

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



TECHNOLOGY TYPE: FIELD PORTABLE ION CHROMATOGRAPH

APPLICATION: MONITORING OF SOLUBLE GASES AND AEROSOL SPECIES IN AMBIENT AIR

TECHNOLOGY NAME: Monitor for Aerosols and Gases in Ambient Air (MARGA) ADI 2080

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ETV Joint Verification Statement

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 permittees), 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 and 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 a field portable ion chromatograph for determining the concentrations of water-soluble gases and aerosol species in ambient air. This verification statement provides a summary of the test results for the Applikon Analytical B.V. Monitor for Aerosols and Gases in Ambient Air ADI 2080 (MARGA).

VERIFICATION TEST DESCRIPTION

This verification evaluated the ability of the MARGA to provide reliable quantitative measurements of soluble gases and aerosol species in air, during continuous and largely unattended operation. The test was conducted over a period of 30 days in the early fall of 2010 and involved continuous operation of duplicate MARGA units at an existing ambient air monitoring site located on EPA's campus in Research Triangle Park, North Carolina. The performance of the MARGA was determined partly through comparisons to modified EPA reference methods for individual gaseous and particulate species. Modifications to the reference methods primarily involved increasing the sampling flow rate to reduce sampling times and minimize measurement bias and uncertainties. Quantitative comparisons of MARGA results to reference results were made for sulfur dioxide (SO₂), nitric acid (HNO₃), and ammonia (NH₃) and the aerosol components sulfate (SO₄²⁻), nitrate (NO₃⁻), and ammonium (NH₄⁺). Hourly MARGA results for these species were averaged over the twice-daily 12-hour reference sampling periods and compared to the results from duplicate filter/denuder reference sampling trains. Hourly MARGA SO₂ results were also compared to continuous pulsed fluorescence SO₂ monitor data. MARGA results for aerosol sodium (Na⁺), calcium (Ca²⁺), and chloride (Cl⁻) were also used in assessing the completeness of MARGA data.

MARGA performance was evaluated based on the quantitative performance goals set for EPA's Clean Air Status and Trends Network (CASTNET) that were incorporated into the test/quality assurance (QA) plan for this verification. The following are the parameters and CASTNET goals on which MARGA performance was evaluated:

Accuracy – The measurement accuracy of each MARGA unit was evaluated based on the slope and intercept of the linear regression of MARGA results against the mean of duplicate 12-hour reference results and on the median absolute relative percent difference (MARPD) between the MARGA results and the mean of duplicate reference measurement results. The CASTNET target goals are a regression slope between 0.80 and 1.2, an intercept within ±10 parts per billion by volume (ppbv) of zero, and MARPD ≤ 40%.

Precision – The precision of the MARGA was determined by comparisons of paired data from the duplicate MARGA units and by comparison of MARGA precision results to pooled results from the reference methods. The CASTNET target goals are MARPD of paired hourly MARGA measurements ≤ 25%, and an MARPD of the paired MARGA data that was less than the 95th percentile of the pooled relative percent difference of the reference method results.

Data Completeness – The MARGA data were evaluated for completeness based on the percentage of the entire test period for which valid hourly data were available within 24 hours of collection and on the average percentage of each reference measurement period that the MARGA unit provided valid data. The CASTNET target goal is for both completion percentages to be ≥ 80%.

Reliability – The reliability of the MARGA units was evaluated in terms of the percentage of the entire test period that each unit was in measurement mode, with a target goal of ≥ 90%. Reliability was also evaluated by whether the MARGA could survive a power outage and return to routine operation within 4 hours and by the average number of site visits per week required to keep the monitor operating (with a goal of ≤ 2 visits per week).

Operational Factors – Performance factors such as maintenance requirements, ease of use, and consumables used/waste generated were assessed from observations by Battelle and EPA field testing staff.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit of the field operations and the laboratory analysis of reference method samples and a data quality audit 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 available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following is a description of the Applikon MARGA, based on information provided by the vendor: The MARGA ADI 2080 is an on-line analyzer for semi-continuous measurement of gases and soluble ions in aerosols. The MARGA utilizes a Wet Rotating Denuder (WRD) to collect acid gases and ammonia by diffusion into an aqueous film. Particles pass through the WRD and are collected in a Steam Jet Aerosol Collector (SJAC). Within the SJAC, a supersaturated environment is created which grows particles by a process known as deliquescence, allowing them subsequently to be collected by inertial separation. As cooling takes place, steam condenses and washes the collected particles into an aqueous sample stream. The aqueous solutions from the WRD and SJAC are subsequently analyzed by ion chromatography (IC) for soluble anions and cations. Software integrated within the MARGA calculates atmospheric concentrations based on air sample flow rate and the ion concentrations in the collected solutions.

