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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**BLACK CARBON MONITORS**
APPLICATION:	**MEASUREMENT OF BLACK CARBON IN AMBIENT AIR**
TECHNOLOGY NAME:	**Model 4 OC-EC Field Analyzer**
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The U.S. Environmental Protection Agency (EPA) has established the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies. Information and ETV documents are available at www.epa.gov/etv.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), and with individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Advanced Monitoring Systems (AMS) Center, one of six verification centers under ETV, is operated by Battelle in cooperation with EPA's National Risk Management Research Laboratory. The AMS Center evaluated the performance of monitors for determining black carbon concentrations in ambient air. This verification statement provides a summary of the test results for the Sunset Laboratory Model 4 OC-EC Field Analyzer.

VERIFICATION TEST DESCRIPTION

The verification test was conducted over a period of approximately 30 days (April 5 to May 7, 2013) and involved the continuous operation of duplicate Model 4 OC-EC analyzers at the Battelle Columbus Operations Special Support Site (BCS3) in Columbus, Ohio. Duplicate reference samples were collected over 12-hour

sampling intervals throughout the testing period, from approximately 7:00 am to 7:00 pm and from approximately 7:00 pm to 7:00 am daily. The reference samples were collected and analyzed by Desert Research Institute for organic carbon (OC) and elemental carbon (EC) using the Interagancy Monitoring of PROtected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) and thermal/optical transmittance (TOT) protocols. Note that in this report the filter samples will be referred to as "reference samples". However, it should be noted that the IMPROVE method is not a true Reference Method in that it is not recognized as an absolute standard. Nonetheless, it is used within the IMPROVE network as the standard method for EC analysis. Thus the method was used in this test as an analytical technique used for comparison to the BC monitors. Other thermal/optical reference methods such as the NIOSH 5040 method may result in different results. The comparability and correlation of the monitoring technology was determined through comparisons to the collocated reference method samples. The precision of the Model 4 analyzers was determined from comparisons of paired data from the duplicate units (identified as "RT3218" and "RT3219". Other performance parameters such as data completeness, maintenance requirements, ease of use, and consumable use were assessed from observations by the Battelle field testing staff. This test was not intended to simulate long-term performance of anlayzers at a monitoring site.

QA oversight of verification testing was provided by Battelle and EPA. Battelle technical staff conducted a performance evaluation audit, and Battelle QA staff conducted a technical systems audit and a data quality audit of 10% of the test data. This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the Model 4 anlayzer is based on information provided by the vendor. This technology description was not verified in this test.

Sunset Laboratory's semi-continuous Model 4 OC-EC Field Analyzer has been developed as a field deployable alternative to integrated filter collection with subsequent laboratory analysis. This instrument can provide time-resolved analyses of OC and EC in airborne particulate matter (PM) on a semi-continuous basis, with OC-EC results comparable to the recognized NIOSH Method 5040 and other thermal optical carbon aerosol methods currently in use. As currently performed, a quartz filter disc is mounted in the oven within the instrument, and samples are collected for the desired time period. Once the collection is complete, the oven is purged with helium, and a stepped-temperature ramp increases the oven temperature to 850 °C, thermally desorbing organic compounds and pyrolysis products into a manganese dioxide (MnO_2) oxidizing oven. As the carbon fragments flow through the MnO_2 oven, they are quantitatively converted to carbon dioxide (CO_2) gas. The CO_2 is swept out of the oxidizing oven with the helium stream and measured directly by a self-contained non-dispersive infrared (NDIR) detector system. A second temperature ramp is then initiated in an oxidizing gas stream and any elemental carbon is oxidized off the filter and into the oxidizing oven and NDIR. The EC is then detected in the same manner as the OC.

The Sunset Laboratory thermal/optical method uses the high light absorbance characteristic of EC to correct for the pyrolysis-induced error. This is done by incorporating a tuned diode laser (red, 660 nm), focused through the sample chamber such that the laser beam passes through the mounted filter in the sample oven. Initial absorbance of the modulated laser beam is recorded. As the oven ramp proceeds, the laser absorbance is monitored continuously by the data system. Any charring of the OC results in an increase in absorbance of the laser. After the initial temperature ramp, when the helium purge is switched to a He/O2 mixture, all of the EC is oxidized off and the laser absorbance is reduced to the background level. When the resulting NDIR data are reviewed with an overlay of the laser absorbance, the point in the second phase oxidizing ramp at which the laser absorbance equals the initial laser absorbance is the split point. Any EC detected, before this point, was formed pyrolytically by charring of the OC. This carbon is subtracted from the EC area observed during the oxidizing phase of the analysis and is assigned as OC. The primary assumption, for this correction, is that the particulate bound EC and the pyrolytically formed EC have the same absorption coefficient. Carefully prepared standard samples suggest that this correction is satisfactory.

