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Environmental Technology Verification Report

Applikon MARGA Semi-Continuous Ambient Air Monitoring System

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The Business of Innovation

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ETV Advanced Monitoring Systems Center

APPLIKON MARGA SEMI-CONTINUOUS AMBIENT AIR MONITORING SYSTEM

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Foreword

The EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

AC	automated colorimetry
ADS	annular denuder system
AMS	Advanced Monitoring Systems Center
ARPD	absolute relative percent difference
CAMD	Clean Air Markets Division (U.S. EPA)
CASTNET	Clean Air Status and Trends Network
CV	coefficient of variation
DL	detection limit
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FEM	Federal Equivalent Method
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectroscopy
IPC	Industrial PC
MARGA	Monitor for Aerosols and Gases in Ambient Air
MARPD	median absolute relative percent difference
NIST	National Institute of Science and Technology
PE	performance evaluation
ppbv	parts per billion (by volume in air)
QA	quality assurance
QC	quality control
QMP	quality management plan
RPD	relative percent difference
RPD_{95}	95th percentile of pooled relative percent difference results
RTP	Research Triangle Park
SJAC	steam jet aerosol collector
TSA	technical systems audit
WRD	wet rotating denuder

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative 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.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of 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 and quality control (QA/QC) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Risk Management Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the Applikon Analytical BV (Applikon) Monitor for Aerosols and Gases in Ambient Air ADI 2080 (MARGA) semi-continuous ambient air monitoring system at an EPA ambient air quality monitoring site in Research Triangle Park (RTP), North Carolina. Semi-continuous ambient air monitoring systems were identified as a priority technology category for verification through the AMS Center stakeholder process.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This report provides results for the verification testing of Applikon BV's MARGA semi-continuous ambient air monitoring system. The following is a description of the MARGA, based on information provided by the vendor. The information provided below was not verified in this test.

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.

The MARGA ADI 2080 consists of:

- Sampling box,
- Analytical box,
- Industrial PC (IPC) with keyboard/mouse and screen,
- ADI 2080 ambient air monitor software,
- Programmable logic control input/output modules, and software,
- Applikon pump modules and stainless steel analyzer cabinet,
- Polypropylene rack with steel inner body,
- Uninterruptable power supply,
- Air pump with mass flow controller.

The MARGA ADI 2080 is constructed with the sampling box located above the analytical box. Air is drawn through the sampling system in the upper box where inorganic gases and aerosols are absorbed and collected into separate aqueous solutions. In the analytical box, the inorganic compounds in the gases and aerosols are determined by IC.

The analytical box also contains an IPC running instrument software that controls all elements of the sampling and analysis. The IPC is equipped with a fold-up liquid crystal display as well as a keyboard with mouse. The MARGA software running on the IPC controls the instrument and provides a user interface. In addition, the analyzer can be checked and controlled remotely via an internet or modem connection. Figure 2-1 shows pictures of the sampling and analytical boxes of the MARGA ADI 2080.

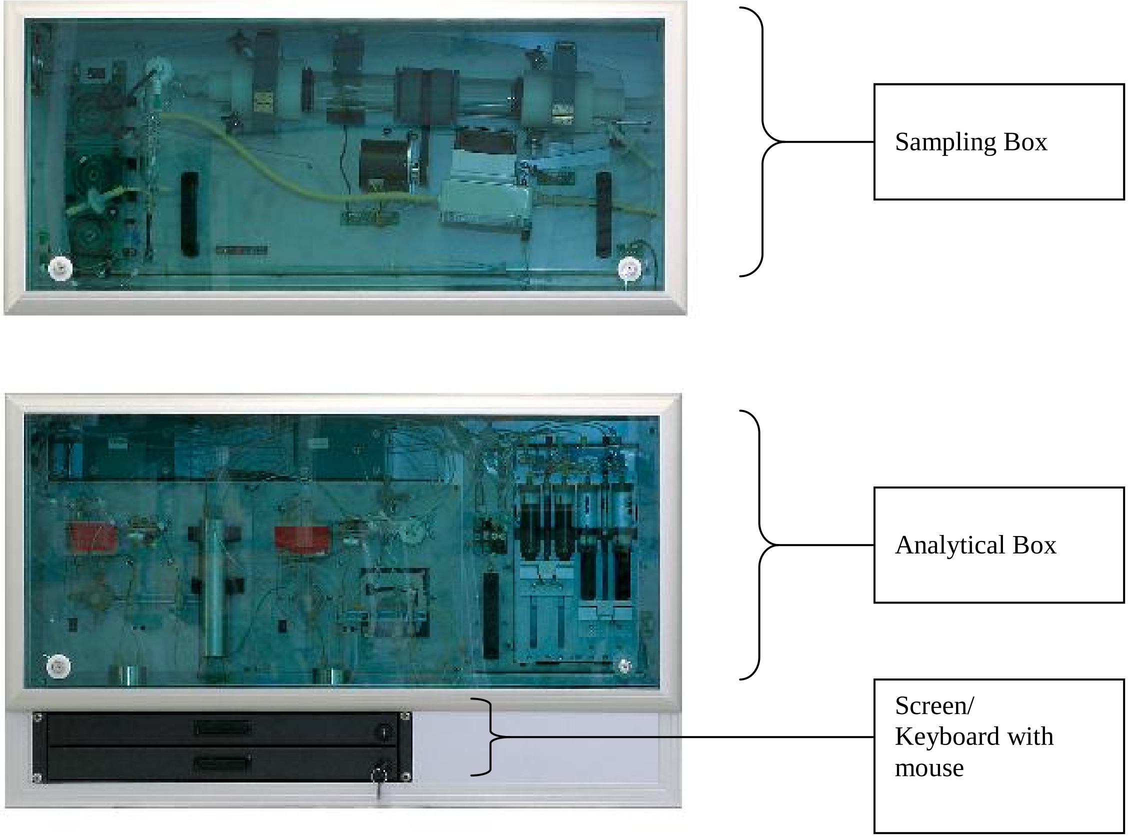

Figure 2-1. MARGA ADI 2080 Sampling and Analytical Boxes

Chapter 3
Test Design and Procedures

3.1 Introduction

EPA's Clean Air Status and Trends Network (CASTNET) is a regional long-term environmental monitoring program, established in 1991 under the Clean Air Act Amendments, which is administered and operated by EPA's Clean Air Markets Division (CAMD). Currently 86 operational CASTNET sites are located in or near rural areas and sensitive ecosystems, to collect data on ambient levels of pollutants where urban influences are minimal. As part of an interagency agreement, the National Park Service sponsors 27 sites which are located in national parks and other Class-I areas designated as deserving special protection from air pollution.

Throughout CASTNET, measurements are made to characterize the ambient concentrations of the following species:

- Sulfur dioxide (SO_2)
- Particulate sulfate (SO_4^{-2})
- Nitric acid (HNO_3)
- Particulate nitrate (NO^{-3})
- Particulate ammonium (NH_4^+)
- Particulate calcium (Ca^{2+})
- Particulate sodium (Na^+)
- Particulate magnesium (Mg^{2+})
- Particulate potassium (K^+)
- Particulate chloride (Cl^-)
- Ozone (O_3)

For all but ozone, ambient air sampling of particles and selected gases is performed by drawing air at a controlled flow rate through open face, three-stage filter packs that use four sequential filters (Teflon®, Nylon®, and dual Whatman® filters impregnated with potassium carbonate). The filter packs are located at 10 meters above the ground surface and accessed using a tilt-down aluminum tower. The filter packs are exchanged every week by a site operator and the exposed filter packs are shipped to a central analytical laboratory for analysis. Although the filter pack approach is simple to use, reliable, inexpensive, and provides sensitive measurements, it suffers from long sampling duration (7-day integrated average) and is subject to bias and uncertainties in species of interest such as gaseous HNO_3 and particle nitrate (NO_3^-) due to reactivity and volatilization issues.[1-3] In addition, due to the time required for chemical analysis and reporting, preliminary concentration data from a CASTNET site are typically not available until 4-6 months after the sample collection date.

Recent advancements in ambient air monitoring instrumentation now provide the capability to observe operating status remotely and to allow real-time or near real-time (within 24 hours) access to monitoring data. The advantages of routine operation of such systems include a more timely data stream and improved air quality assessment capability. Real-time, multi-pollutant monitoring in rural areas will help the EPA better characterize the extent of regional transport of pollutants (i.e., particulate matter and gaseous precursors), provide improved regional dry deposition estimates, and help in both the development and validation of air quality models.

This verification test was conducted according to amended procedures specified in the ETV *Test/QA Plan for Verification of Semi-Continuous Ambient Air Monitoring Systems.*[4] Amendments to this test/QA plan are described in Section 4.1 of this report. The purpose of this verification test was to generate performance data on semi-continuous ambient air monitoring technologies so organizations and users interested in installing and operating these systems can make informed decisions about their potential benefit. The test was conducted over a period of 30 days and involved the continuous operation of duplicate MARGA units at an existing ambient air monitoring site located on the EPA campus in RTP. The accuracy of the MARGA was determined 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 overall sampling times and help minimize measurement bias and uncertainties, while still meeting the data quality objectives of this verification test. The precision of the MARGA was determined from comparisons of paired data from the duplicate units, and through comparisons to pooled results of the reference methods. Other performance parameters such as data completeness, maintenance requirements, ease of use, and operational costs were assessed from observations by the Battelle or EPA field testing staff. This test was not intended to simulate long-term (e.g., multi-year) performance of semi-continuous monitoring technologies at a monitoring site. As such, performance and maintenance issues associated with long-term use of the MARGA are not addressed in this report.

The MARGA was verified by evaluating the following parameters:

- Accuracy as compared to reference measurements
- Precision between duplicate units
- Data completeness
- Reliability
- Operational factors such as ease of use, maintenance and data output needs, power and other consumables use, and operational costs.

The MARGA was previously verified in a separate test conducted at the Burdens Creek Air Monitoring Site in RTP, NC from October 1 to 31, 2008. The results of that verification test are available at http://www.epa.gov/nrmrl/std/etv/pubs/600r09083.pdf. The subject of this report is a second field test of the MARGA that was conducted in the autumn of 2010 at an ambient air monitoring site on EPA's campus in RTP, NC. That site is located within approximately 200 m of the Burdens Creek site used for the 2008 test. In contrast to the first field test in which the monitoring systems were operated and maintained by the vendor throughout the field period, during this field test two MARGA units were operated by EPA staff.