VERIFICATION RESULTS

Table VS-1 summarizes the results of the MARGA verification. A bolded entry in Table VS-1 indicates that the CASTNET performance goal was met. Table VS-1 shows that the great majority of performance goals were met by both MARGA units, with the regression slopes for HNO₃ and NO₃⁻, and the MARPD accuracy for NO₃⁻, being the key exceptions.

Table VS-1. Summary of Verification Results for the MARGA ADI 2080

Parameter	Comparison	Results				
		Analyte	MARGA 1		MARGA 2	
	Slope		Intercept (µg/m ³)	Slope	Intercept (µg/m ³)	
Accuracy	Regression analysis comparison to reference samples	SO ₂	1.16	0.16	1.08	0.13
		HNO ₃	0.780	0.35	0.596	0.28
		NH ₃	0.930	-0.14	0.987	-0.08
		SO ₄ ²⁻	1.02	0.30	0.986	0.22
		NO ₃ ⁻	2.48	-0.15	1.73	-0.05
		NH ₄ ⁺	1.02	-0.23	0.993	-0.25
		SO ₂ ^a	0.962	0.50	0.890	0.44
Accuracy	Calculation of MARPD between MARGA results and reference method results		MARPD			
				MARGA 1	MARGA 2	
		SO ₂		31.2%	18.9%	
		HNO ₃		34.1%	25.8%	
		NH ₃		33.1%	18.2%	
		SO ₄ ²⁻		17.3%	9.1%	
		NO ₃ ⁻		86.9%	58.7%	
NH ₄ ⁺		19.2%	25.3%			
SO ₂ ^a		19.8%	14.1%			

^a Comparison to continuous FEM analyzer (1 hr data), all other comparisons relative to 12-hr denuder/filter pack.

Table VS-1. (Continued)

Parameter	Comparison	Results				
Precision	Comparison of results from duplicate monitoring systems	Analyte			1-Hour MARPD	
		SO ₂			10.4%	
		HNO ₃			24.8%	
		NH ₃			22.4%	
		SO ₄ ²⁻			6.5%	
		NO ₃ ⁻			27.3%	
NH ₄ ⁺			6.3%			
Precision	Comparison of MARPD of 12-hour average MARGA data and 95 th percentile of pooled RPD results from reference measurements (RPD ₉₅)	Analyte	Ref. Method RPD₉₅	MARGA 12-Hour MARPD		
		SO ₂	20.5%	8.7%		
		HNO ₃	29.9%	26.5%		
		NH ₃	40.7%	18.8%		
		SO ₄ ²⁻	11.4%	6.8%		
		NO ₃ ⁻	59.9%	23.9%		
NH ₄ ⁺		13.0%	6.5%			
Data completeness	Ratio of number of hourly data points successfully collected to number of potential hourly data points that could have been collected	Analyte	% of Valid Data		Average % of Valid Data per Reference Sampling Period (e.g., per 12 hours)	
			MARGA 1	MARGA 2	MARGA 1	MARGA 2
		SO ₂	99.3%	96.3%	99.4%	96.3%
		HNO ₃	99.3%	96.3%	99.4%	96.5%
		NH ₃	99.3%	96.3%	99.4%	96.3%
		SO ₄ ²⁻	99.3%	96.1%	99.4%	96.1%
		NO ₃ ⁻	99.3%	96.1%	99.4%	96.1%
		NH ₄ ⁺	99.3%	96.3%	99.4%	96.3%
		Na ⁺	99.3%	96.3%	99.2%	96.5%
		Ca ²⁺	99.4%	96.3%	99.2%	96.8%
Cl ⁻	99.3%	96.1%	-- ^b	-- ^b		
Reliability	Percentage of time in operating mode	MARGA 1: 99.4% MARGA 2: 96.8%				
Reliability	Time to start-up after power interruption	MARGA 1: < 1 hour MARGA 2: Not tested				
Reliability	Number of site visits per week	MARGA 1: Approximately one MARGA 2: Approximately one				

^b Not applicable; Cl⁻ was never detected in both reference method samples for a given sampling period.

Table VS-1. (Continued)

Parameter	Comparison	Results
Ease of use	Operator observations	Installation of two MARGA units completed in a few days Full operational readiness of two units required extensive effort, including correction of apparent bacterial contamination Routine operations of the instrument were easy with the only regularly scheduled tasks being solution preparation and changing, and filter replacement
Maintenance	Operator observations	Routine maintenance consisted of preparing and changing/refilling solutions and replacement of particle filters Non-routine maintenance included SJAC pump motor replacement, and cleaning of sample inlets.
Consumables/waste generated	Operator observations	Cation and anion eluents, absorbing solution, suppressor regenerant, and internal standard periodically refilled Internal filters replaced weekly Approximately 31 liters of waste solutions generated weekly by each MARGA unit

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