VERIFICATION RESULTS (An unexplained anomaly in the signal of one of the duplicate Model 4 analyzers was discovered during data processing. Results presented here include both uncorrected and corrected values.)

		TOR		TOT	
Comparability- Regression analysis comparison to reference samples	**Analyzer/Mode**	**Slope**	**Intercept**	**Slope**	**Intercept**
	RT3218 Thermal	0.797 (0.044)	0.280 (0.028)	1.057 (0.053)	0.293 (0.025)
	RT3219 Thermal	0.903 (0.063)	0.346 (0.040)	1.215 (0.073)	0.355 (0.035)
	RT3219 Corrected Thermal	0.819 (0.043)	0.290 (0.027)	1.080 (0.053)	0.306 (0.025)
	RT3218 Optical	0.656 (0.034)	0.134 (0.021)	0.874 (0.036)	0.143 (0.017)
	RT3219 Optical	0.701 (0.034)	0.140 (0.022)	0.934 (0.038)	0.150 (0.018)

		RPD[a]	
Comparability- Calculation of Relative Percent Difference (RPD) between Model 4 OC-EC results and reference method results	**Analyzer/Mode**	**TOR**	**TOT**
	RT3218 Thermal	45.4%	80.6%
	RT3219 Thermal	66.2%	101.4%
	RT3219 Corrected Thermal	45.7%	77.6%
	RT3218 Optical	-3.7%	23.6%
	RT3219 Optical	2.1%	31.2%

		r^2	
Correlation - Regression analysis comparison to reference samples	**Analyzer/Mode**	**TOR**	**TOT**
	RT3218 Thermal	0.854	0.876
	RT3219 Thermal	0.783	0.827
	RT3219 Corrected Thermal	0.865	0.878
	RT3218 Optical	0.878	0.910
	RT3219 Optical	0.882	0.914

		RPD (# of Observations)			
		Thermal		Optical	
Precision - Comparison of results from duplicate monitoring systems		**2-hour**	**12-hour**	**2-hour**	**12-hour**
	Uncorrected	19.9% (N=168)	14.3% (N=38)	5.7% (N=91)	6.3% (N=16)
	Corrected	12.4% (N=157)	9.7% (N=36)	--	--

Precision – Regression analysis of results from duplicate monitoring systems	**Mode**	**Period**	**Slope**	**Intercept**	**r^2**
	Thermal Uncorrected	2-hour	1.075 (0.021)	0.064 (0.017)	0.880
		12-hour	1.104 (0.055)	0.044 (0.040)	0.872
	Thermal Corrected	2-hour	1.000 (0.016)	0.024 (0.013)	0.912
		12-hour	0.980 (0.036)	0.035 (0.027)	0.925
	Optical	2-hour	1.057 (0.002)	0.002 (0.001)	0.999
		12-hour	1.065 (0.004)	-0.001 (0.002)	0.999

Data Completeness	**Analyzer**	**Period**	**Total Periods**	**Valid Measurements**	**% Complete**
	RT3218	2-hour	378	372	98%
		12-hour	63	62	98%
	RT3219	2-hour	378	372	98%
		12-hour	63	62	98%

VERIFICATION RESULTS (Cont.)

Maintenance	• Routine maintenance consisted of replacing filters approximately weekly.
Consumables/waste generated	• Three different compressed gas cylinders required to operate the units • Internal filters replaced weekly.
Ease of use	• Installation of two Model 4 units with inlets completed in ~4 hours. • Calibration of units completed in ~3-4 hours, after allowing the units to operate overnight. • Routine operation required no effort other than brief daily instrument checks and approximately weekly data downloads. • Data processed using vendor software to generate csv data files.

[a] For these calculations, reference method results below twice the method detection limit were excluded. For perfect agreement between the Model 4 analyzers and the reference method results, the RPD would be zero. In general, the measured concentrations from the Model 4 analyzers were higher than those from the reference method resulting in positive RPD values. It should be noted that only about two thirds of the TOR reference method results and fewer than half the TOT reference method results were above twice the detection limit.

Signed by Spencer Pugh 4/17/14
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Signed by Cynthia Sonich-Mullin 5/7/14
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