Consistent with the CASTNET performance requirements specified in the test/QA plan[4] and listed in Appendix A of this report, MARGA performance was verified for measurement of SO_2, HNO_3, and NH_3 in the gas phase and NO_3^-, SO_4^{2-}, and NH_4^+ in the particle phase, and data completeness was also evaluated for Cl^-, Ca^{2+}, and Na^+ in the particle phase.

3.2 Test Procedures

During testing, duplicate MARGA units were installed inside an environmentally controlled instrument trailer at the EPA ambient air monitoring site. The two MARGA units operated continuously over the 30-day testing period, and were operated and maintained by EPA staff after training by the vendor. Maintenance performed on the MARGA units was conducted and documented by EPA staff, and is reported in Section 6.5 of this report. Hourly measurements for all analytes were reported by the two MARGA units, stored by the MARGA software, and subsequently provided to Battelle.

Annular Denuder Systems (ADS) based on Compendium Method IO-4.2[5] were used as the reference comparison method and consisted of a sodium carbonate (Na_2CO_3) coated denuder and phosphorous acid (H_3PO_3) coated denuder in series for the collection of acid and base gases, respectively, followed by a Teflon filter for the collection of particulate matter, a nylon filter for the collection of volatilized particulate nitrate, and a citric acid coated cellulose filter for the collection of volatilized particulate ammonium. The denuder/filter pack samplers were installed on the roof of the trailer housing the MARGA units being tested and collected ambient air samples at a flow rate of 10 liters per minute (L/min). Figure 3-1 shows the sampling trailer with denuders and filter pack samplers set up on the roof. Figure 3-2 shows a closer view of the duplicate denuder/filter pack samplers installed on the trailer roof, and Figure 3-3 shows a denuder/filter pack train installed inside one of the samplers. During operation, ambient air entered through an inlet cyclone with a 2.5 micron cut point and was drawn upward through the denuder/filter pack train. Heaters and a circulating fan were used to provide a small degree of temperature regulation inside each sampler housing to avoid extreme temperature conditions.

Figure 3-1. Sampling trailer with denuder/filter pack samplers.

Figure 3-2. Denuder/filter pack samplers.

Figure 3-3. Installed denuder/filter pack sampling train.

The denuders and filter packs, including field blanks, were prepared by MACTEC Engineering and Consulting (MACTEC) in their Gainesville, FL facilities and shipped by MACTEC to a Battelle staff member in RTP. At the field site, the sampling media were stored at room temperature in their original shipping containers until used for sampling. Prior to use, the denuders and assembled filter packs were sealed or capped, to prevent contamination. Specific sample handling procedures were implemented to avoid contamination of the denuder/filter pack components during assembly of the sampling trains and changeout of sampling media. Clean lint-free gloves were used when handling the denuder/filter pack components. Special care was taken to avoid breathing on components of the denuder/filter pack reference samples, to minimize ammonia contamination.

All denuder/filter pack samples were collected by Battelle staff, who were trained in assembly and sampling of the denuder/filter pack trains by MACTEC staff. After sampling, the denuder/filter pack trains were retrieved, disassembled on-site, sealed, and stored under refrigeration until return express shipment to MACTEC’s analytical laboratory for extraction and analysis. Each shipping container held enough sampling media for approximately two days of sampling, so three to four overnight return sample shipments to MACTEC were made each week. Collected samples were not shipped over the weekend, to avoid delays. Freezer packs were included in the return shipments to maintain all collected sampling media cold until receipt at the analytical laboratory.

At MACTEC's analytical laboratory, the filters and denuders were extracted using deionized water and analyzed for target analytes. Denuder extracts were analyzed for SO_2 (as SO_4^{2-}), HNO_3 (as NO_3^-), and NH_3 (as NH_4^+). The Teflon filter extracts were analyzed for SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, and K^+. The nylon filter extracts were analyzed for NO_3^-, and the backup cellulose filter extracts were analyzed for NH_4^+. The analyte results from these filters were summed with those from the corresponding Teflon filter to determine the total particulate NO_3^- and NH_4^+, respectively. Analysis for most of the target analytes was performed by IC based on the procedures described in EPA Method 300.0.[6] Additional analysis for NH_4^+ was performed by automated colorimetry (AC) based on the procedures described in EPA Method 350.1.[7] The particulate metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) according to EPA Method 6010B.[8] Additionally, the MARGA units were collocated with a Federal Equivalent Method (FEM) continuous pulsed fluorescence analyzer for SO_2, which was operated and maintained by EPA staff, who provided the resulting SO_2 data from the testing period.

3.3 Field Site

The EPA ambient air monitoring site is located on the EPA campus in RTP and is maintained by EPA staff. The site consists of several instrument trailers and a 10-m meteorological tower installed in an open area within surrounding forested land, and is subject to restricted access at all times. A variety of routine measurements are performed at this site and it is periodically used for special studies. The MARGA units evaluated during this verification were housed in an environmentally controlled trailer, located at least 200 meters away from the nearest building. The denuder/filter pack reference method samplers were located on a platform on the roof of the trailer. Pumps for the denuder/filter packs were located in weatherproof boxes adjacent to the denuder/filter pack samplers on the trailer roof. Continuous SO_2 measurements were made by EPA using a pulsed fluorescence FEM analyzer located in a separate trailer approximately 30 meters from the trailer housing the MARGA units.

3.4 Verification Schedule

The MARGA verification field test took place from September 8 through October 8, 2010. Duplicate denuder/filter pack reference samples were collected over 12-hour sampling intervals throughout the 30-day testing period, from 7:00 am to 7:00 pm and from 7:00 pm to 7:00 am daily. Denuder/filter pack reference measurements began on September 8 at 7:00 pm and concluded on October 8 at 7:00 pm.

Duplicate MARGA units were installed by the vendor and had been operating at the site for several weeks prior to the start of the verification test. The vendor performed routine and non-routine maintenance on both units to prepare them for the start of the verification test. The continuous FEM SO_2 analyzer used to provide additional reference SO_2 measurements was also installed and operating at the site long before the start of the MARGA evaluation.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures and all verification testing were performed in accordance with test/QA plan for this verification test[4] and the quality management plan (QMP) for the AMS Center[9] except where noted below. QA/QC procedures and results are described below.

4.1 Amendments/Deviations

An amendment to the existing test/QA plan[4] for MARGA verification was established and approved prior to the verification field test. That amendment[10] updated the test/QA plan by revising the schedule, procedures, and description of roles and responsibilities to accurately present the verification effort described in this report. That amendment was distributed to all Battelle, EPA, and MACTEC personnel involved in the verification, and to Applikon, the vendor of the MARGA.

Four deviations to the test/QA plan were prepared, approved, and retained in the test documentation. Those deviations established the following modifications and corrections to the test/QA plan and the test procedures:

- Setting the reference method sampling intervals as 7:00 am to 7:00 pm and 7:00 pm to 7:00 am, rather than 6:00 am to 6:00 pm and 6:00 pm to 6:00 am, to more closely match local diurnal variations in pollutant concentrations.
- Relaxing the tolerance on the temperature of the refrigerator used to store collected reference samples in the field from the 4 (±2) °C tolerance stated in the test/QA plan, which is appropriate for a full-size laboratory-grade refrigerator but unnecessary for the sample storage in question. A storage temperature range of less than 10 °C was acceptable.
- Correcting an erroneous reference in the test/QA plan to a phosphorous acid coated denuder, instead of the cellulose final filter actually used in the reference sampler.
- Requiring documentation in the test records of training of the field testing staff. Appropriate forms were used to document training by Applikon of EPA personnel in operation of the MARGA, and training by MACTEC of Battelle personnel in operation of the reference method samplers.

4.2 Reference Methods

The following sections describe the QA/QC procedures employed in the collection and analysis of reference samples.

4.2.1 Denuder/Filter Pack Sampling

This verification test included a comparison of MARGA results to those of the denuder/filter pack reference measurements. During each week of sample collection one set of reference sampling media were reserved as field blank samples. The field blanks remained in the shipping containers and were not handled in the field, but were extracted and analyzed like normal samples in the laboratory. Table 4-1 presents a summary of the denuder/filter pack field blank analyses. With the exception of the H_3PO_3 denuder, few of the field blanks exhibited analyte levels above the detection limit, and none of the field blanks exhibited analyte levels above twice the detection limit. In the case of the H_3PO_3 denuder, all five of the field blanks were above the detection limit and four of the five field blanks exhibited levels of NH_3 above twice the detection limit. The cause of this apparent contamination was not determined, however, the average of the measured NH_3 blank values (i.e., 1.1 µg) was subtracted from all H_3PO_3 denuder results to account for the apparent contamination. This blank value was corrected by subtracting 0.15 µg/m^3 from the results.

Table 4-1. Summary of Reference Method Field Blank Analyses

Medium	Analyte	Det. Limit (µg)	# of Blank Samples	# above D.L.	Average (µg) (St. Dev.)[a]
Teflon filter	NH_4^+	0.5	5	0	--
	NO_3^-	0.2	5	0	--
	SO_4^{2-}	1	5	0	--
Nylon filter	NO_3^-	0.2	5	0	--
	SO_4^{2-}	1	5	2	1.1 (0.1)
Cellulose filter	NH_4^+	0.5	5	2	0.8 (0.3)
Na_2CO_3 denuder	NO_3^-	0.16	5	0	--
	SO_4^{2-}	0.8	5	1	1.2
H_3PO_3 denuder	NH_3	0.4	5	5	1.1 (0.4)

[a] Average of the results above the detection limit.

4.2.2 Denuder/Filter Pack Analysis

The analyses of the denuder/filter pack samples were conducted by IC based on EPA Method 300.0, by AC based on EPA Method 350.1, and by ICP-AES based on Method 6010B.

Analyses of these samples were subject to the data quality criteria of the respective methods, which included duplicate analysis of individual samples, as well as blanks and calibration check standards with every batch of samples analyzed. For each duplicate analysis the absolute relative percent difference (ARPD) between the measured results was calculated.

Table 4-2 summarizes the results of the duplicate analysis of samples for the collected components of denuder/filter pack reference samples. For these analytes, for all the sampling media, the mean and maximum ARPD values were well below the 20% acceptance criterion stated in the test/QA plan for this verification test.

