtained. One of the five samples provided by NIST, ACG00661, was discarded because data from the reference laboratories had a relative difference greater than 15%. For sample ACG00682, one reference laboratory reported a scuff on the punch, suggesting the possibility of sample loss. All of the samples were orange after the total carbon analyses indicating a large amount of inorganic material. Most of the misses were with the NIST split samples, suggesting that the evaluation criteria may not be suitable. Reported elemental carbon variability may have been due to sample uniformity, complexity of the composition, leakage (undefined border), variability of the loading or the small differences in the thermal programs.

Sample Number	SRM 1649a (mg)
ACG00164	3.6157
ACG00167	3.4278
ACG00238	3.2306
ACG00661	3.1577
ACG00682	3.4173

Relative percent difference was calculated using the following formula:

$$\% \text{ RPD} = \frac{(\text{observed value} - \text{average value of reference labs}) * 100}{\text{Average value of observed value and average of reference labs}}$$

III Conclusion and Recommendation:

In summary, RTI missed 4 data points out of a 37 total measurements. RTI's result for the EPA trip blank was excellent, 0.14 ug/cm², showing little, if any, background contamination. This measurement is below the statistical error at this level. For the sucrose and KHP solutions, RTI was outside the accuracy criteria for the SS4 sucrose solution and for the precision criteria for the SS2 and SS4 duplicate pair. The error appears to be a pipetting error because one value was low and the other high. Also, the other duplicate samples, SS5 and SS8, and the RTI's internal duplicates for SS1, SS8 and sample MSP-030 were excellent (RTI's raw data). RTI had excellent agreement with the remaining performance evaluation solutions and missed only 2 on the split filter samples. These two misses on the RTP split filters missed the 20% evaluation criteria by less than 2%. Overall evaluation of the RTI carbon analysis performance has been determined to be satisfactory with 89% of the reported data within the evaluation criteria.

Laboratory	Total Measurements	Measurements Within Criteria	Completeness (%)
RTI	37	33	89
Laboratory 1	35	32	91
Laboratory 2	21	20	95
Laboratory 3	15	15	100
Laboratory 4	14	13	93

Complete Data

file:RTI_Final2.XLS

Lab	Sample	OC (ug/cm2)	AVE OC (ug/cm2)	OC Difference	EC (ug/cm2)	AVE EC (ug/cm2)	EC Difference	TC (ug/cm2)	AVE TC (ug/cm2)	TC Difference	
Part 1: Trip Blanks											
1a - EPA Trip Blank											
lab 1	B-1			(-0.01)			(-0.04)			-0.05	OK
RTI				(0.14)			(0)			0.14	OK
1b - NIST Trip Blanks											
				(Difference)			(Difference)			(Difference)	
lab 1	ACG00330	3.75	3.02	0.73	0.12	0.07	0.05	3.87	3.09	0.78	OK
lab 4		2.29		-0.73	0.02		-0.05	2.31		-0.78	OK
RTI		2.66		-0.36	0		-0.07	2.66		-0.43	OK
lab 1	ACG00869	3.48	2.49	0.99	0.24	0.12	0.12	3.72	2.61	1.11	greater than 1
lab 4		1.5		-0.99	0		-0.12	1.5		-1.11	OK
RTI		1.6		-0.89	0		-0.12	1.6		-1.01	OK

lab 2		21.05		-4.63OK	1.67		0.10OK	22.72		-4.01OK
lab 3		22.2		0.69OK	1.7		0.13OK	24		1.47OK
RTI		23.16		4.93OK	1.03		-0.54OK	24.18		2.22OK
lab 1	MSP-029	13.84	12.69	8.67OK	1.25	1.48	-0.23OK	15.09	14.17	6.26OK
lab 2		11.83		-7.01OK	1.6		0.12OK	13.43		-5.39OK
lab 3		12.4		-2.31OK	1.6		0.12OK	14		-1.23OK

Lab	Sample	OC (ug/cm2)	AVE OC (ug/cm2)	Difference (%RPD)	EC (ug/cm2)	AVE EC (ug/cm2)	Difference (Difference)	TC (ug/cm2)	AVE TC (ug/cm2)	Difference (%RPD)
RTI		11.86		-6.76OK	0.92		-0.56OK	12.8		-10.34OK
lab 1	MSP-030	14.89	14.32	3.93OK	0.88	1.14	-0.26OK	15.75	15.45	1.94OK
lab 2		13.66		-4.69OK	1.13		-0.01OK	14.79		-4.34OK
lab 3		14.4		0.58OK	1.4		0.26OK	15.8		2.26OK
RTI		14.05		-1.88OK	0.7		-0.44OK	14.76		-4.55OK

Part 3b - NIST Samples

lab 1	ACG00164	76.93	75.75	1.55OK	29.44	26.13	11.91OK	106.36	101.88	4.31OK
lab 4		74.57		-1.57OK	22.82		-13.52OK	97.39		-4.50OK
RTI		72.66		-4.16OK	26.29		0.61OK	98.95		-2.91OK
lab 1	ACG00167	69.89	66.31	5.25OK	26.85	25.42	5.48OK	96.73	91.70	5.34OK
lab 4		59.08		-11.54OK	23.5		-7.84OK	82.59		-10.45OK
lab 2		69.97		5.37OK	25.9		1.88OK	95.77		4.35OK
RTI		69.14		4.17OK	23.5		-7.84OK	92.64		1.02OK
lab 1	ACG00238	68.83	63.28	8.41OK	19.15	22.60	-16.53outside 15%	97.99	89.25	9.34OK
lab 4		62.16		-1.78OK	21.29		-5.97OK	83.55		-6.59OK
lab 2		58.84		-7.27OK	27.36		19.06outside 15%	86.2		-3.47OK
RTI		67.19		6.00OK	19.57		-14.37OK	86.76		-2.83OK
lab 1	ACG00682	58.22	54.09	7.35OK	26.39	21.91	18.55outside 15%	84.61	76.17	10.49OK
lab 4		55.7		2.93OK	16.92		-25.70outside 15%	73.13		-4.08OK
lab 2		48.36		-11.19OK	22.42		2.30OK	70.78		-7.34OK
RTI		62.03		13.67OK	20.33		-7.48OK	82.36		7.80OK