Table 4-2. Results of Duplicate Analyses of Denuder/Filter Pack Reference Samples

Medium	Analyte	# of Samples	Mean ARPD	Max. ARPD
Teflon filter	NH_4^+	7	1.4%	6.6%
	NO_3^-	6	1.6%	6.7%
	SO_4^{2-}	6	0.2%	0.6%
Nylon filter	NO_3^-	6	2.9%	7.4%
	SO_4^{2-}	6	7.3%	12.5%
Cellulose filter	NH_4^+	11	2.8%	10.0%
Na_2CO_3 denuder	NO_3^-	13 (3)[a]	1.2%	2.8%
	SO_4^{2-}	13 (2)[a]	1.1%	4.3%
H_3PO_3 denuder	NH_3	10	0.7%	2.2%

[a] Number of duplicate pairs below detection limit.

4.2.3 Gas Analyzers

The SO_2 continuous FEM analyzer used for this verification test was already in operation at the test site and was included in EPA's routine QC activities at the site. Quality control activities associated with the SO_2 continuous FEM analyzer included multipoint calibrations of the analyzer, routine zero/span checks, and biweekly precision checks. No additional QC activities were implemented specifically for this verification test although documentation of the QC activities performed during testing was provided to Battelle by EPA.

4.3 Audits

Three types of audits were performed during the verification test: a performance evaluation (PE) audit of the denuder/filter pack reference method sampling and analysis, a technical systems audit (TSA) of the verification test performance, and a data quality audit. Audit procedures are described further below.

4.3.1 Performance Evaluation Audit

A PE audit of the denuder/filter pack reference method sampling procedures was performed by measuring the sample flow rate through each of the denuder/filter pack sampling systems during sampling. The flow rate was measured using a NIST-traceable flow transfer standard (BIOS DryCal, Serial No. 103777). The results of those checks are summarized in Table 4-3, and indicated that the sampler flow rates were within the target ±5% tolerance of the nominal 10 L/min flow rate.

Table 4-3. Summary of Denuder/Filter Pack Flow Rate PE Audit

Date	Reference Sampler	Measured Flow (L/min)	Difference from Nominal
9/9/10	#1	9.85	-1.5%
9/9/10	#2	9.72	-2.8%

Additionally, a PE audit of the analytical methods was performed by supplying the analytical laboratory with samples prepared from independent NIST-traceable standard solutions. Those PE samples were prepared to be within the concentration range of sample extracts resulting from the reference method field sampling. The PE samples, along with blank solutions also supplied by Battelle, were analyzed and the results are summarized in Table 4-4. The target acceptance criteria for the PE audit results were ±5% for the IC and ICP-AES results and ±10% for the AC results. In all cases, the results of the PE audit met the stated acceptance criteria.

Table 4-4. Summary of PE Audits of Analytical Methods

Analyte	Analytical Method	Standard Concentration (µg/mL)	Measured Concentration (µg/mL)	Percent Difference
NH_4^+	AC	0.80	0.801	0.1%
NH_4^+	AC	0	0.02	--
Na^+	ICP-AES	0.50	0.516	3.3%
Na^+	ICP-AES	0	0.005	--
K^+	ICP-AES	0.50	0.523	4.5%
K_+	ICP-AES	0	0.005	--
Ca_2^+	ICP-AES	0.50	0.525	5.0%
Ca_2^+	ICP-AES	0	0.003	--
Mg_2^+	ICP-AES	0.50	0.523	4.6%
Mg_2^+	ICP-AES	0	0.003	--
NO_3^-	IC	1.50	1.509	0.6%
NO_3^-	IC	0	0.008	--
SO_4^{2-}	IC	1.50	1.506	0.4%
SO_4^{2-}	IC	0	0.04	--
Cl^-	IC	1.50	1.502	0.1%
Cl^-	IC	0	0.02	--

4.3.2 Technical Systems Audit

A Battelle QA Officer performed two TSAs as part of this verification test. The first TSA was performed at the MACTEC facilities in Gainesville, FL in a reference method validation effort conducted prior to the beginning of the verification test. That TSA focused on observation of the reference method sampling and analytical laboratory QA/QC procedures in preparation for the field test. The second TSA was performed during the first week of the verification field test and focused on the sampling material handling, sample collection, and field data recording procedures. The purpose of these audits was to ensure that the verification test was being performed in accordance with the AMS Center QMP,[8] the amended test/QA plan for this verification test,[4,9] published reference methods,[5-7] and any SOPs used by the analytical laboratory. In these audits, the Battelle QA Officer observed the reference method sampling and sample recovery, compared the actual test procedures being performed to those specified or referenced the test/QA plan, reviewed data acquisition and handling procedures, inspected documentation of reference sample chain of custody; and reviewed test record books. He also conferred with the EPA and MACTEC testing staff.

As noted in Section 4.1, the test/QA plan was amended to cover changes from the first round of testing that were implemented in the second round of testing. Also as noted in Section 4.1, four deviations from the test/QA plan were identified and documented.

4.3.3 Data Quality Audit

At least 10% of the data acquired during the verification test were audited. Battelle’s Quality Manager, or designee, traced the data from the acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked. Only minor data issues were noted in the data quality audit, with no effect on the overall quality of the verification results.

4.4 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center. The results of the audits were submitted to the EPA.

4.5 Data Review

All data received from EPA for the two MARGA units and the SO_2 analyzer, and from MACTEC for the denuder/filter pack reference measurements, underwent 100% review and validation by Battelle technical staff before being used for any statistical calculations. Based on review of MARGA data files and operator logs, a small number of hourly MARGA measurements were excluded from the data analysis because of instrument malfunction or interference from maintenance activities. Those data are detailed in Section 6.5.1. All denuder/filter pack and continuous SO_2 reference data were found to be valid and were included in the data analysis.

Records generated in the verification test received a one-over-one review before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.1 are presented in this chapter. Consistent with the test/QA plan[4] and the CASTNET performance requirements (Appendix A), before any statistical comparisons were made the MARGA detection limit for each analyte was estimated based on instrument operating conditions and review of QC data. The MARGA detection limits for the target analytes (in $\mu g/m^3$) were SO_2, 0.04; HNO_3, 0.10; NH_3, 0.05; SO_4^{2-}, 0.06; NO_3^-, 0.10; and NH_4^+, 0.05. In some cases the MARGA reported a zero value for a target analyte when no peak was reported for the analyte in the IC analysis. When a zero value had an associated validation indicator of V (valid) or U (uncertain, indicating the internal standard was > 5% out of expected range), the zero value was replaced with one-half of the respective detection limit. In the few cases when a zero value had an associated validation indicator of I (invalid) the data point was excluded from the data analysis.

For comparison of hourly data between the two MARGA units (Section 5.2), individual hourly MARGA values below twice the analyte detection limit were excluded before data comparison. However, in calculating 12-hour MARGA averages for comparison to the denuder/filter pack reference method results, all hourly MARGA data (including half-detection-limit values assigned as described above) were included in the MARGA averages. There were usually 12 hours, and always at least seven hours, of MARGA data for any analyte in any 12-hour averaging period.

5.1 Accuracy

The accuracy of the MARGA units was evaluated in two ways (i.e., linear regression, and calculation of the median ARPD (MARPD) relative to the reference data) for each of the target analytes (SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+).

5.1.1 Regression Analysis

Accuracy was determined from a linear least squares regression analysis of the measured concentrations of the target analytes determined from the MARGA units and the corresponding reference methods. For comparison to the denuder/filter pack reference samples, average concentrations from each of the two MARGA units were determined separately for each of the 12-hour sampling periods during the testing period, by averaging the 1-hour MARGA results over the corresponding sampling periods. For each of the two MARGA units, these averages were plotted separately against the mean of the corresponding duplicate reference method measurements. The slope and intercept of these plots were determined from a linear regression analysis and are reported independently for each of the two units, and for each target analyte. For comparison to the continuous reference measurements of SO_2, 1-hour average concentration readings from each MARGA unit were plotted against the corresponding 1-hour average reference measurements. Again, the slope and intercept of these plots were determined from a linear regression analysis and are reported independently for each of the duplicate monitoring systems. Consistent with CASTNET requirements (Appendix A), for both regression analyses (i.e., with 12-hour denuder/filter pack and 1-hour continuous SO_2 reference data), any reference values below twice the respective MARGA detection limit were excluded from the analysis.

5.1.2 MARPD Analysis

The accuracy of each MARGA unit relative to the denuder/filter reference method was calculated as the MARPD of the results determined using Equation 1:

$$ARPD = \left| \frac{C_i - \overline{C(ref)_i}}{\overline{C(ref)_i}} \right| \cdot 100 \qquad (1)$$

where C_i and $\overline{C(ref)_i}$ are the average target analyte concentration measured by a MARGA unit and the mean of the analyte concentrations measured by the duplicate reference method samples, respectively, for the i^{th} reference sampling period. The same equation was used to determine the MARPD for the comparison of MARGA and reference hourly SO_2 data, with the hourly reference SO_2 value taking the place of the $\overline{C(ref)_i}$ value.

The MARPD analysis of the MARGA units was based on the same data sets used for the regression analysis (Section 5.1.1.), i.e., including all sampling periods for which concentrations determined by the relevant reference method were greater than twice the MARGA detection limit.

5.2 Precision

The precision of the MARGA units was evaluated in two ways (i.e., as the MARPD of paired hourly results from the duplicate MARGA units, and by comparison of the MARPD of paired 12-hour average MARGA results to the MARPD of the paired denuder/filter reference method results) for each of the target analytes (SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+). Consistent with CASTNET requirements (Appendix A), for this comparison any data below twice the respective MARGA detection limit were excluded from the analysis.

5.2.1 Comparison of Paired Results

The MARPD between the paired measurements from the duplicate MARGA units was calculated as the median value of the ARPD values determined using Equation 2:

$$ARPD = \frac{\left|C(1)_i - C(2)_i\right|}{[C(1)_i + C(2)_i]/2} \cdot 100 \qquad (2)$$

where $C(1)_i$ and $C(2)_i$ are the target analyte concentration measured by the first and second of the two MARGA units. This equation was used to calculate MARPD for both the paired MARGA hourly data and the paired MARGA 12-hour average data. Precision was assessed independently for each target analyte.

5.2.2 Comparison to Pooled Reference Method Results

Precision was also assessed through comparisons of the MARGA MARPD determined by Equation 2 to the 95th percentile of the pooled relative percent difference of the duplicate reference method measurements. Precision was assessed independently for each target analyte.

5.3 Data Completeness

Data completeness was assessed in two ways, based on the overall data return achieved by each MARGA unit during the testing period. For each of the duplicate MARGA units, this calculation used the total hours of data reported as valid by the unit and available within 24 hours, divided by the total possible hours of data in the entire 30-day field period (i.e., 720 hours). Also, data completeness was assessed based on the number of hours of data reported as valid by the unit within each 12-hour reference method sampling period. The performance goals for both of these measures of data completeness were $\geq$ 80%. The causes of any substantial incompleteness of data return were established from operator observations and MARGA diagnostics, and noted in the discussion of data completeness results.

5.4 Reliability

Instrument reliability was assessed in two ways. Firstly, reliability was assessed in terms of the percentage of time that each MARGA unit operated in measurement mode over the duration of the test period. This assessment is reported independently for the two duplicate MARGA units. Additionally, reliability was assessed in terms of the ability of the MARGA to perform a controlled shutdown in the case of a power failure, followed by an automated return to measurement mode within 4 hours after power has been restored. For this assessment, the testing staff imposed an abrupt power outage at the test site and monitored the performance of one of the MARGA units during and after the power outage. That shutdown test was conducted on October 28, i.e., after completion of the 30-day period of reference method sampling, to avoid jeopardizing MARGA performance during the test.

5.5 Operational Factors

Operational factors including ease of installation, ease of use, extent of operator attention, routine and non-routine maintenance, data output, consumables use, and waste generation were evaluated based on observations recorded by the EPA operators of the MARGA units, and explained by the vendor as needed. Both a laboratory record book and an electronic log were maintained at the test site, and were used to enter daily observations on these factors. Examples of information recorded in the record book include the daily status of diagnostic indicators for the MARGAs; use or replacement of any consumables; the effort or cost associated with maintenance, inlet cleaning, or repair; the duration and causes of any down time or data acquisition failure; and observations about ease of use of the MARGA units.

Chapter 6
Test Results

Figures 6-1 through 6-6 show time sequence plots of the duplicate MARGA data recorded during the verification testing period for SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+, respectively. For comparison the mean denuder/filter pack reference method results for the respective sampling periods are also presented in these figures. Note that the reference method results for NH_3 have been corrected by subtraction of the 0.15 µg/m^3 blank value noted in Section 4.2.1. Figure 6-7 shows the SO_2 data from the two MARGA units along with the SO_2 data from the continuous FEM analyzer at the field site.

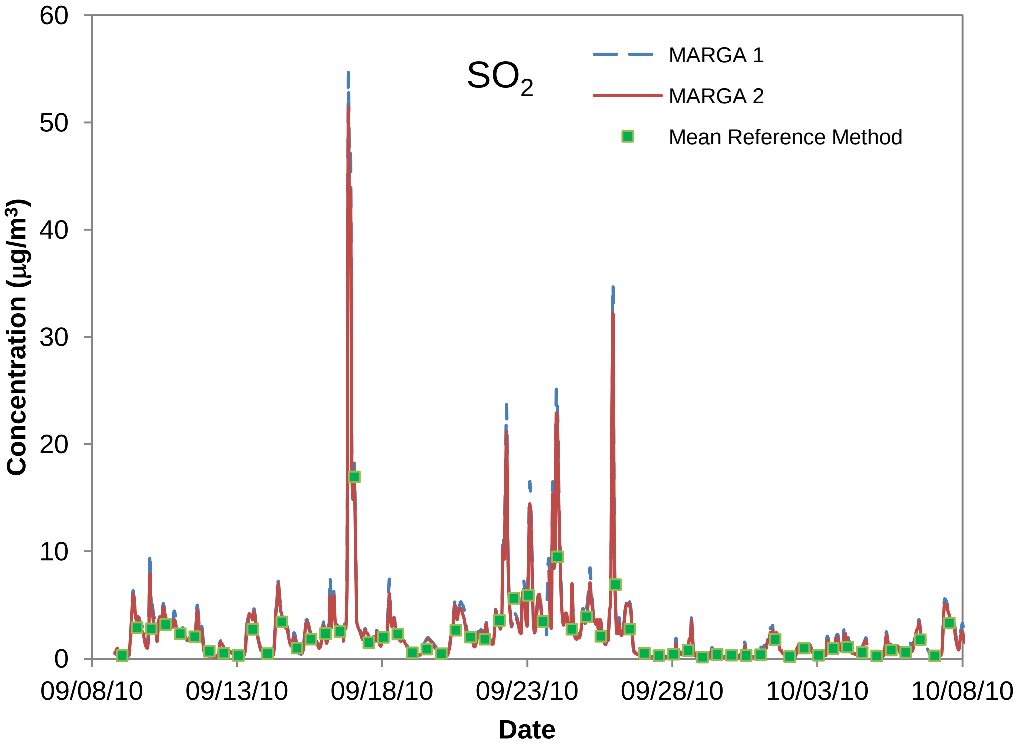

Figure 6-1. Time sequence plot of SO_2 measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

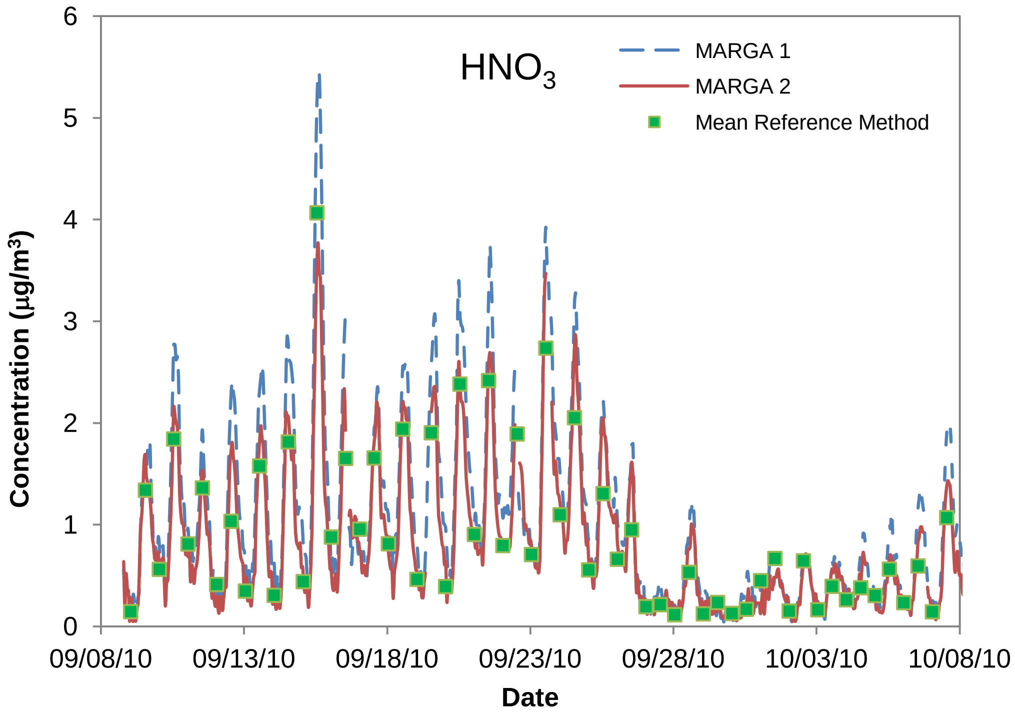

Figure 6-2. Time sequence plot of HNO_3 measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

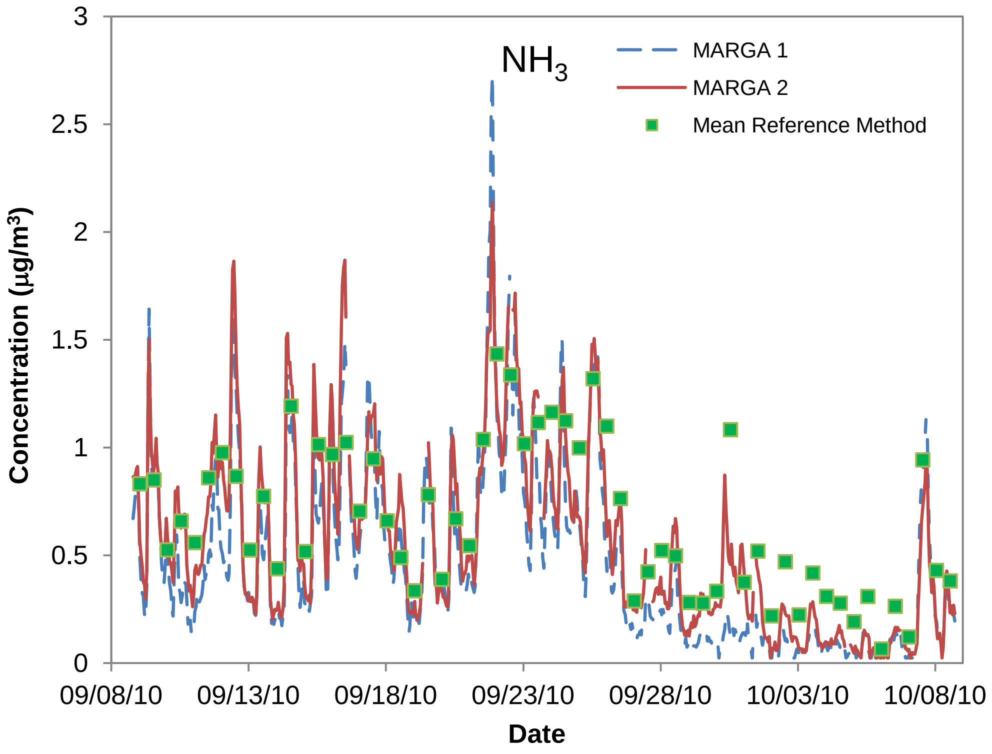

Figure 6-3. Time sequence plot of NH_3 measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

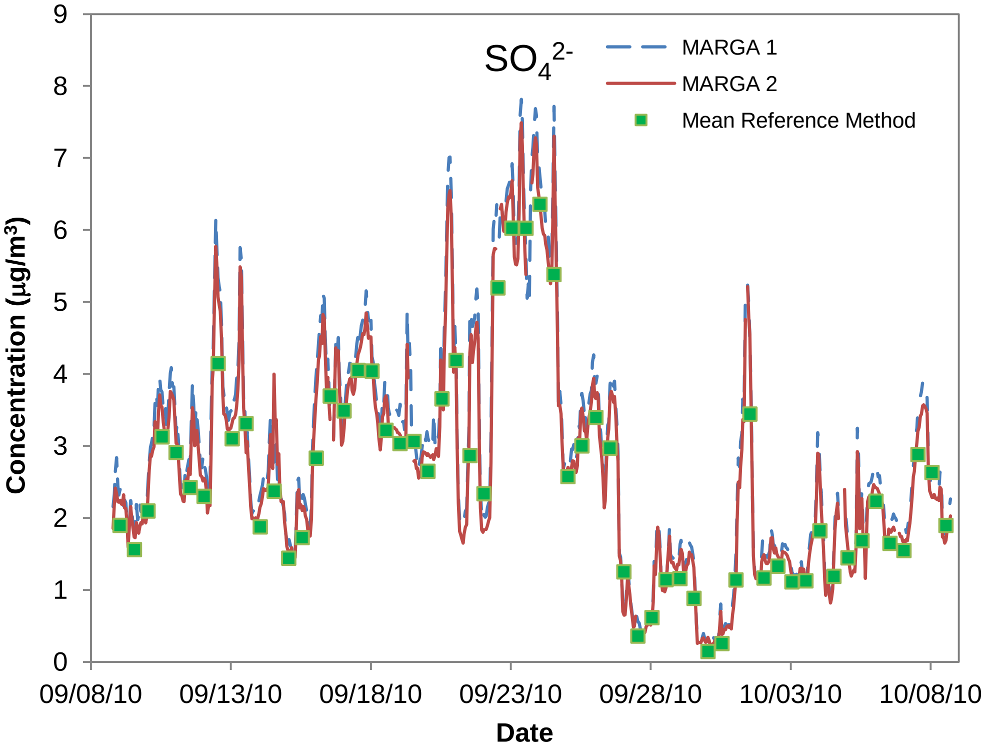

Figure 6-4. Time sequence plot of SO_4^{2-} measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

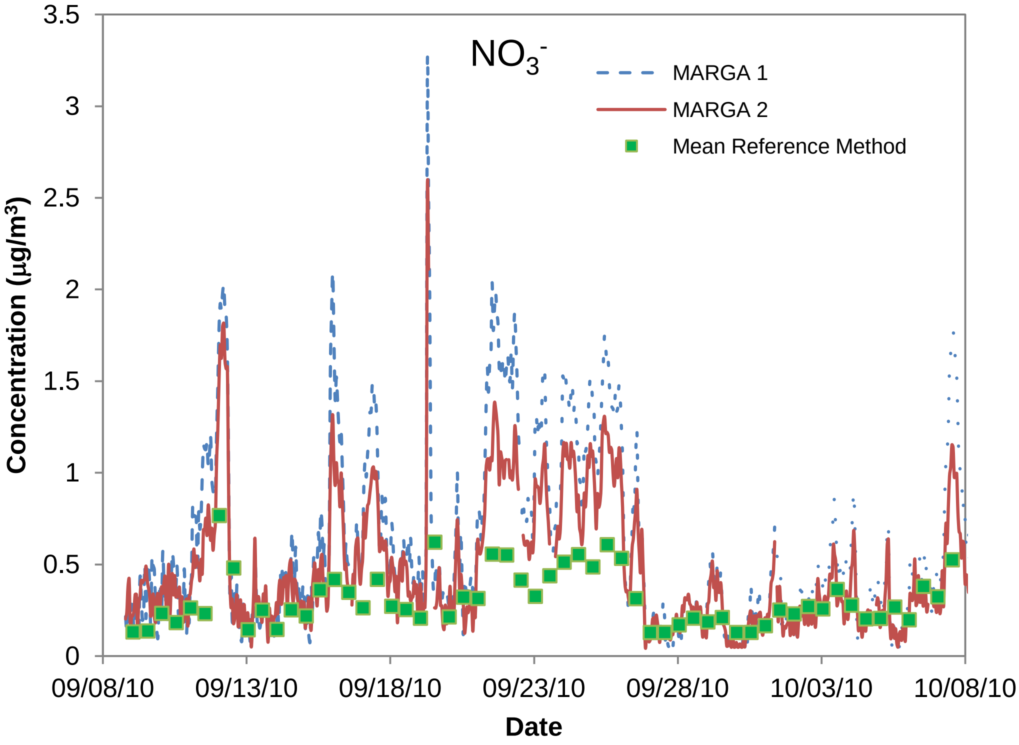

Figure 6-5. Time sequence plot of NO_3^- measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

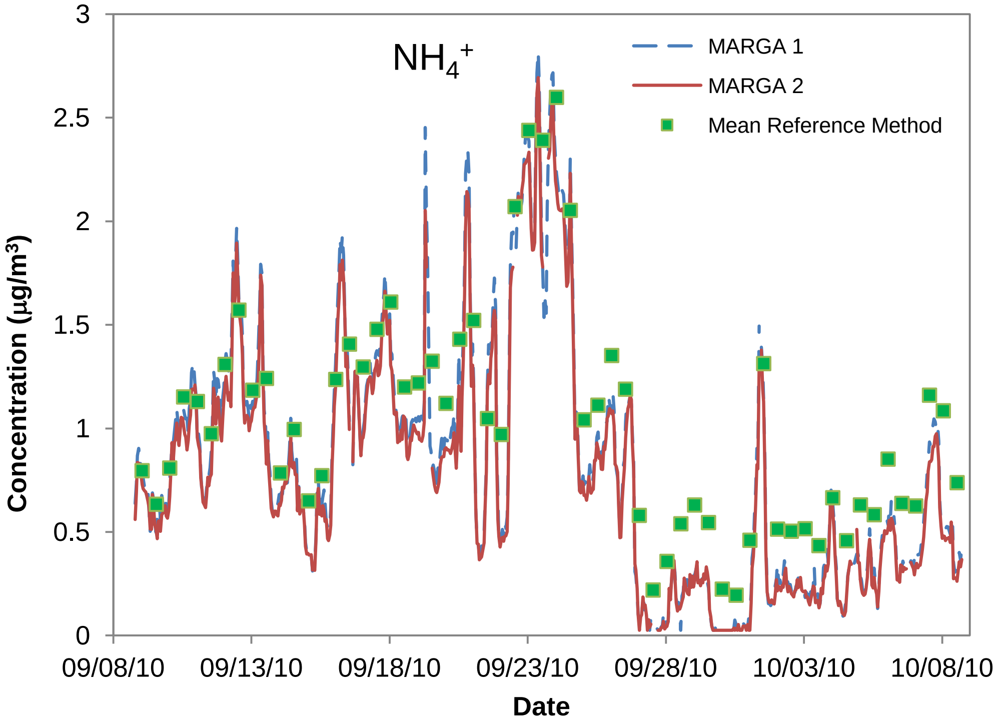

Figure 6-6. Time sequence plot of NH_4^+ measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

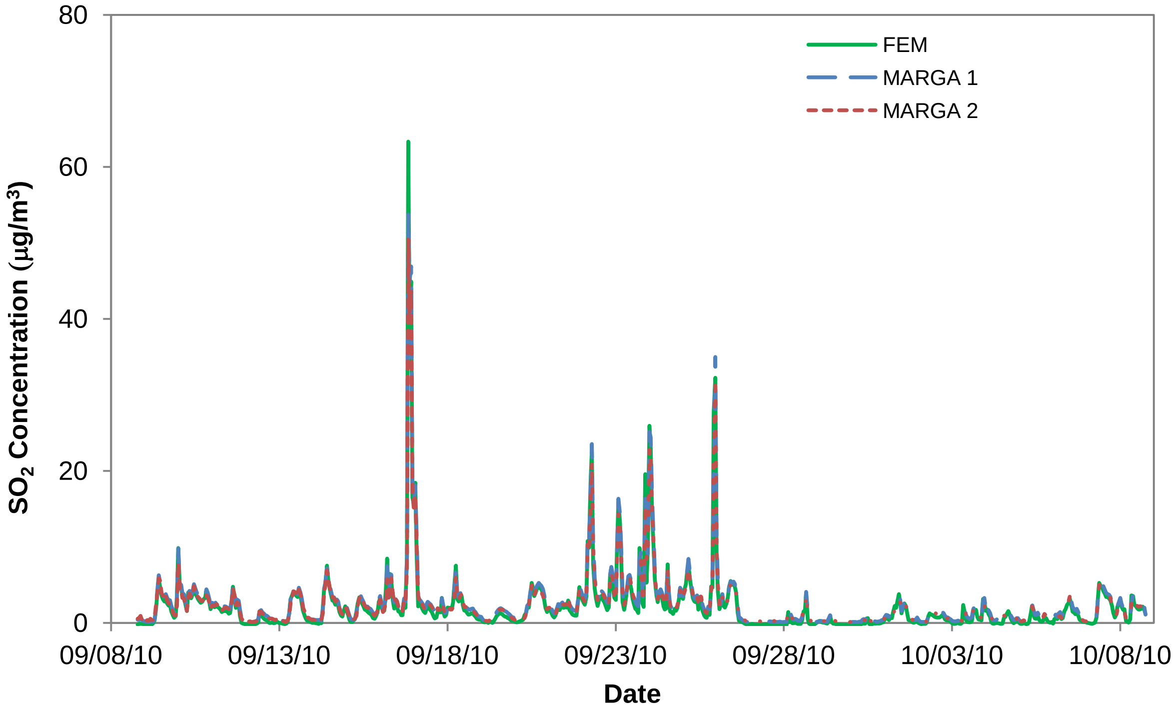

Figure 6-7. Time sequence plot of hourly SO_2 measurement results from duplicate MARGA and continuous SO_2 FEM measurements.

Figure 6-8 shows linear regression plots comparing the duplicate denuder/filter pack reference results for each of the target analytes. Close agreement of the results from the duplicate reference method sampling trains for all analytes is evident from Figure 6-8.The results of the verification tests of the MARGA semi-continuous ambient air monitoring system are presented below for each of the performance parameters.

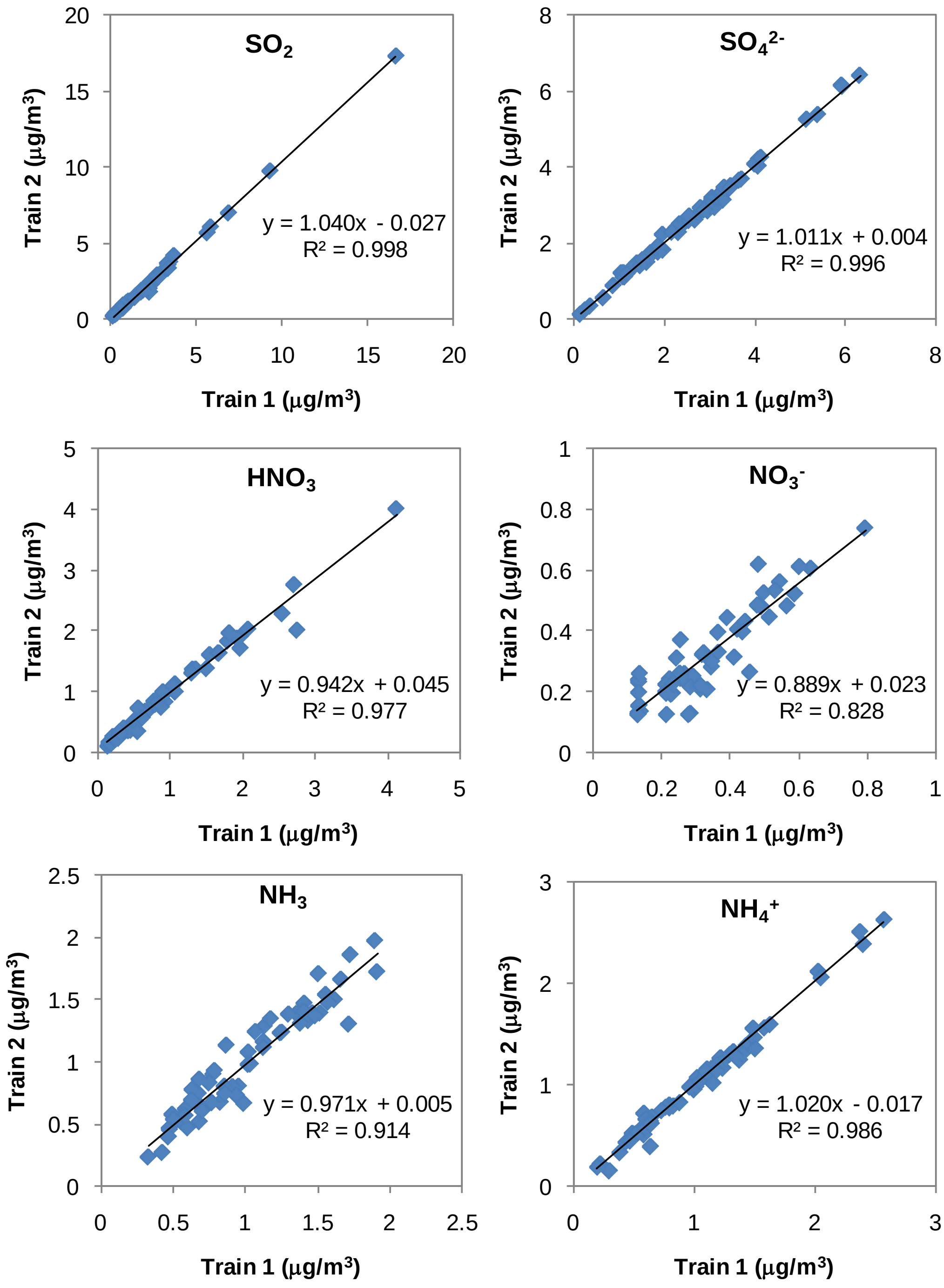

Figure 6-8. Regression Plots of Data from Duplicate Reference Method Sampling Trains for Target Analytes.

6.1 Accuracy

The accuracy of the MARGA units was determined in two ways. Firstly, accuracy was determined from a linear least squares regression analysis of the measured concentrations of the target analytes determined by the MARGA units and by the corresponding reference methods as described in Section 5.1.1. Also, accuracy was determined from the MARPD of the differences between the MARGA data and the mean of the reference method data, as described in Section 5.1.2. The results of these analyses are presented below.

6.1.1 Regression Analysis

Figure 6-9 shows regression plots of the results from the duplicate MARGA units versus the mean denuder/filter pack reference results for each of the target analytes. Figure 6-10 shows a corresponding regression plot of the hourly MARGA SO_2 results against the continuous FEM SO_2 results.

Table 6-1 presents a summary of the linear regression analysis of these data for each target analyte. The CASTNET performance goals for semi-continuous ambient air monitoring systems (Appendix A) include that the slope of the regression analysis be between 0.80 and 1.20, and that the intercept be between -10 ppb and + 10 ppb for each analyte. Table 6-2 summarizes the performance of the duplicate MARGA units relative to these goals for each target analyte (each check mark indicating a goal was met). (Note that the intercept values in Table 6-1 were converted to ppb from µg/m^3 for comparison to the CASTNET intercept performance goal.) Tables 6-1 and 6-2 show that the CASTNET regression goals were met except for the HNO_3 and NO_3^- slopes with both MARGA units. The HNO_3 slopes were below 0.8 with both units, and the NO_3^- slopes were above 1.2 with both units.

Table 6-1. Summary of Regression Analysis Results for the MARGA Units

Target Analyte	MARGA 1			MARGA 2		
	Slope	**Intercept µg/m^3**	**r^2**	**Slope**	**Intercept µg/m^3**	**r^2**
SO_2	1.16	0.16	0.994	1.08	0.13	0.990
HNO_3	0.780	0.35	0.884	0.596	0.28	0.883
NH_3	0.930	-0.14	0.732	0.987	-0.08	0.803
SO_4^{2-}	1.02	0.30	0.995	0.986	0.22	0.994
NO_3^-	2.48	-0.15	0.774	1.73	-0.05	0.786
NH_4^+	1.02	-0.23	0.959	0.993	-0.25	0.958
SO_2[a]	0.962	0.50	0.979	0.890	0.44	0.982

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

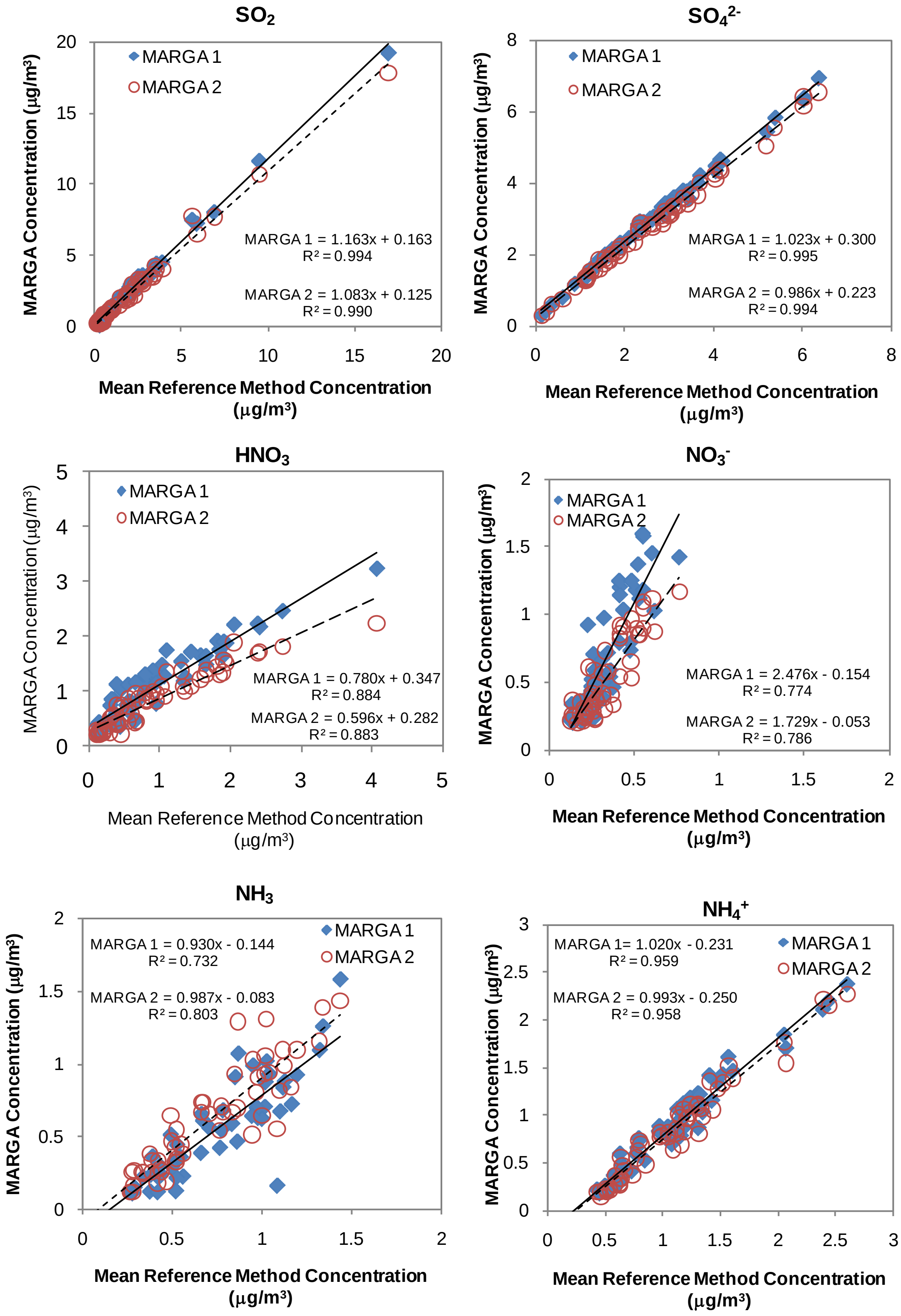

Figure 6-9. Regression plots of MARGA data versus mean denuder/filter reference method data for SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+.

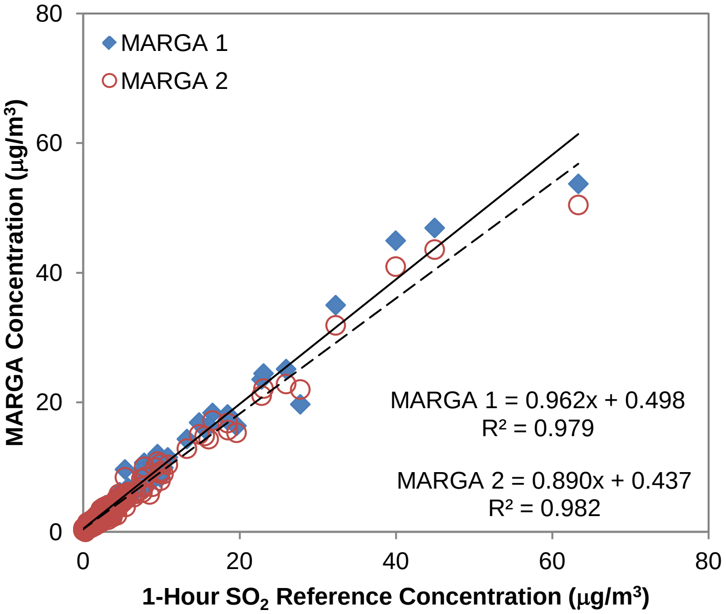

Figure 6-10. Regression plots of hourly MARGA data versus hourly FEM data for SO_2

Table 6-2. MARGA Regression Analysis Results versus CASTNET Performance Goals

Target Analyte	MARGA 1		MARGA 2	
	Slope	Intercept	Slope	Intercept
SO_2	✓	✓	✓	✓
HNO_3		✓		✓
NH_3	✓	✓	✓	✓
SO_4^{2-}	✓	✓	✓	✓
NO_3^-		✓		✓
NH_4^+	✓	✓	✓	✓
SO_2[a]	✓	✓	✓	✓

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

6.1.2 MARPD Analysis

Table 6-3 presents a summary of the calculated MARPD results and indicates whether the results meet the CASTNET performance goals for each target analyte for each of the duplicate MARGA units. The MARPD results of the paired denuder/filter pack reference data for each analyte are also included in Table 6-3 to show the precision of the reference data. In all cases, the duplicate reference method measurements easily met the CASTNET precision goal of MARPD ≤ 25%, confirming that the reference measurements provide a sound basis for comparison to the MARPD of the MARGA units. Both MARGA units met the CASTNET accuracy goal of ≤ 40% MARPD for SO_2, HNO_3, NH_3, SO_4^{2-}, and NH_4^+, but not for NO_3^-.

Table 6-3. Calculated MARPD Results for Reference Data and MARGA Units

Target Analyte	Reference Method MARPD	MARGA 1 MARPD	MARGA 1 CASTNET Goal	MARGA 2 MARPD	MARGA 2 CASTNET Goal
SO_2	4.8%	31.2%	✓	18.9%	✓
HNO_3	7.2%	34.1%	✓	25.8%	✓
NH_3	10.0%	33.1%	✓	18.2%	✓
SO_4^{2-}	2.8%	17.3%	✓	9.1%	✓
NO_3^-	9.3%	86.9%		58.7%	
NH_4^+	3.2%	19.2%	✓	25.3%	✓
SO_2[a]	NA	19.8%	✓	14.1%	✓

[a] Comparison to continuous FEM analyzer (1-hr data), all other comparisons relative to 12-hr denuder/filter pack.
NA: Not applicable.

To assess if the MARGA's failure to meet the CASTNET goals for NO_3^- was the result of expected measurement error, a Wilcoxon matched pair test was performed. For this analysis, the NO_3^- values from each MARGA for each valid reference method measurement period were paired with the corresponding mean reference method value. The differences in the paired values were ranked and the Wilcoxon rank sum statistic was determined. This value was then used to determine if the observed differences were likely to be random (e.g., large p-value), or the result of actual differences between the data sets (e.g., small p-value) based on a two-tailed distribution. For each MARGA unit, the Wilcoxon statistic indicated an actual difference between the MARGA and reference data sets ($p < 0.001$).

Although not evaluated as part of the ETV performance test, it is noteworthy that the sum of $HNO_3 + NO_3^-$ from MARGA measurements showed regression slopes relative to the corresponding sum from reference measurements that were closer to 1.0 (i.e., slopes of 1.06 and 0.83 for MARGA units 1 and 2, respectively) than did the separate HNO_3 and NO_3^- comparisons.

6.2 Precision

Precision of MARGA measurements was assessed in two ways as described in Section 5.2. Firstly, the MARPD of paired hourly measurements from the duplicate MARGA units was calculated for each of the target analytes, when both measurements exceeded twice the detection limit for the respective analyte. Table 6-4 presents a summary of the MARPD results for the duplicate MARGAs. This table also presents a summary of the number of hourly data points for each analyte where both MARGA results exceeded twice the detection limit as well as the number of hourly data points below twice the detection limit for each MARGA. For all analytes except NO_3^-, the duplicate MARGAs met the CASTNET precision goal of MARPD ≤ 25%.

Additionally, the MARPD of the duplicate MARGA results was calculated for each 12-hour reference sampling period and compared to the 95th percentile of the pooled RPD results (RPD_{95}) of the duplicate denuder/filter pack reference measurements (Table 6-5). The CASTNET performance goal for this measure of precision is for the MARPD of the MARGA units to be less than the corresponding 95th percentile of the reference data. Table 6-5 shows that the MARGA units met this performance goal for all target analytes.

Table 6-4. Summary of Calculated MARPD Results for Duplicate MARGA Units

Target Analyte	MARPD	Number of Hourly Data with Both Monitors above 2 x DL	Number of Hourly Data below 2 x DL	
			MARGA 1	MARGA 2
SO_2	10.4%	691	4	28
HNO_3	24.8%	582	62	129
NH_3	22.4%	561	138	103
SO_4^{2-}	6.5%	666	4	53
NO_3^-	27.3%	520	129	157
NH_4^+	6.3%	636	59	81

Table 6-5. Comparison of MARPD of 12-Hour Average MARGA Measurements with 95th Percentile of Pooled RPD Results of Duplicate Reference Measurements

Target Analyte	Reference RPD_{95}	MARGA MARPD (%)	Met CASTNET Goal
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%	✓

6.3 Data Completeness

The data completeness for the duplicate MARGA systems was calculated in two ways as described in Section 5.3. Data completeness was calculated both as the percentage of valid hourly data collected during the entire 30-day verification testing period and as the average number of hours and percentage of valid data collected during each 12-hour reference period when detectable levels were observed in both reference method samples. Completeness was calculated independently for each MARGA and for each target analyte. Table 6-6 summarizes the data completeness results and shows that the 80% completeness goals were easily met for all analytes on both MARGA units, with the exception of the average percentage of valid data collected during each reference period for Na^+.

Table 6-6. Summary of Data Completeness for MARGA Units

Target Analyte	% of Valid Data		Average Hours (%) of Valid Data per Reference Sampling Period (i.e., per 12 hours)	
	MARGA 1	MARGA 2	MARGA 1	MARGA 2
SO_2	99.3%	96.3%	11.9 (99.4%)	11.6 (96.3%)
HNO_3	99.3%	96.3%	11.9 (99.4%)	11.6 (96.5%)
NH_3	99.3%	96.3%	11.9 (99.4%)	11.6 (96.3%)
SO_4^{2-}	99.3%	96.1%	11.9 (99.4%)	11.5 (96.1%)
NO_3^-	99.3%	96.1%	11.9 (99.4%)	11.5 (96.1%)
NH_4^+	99.3%	96.3%	11.9 (99.4%)	11.6 (96.3%)
Na^+	99.3%	96.3%	11.9 (99.2%)	11.6 (96.5%)
Ca^{2+}	99.4%	96.3%	11.9 (99.2%)	11.5 (96.8%)
Cl^-	99.3%	96.1%	NA	NA

NA – Not applicable, Cl^- was never detected in both reference method samples for a given sampling period.

6.4 Reliability

MARGA reliability was assessed in three ways. Firstly, reliability was assessed in terms of the percentage of time that the monitoring systems operated in measurement mode over the duration of the test period, with a performance goal of at least 90%. Secondly, reliability was assessed in terms of the ability of the MARGA to perform a controlled shut-down in the case of a power failure, followed by an automated return to measurement mode within 4 hours after power had been restored. For this assessment, the testing staff imposed a temporary power outage at the test site and monitored the performance of one of the duplicate MARGA systems during and after the power outage. Finally, the number of operator site visits per week that were required to keep the MARGA units operating during the 30-day field period was recorded, with a goal of no more than 2 visits per week. Site visits were required only for routine maintenance of the MARGA units, as described in Section 6.5. These three assessments of reliability are reported independently for the duplicate MARGA units in Table 6-7.

Table 6-7. Summary of MARGA Reliability Assessments

Unit	% of Time in Operating Mode	Time to Start-up after Power Interruption	Site Visits per Week
MARGA 1	99.4%	< 1 hour[a]	Approximately one[b]
MARGA 2	96.8%	Not tested	Approximately one[b]

[a] Power was turned off at 1:51 pm on October 28, 2010 and the MARGA completed a controlled shutdown at 2:08 pm. Power was restored at 2:13 pm and the MARGA restarted and returned to measurement mode at 2:31 pm.

[b] See Section 6.5.

6.5 Operational Factors

This section addresses the maintenance, consumables, waste generation, ease of use, and other factors relevant to automated field operation of the MARGA.

6.5.1 Ease of Use

The two MARGA units were installed at the field site by the two EPA operators with the assistance of a representative of Applikon. The physical installation was completed over a few days. However, extensive effort was needed over a few weeks to bring the two units to a state of readiness for the verification test, and that readiness was achieved with the assistance of an Applikon representative only a few days before the start of the field period. A primary issue affecting MARGA response was apparent bacterial contamination of unknown origin. Multiple approaches, including thorough cleaning of several MARGA components and addition of a third bacterial filter to the water purification system used for MARGA reagent preparation, were tried simultaneously and were ultimately successful. Final MARGA preparation efforts included replacement of a pump motor in MARGA unit 2 immediately before the start of reference method sampling on September 8, 2010.

During the 30-day field period the two MARGA units operated largely unattended and almost entirely without interruption. An EPA site operator visited the field site on 20 of the 30 test days, but on most of those days conducted only brief (< 0.5 hour) performance inspections that were not required for operation of the MARGA units and that did not interrupt ambient monitoring. The MARGA operations and data were also monitored remotely on a daily basis by an Applikon representative. Routine maintenance (Section 6.5.2) did not cause any loss of MARGA monitoring data. Non-routine maintenance activities (Section 6.5.3) did result in some loss of MARGA data.

6.5.2 Routine Maintenance

Routine maintenance consisted of preparation and change out of absorbing solution, cation and anion IC eluents, internal standard, and suppressor regenerant. The absorbing solution was refilled in each MARGA unit seven times during the 30-day field period. In a few cases the absorbing solution was refilled more frequently than needed, to avoid the necessity of visiting the site on a weekend. The eluents were refilled twice, and the internal standard and regenerant were each refilled once, during the field period. Additionally, inlet particle filters were changed twice during the field period. Refilling solutions took 10 minutes or less, and filter changes took five minutes or less, with no interruption of MARGA operation for these activities. The site operators made no effort to consistently refill all solutions and change particle filters on the same day, but those activities could have been combined in one site visit per week. Approximately six man-hours were needed per week for routine maintenance including solution preparation, laboratory cleanup after reagent preparation, refills, filter changes, and disposal of waste solutions.

6.5.3 Non-Routine Maintenance

Non-routine maintenance of the MARGA units consisted of cleaning of the MARGA sample inlets, conducting air flow calibrations, and responding to occasional minor malfunctions with MARGA unit 2. These activities required approximately one hour per week. Both non-routine maintenance and the minor malfunctions caused loss of monitoring data; these occurrences are summarized in Table 6-8. Also shown in that table is the number of hourly MARGA monitoring periods lost due to the activity or malfunction.

Table 6-8 shows four hours of data were lost in the 30-day field period for MARGA unit, whereas 27 total hours of data were lost for MARGA unit 2. In most cases data loss occurred for both gaseous and aerosol species with a given MARGA unit; the few exceptions are noted in Table 6-8. Four hours of data from MARGA unit 1, and six hours of data from MARGA unit 2, were lost due to inlet cleaning and flow calibration conducted on three test days. These activities were conducted to assure correct sampling and comparability with the two MARGA inlets, and do not indicate a fault with the MARGA units themselves. Of the remaining 21 hours of data lost for MARGA unit 2, 20 hours were lost due to incorrect syringe drive operation or stoppage of the MARGA operational cycle. MARGA operation was readily restored, or resumed on its own, after these occurrences, but the ultimate cause of these occurrences was not investigated as part of the test. One hour of aerosol data lost for MARGA unit 2 occurred in the very first hour of the field period, and was likely a result of the replacement of the pump motor immediately before the start of the field period.

Table 6-8. Summary of Non-Routine Maintenance Activities and Malfunctions for MARGA Units During Verification Testing

Date	Affected MARGA Unit	Malfunction or Activity	Data Lost[a]
9/8/10	2	"SJAC fill open time short"; likely due to pump motor replacement immediately before start of test.	19:00 (aerosol only)
9/16/10	1 and 2	Inlet cleaning and air flow calibration check.	15:00, 16:00
9/19/10	2	Unit stopped due to software problem; "error in setting the outputs (timeout)".	10:00 – 13:00
9/22/10	1 and 2	Inlet cleaning and air flow calibration check.	14:00 (MARGA unit 1) 13:00-15:00 (MARGA unit 2)
9/23/10	2	Syringe problem.	15:00 – 18:00
9/27/10	2	Syringe too fast due to software problem.	13:00 – 16:00 (gases) 13:00-17:00 (aerosol)
10/1/10	1 and 2	Inlet cleaning and air flow calibration check.	11:00
10/4/10	2	Syringe speed event due to communication error; data quality uncertain.	19:00 – 22:00
10/6/10	2	Unit stopped and restarted; cause unknown.	19:00 – 21:00

a: Start times (local time) of affected MARGA hourly sampling periods.

6.5.4 Consumables/Waste Generation

The consumables required by the two MARGA units included absorbing solution (deionized water containing 10 parts per million hydrogen peroxide (H_2O_2)), cation eluent (nitric acid solution), anion eluent (sodium carbonate and sodium bicarbonate solution), an internal lithium bromide standard solution, suppressor regenerant (phosphoric acid solution), and inlet particle filters. Each MARGA unit consumed the absorbing solution at a rate of approximately 20 L per week, and the cation and anion eluents at a rate of approximately 5 L of each per week. Internal standard and suppressor regenerant were consumed at approximately 0.7 and 0.6 L per week, respectively, for each unit. Thus approximately 31.3 L of waste solutions was generated by each MARGA unit per week. All waste solutions are considered non-hazardous and do not require any special treatment for disposal. The particle filters were changed twice during the 30-day field period and are simply thrown away.

Chapter 7
Performance Summary

Table 7-1 presents a summary of the results of the verification of the MARGA systems during this verification test. Bolded entries indicate that the CAMD performance goal specified in the test/QA plan[4] was met. Table 7-1 shows that the great majority of performance goals were met by both MARGA units, with the regression slopes for HNO_3 and NO_3^-, and the MARPD accuracy for NO_3^-, being the key exceptions.

Table 7-1. Summary of Verification Test Results for the MARGA

<table>
<tr><th rowspan="3">Parameter Evaluated</th><th rowspan="3">Method of Evaluation</th><th colspan="5">Results</th></tr>
<tr><th rowspan="2">Analyte</th><th colspan="2">MARGA 1</th><th colspan="2">MARGA 2</th></tr>
<tr><th>Slope</th><th>Intercept ($\mu g/m^3$)</th><th>Slope</th><th>Intercept ($\mu g/m^3$)</th></tr>
<tr><td rowspan="7">Accuracy</td><td rowspan="7">Regression analysis comparison to reference samples</td><td>SO_2</td><td>**1.16**</td><td>**0.16**</td><td>**1.08**</td><td>**0.13**</td></tr>
<tr><td>HNO_3</td><td>0.780</td><td>**0.35**</td><td>0.596</td><td>**0.28**</td></tr>
<tr><td>NH_3</td><td>**0.930**</td><td>**-0.14**</td><td>**0.987**</td><td>**-0.08**</td></tr>
<tr><td>SO_4^{2-}</td><td>**1.02**</td><td>**0.30**</td><td>**0.986**</td><td>**0.22**</td></tr>
<tr><td>NO_3^-</td><td>2.48</td><td>**-0.15**</td><td>1.73</td><td>**-0.05**</td></tr>
<tr><td>NH_4^+</td><td>**1.02**</td><td>**-0.23**</td><td>**0.993**</td><td>**-0.25**</td></tr>
<tr><td>SO_2[a]</td><td>**0.962**</td><td>**0.50**</td><td>**0.890**</td><td>**0.44**</td></tr>
<tr><td rowspan="9">Accuracy</td><td rowspan="9">Calculation of MARPD between MARGA results and reference method results</td><th rowspan="2" colspan="2">Analyte</th><th colspan="3">MARPD</th></tr>
<tr><th>MARGA 1</th><th colspan="2">MARGA 2</th></tr>
<tr><td colspan="2">SO_2</td><td>**31.2%**</td><td colspan="2">**18.9%**</td></tr>
<tr><td colspan="2">HNO_3</td><td>**34.1%**</td><td colspan="2">**25.8%**</td></tr>
<tr><td colspan="2">NH_3</td><td>**33.1%**</td><td colspan="2">**18.2%**</td></tr>
<tr><td colspan="2">SO_4^{2-}</td><td>**17.3%**</td><td colspan="2">**9.1%**</td></tr>
<tr><td colspan="2">NO_3^-</td><td>86.9%</td><td colspan="2">58.7%</td></tr>
<tr><td colspan="2">NH_4^+</td><td>**19.2%**</td><td colspan="2">**25.3%**</td></tr>
<tr><td colspan="2">SO_2[a]</td><td>**19.8%**</td><td colspan="2">**14.1%**</td></tr>
</table>

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

Table 7-1. (Continued)

Parameter Evaluated	Method of Evaluation	Results	
		Analyte	**1-Hour MARPD**
Precision	Comparison of results from duplicate monitoring systems	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%**

Parameter Evaluated	Method of Evaluation	Results		
		Analyte	**Ref. Method RPD_{95}**	**MARGA 12-Hour MARPD**
Precision	Comparison of MARPD of 12-hour average MARGA data and 95th percentile of pooled RPD results from reference measurements (RPD_{95})	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%**

Parameter Evaluated	Method of Evaluation	Results				
		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**
Data completeness	Ratio of number of hourly data points successfully collected to number of potential hourly data points that could have been collected	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%**	NA	NA

Parameter Evaluated	Method of Evaluation	Results
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**

Table 7-1. (Continued)

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 refilling reagent solutions, disposal of waste solutions, and replacement of particle filters; approximately 6 man-hours per week • Non-routine maintenance included flow checks, cleaning of sample inlets, and responding to minor infrequent problems; approximately 1 man-hour per week
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

Chapter 8
References

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2. Harrison, R.M., Kitto, A.M.N. 1990. "Field Intercomparison of Filter Pack and Denuder Sampling Methods for Reactive Gaseous and Particulate Pollutants", Atmos. Environ. 24A(10): 2633-2640.

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Appendix A

Performance Objectives for CASTNET Semi-Continuous Ambient Air Monitoring Systems

Goal	**Analytes**	**Description**	**Target**
Accuracy Goal 1	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+	Slope (m) of linear regression by least-squares method of mean value of reference measurements paired with measurement of each instrument. All data with mean reference values below 2 times the instrument detection limit (IDL) are excluded.	$0.80 \le m \le 1.20$
Accuracy Goal 2	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+	Intercept (b) of linear regression by least-squares method of mean value of reference measurements paired with measurement of each instrument. All data with mean reference values below 2 times the IDL are excluded.	-10 ppb $\le b \le 10$ ppb
Accuracy Goal 3	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+	The median absolute relative percent differences (MARPD) between the mean value of reference measurements paired with measurement of each instrument.	MARPD ≤ 40%
Accuracy Goal 4 (If the instrument does not meet Accuracy Goal 3)	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+	Perform Wilcoxon matched pairs test to determine if the failure to achieve Accuracy Goal 3 is due to expected measurement variation. The ratio of observed differences in the two data sets (i.e., reference and instrument) to expected random differences in the same two data sets.	p-value ≤ 0.05
Precision Goal 1	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+	MARPD between paired instrument measurements. All data with mean instrument values below 2 times the IDL are excluded.	MARPD ≤ 25%
Precision Goal 2	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+	Median absolute relative percent difference between paired instrument measurements ($RPD_{0.5}$) is less than the 95th percentile of the pooled RPD of the reference method ($RPD_{REF0.95}$).	$RPD_{0.5} \le RPD_{REF0.95}$
Completeness Goal 1	SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+, Na^+, Ca^{2+}, and Cl^-	Percentage of test period for which valid data, as indicated by the instrument, is available within 24 hours of collection.	$T_{valid} \ge 80\%$
Completeness Goal 2	SO_2, HNO_3, NH_3, SO_{42-}, NO_{3-}, and NH_{4+}, Na^+, Ca^{2+}, and Cl^-	Completeness of data record for comparison with reference measurements for each test period, when detected by reference measurements (i.e., hours of valid measurements for each valid reference measurement period).	$T_{Reference} \ge 80\%$
Reliability Goal 1	Instrument measurement mode	Percentage of time instrument is in measurement mode for test period	$T_{Measurement} \ge 90\%$
Reliability Goal 2	Power failure tolerance	In the event of a power failure the instrument has sufficient back-up power to perform a controlled shutdown, restarts, and instrument returns to measurement mode within 4 hours after power has returned.	Yes/No
Reliability Goal 3	Operator attendance	Average number of site visits per week required to keep instrument operating.	$N \le 2$