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Environmental Technology Verification Report

Applikon MARGA Semi-Continuous Ambient Air Monitoring System

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

APPLIKON MARGA SEMI-CONTINUOUS AMBIENT AIR MONITORING SYSTEM

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water 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, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and groundwater; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environ¬ment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director

National Risk Management Research Laboratory

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List of Abbreviations

AC	automated colorimetry
AMS	Advanced Monitoring Systems Center
ADS	annular denuder system
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
NCSU	North Carolina State University
NIST	National Institute of Science and Technology
PE	performance evaluation
ppb	parts per billion
QA	quality assurance
QC	quality control
QMP	quality management plan
RPD	relative percent difference
RPD_{95}	95th percentile of pooled 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 Applikon BV's Monitor for Aerosols and Gases in Ambient Air (MARGA) semi-continuous ambient air monitoring system at the Burdens Creek ambient air quality monitoring site in Research Triangle Park, 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 ambient air monitor components:

- ☐ A sampling box
- ☐ An 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 analyzer consists of two boxes: the upper sampling box and the lower 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 in the process 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.

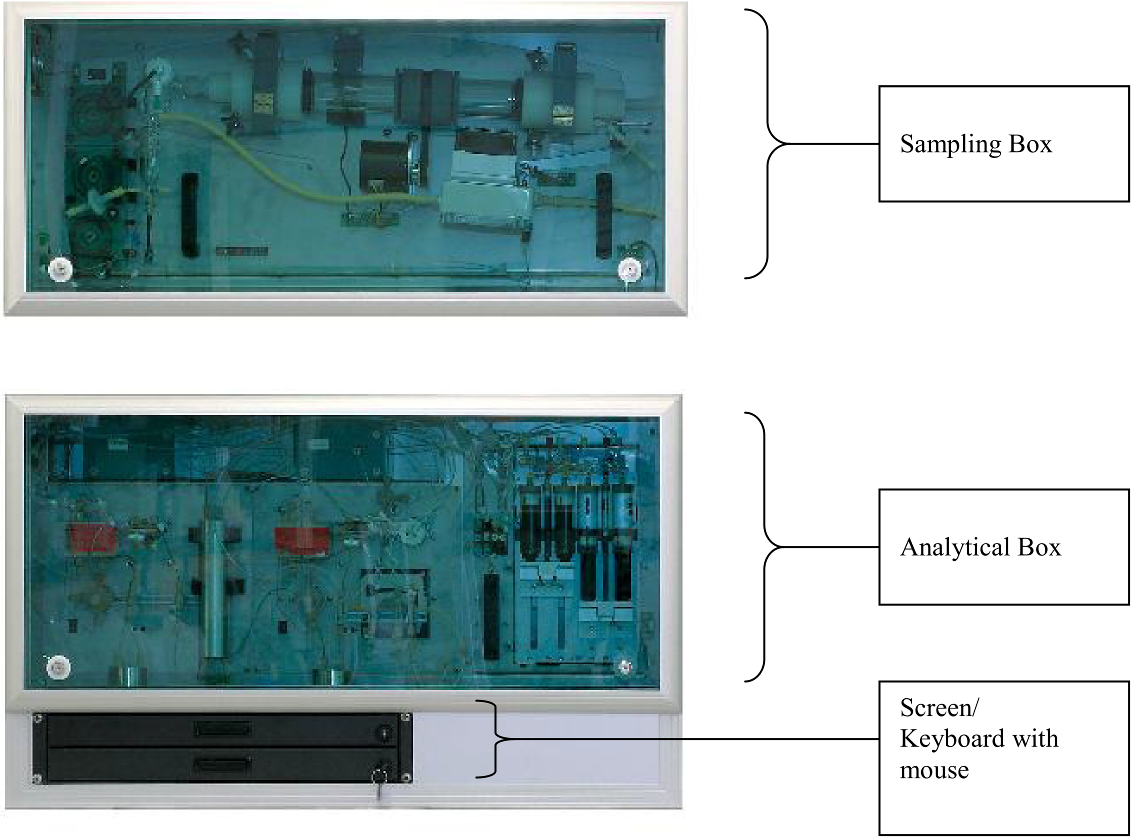

Figure 2-1. MARGA ADI 2080 Sampling and Analytical Boxes

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). Presently there are a total of 86 operational CASTNET sites located in or near rural areas and sensitive ecosystems collecting 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})
- Particulate nitrate (NO^{-3})
- Nitric acid (HNO_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 an open face, three-stage filter pack that uses 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 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 from 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 much more timely data stream and improved air quality assessment capability. Real-time, multi-pollutant monitoring in rural areas will help to 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 procedures specified in the ETV *Test/QA Plan for Verification of Semi-Continuous Ambient Air Monitoring Systems.*[4] 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 and, specifically, use in CASTNET. The test was conducted over a period of approximately 30 days and involved the continuous operation of duplicate semi-continuous monitoring technologies at an existing ambient air monitoring station located near EPA laboratories in Research Triangle Park (RTP), North Carolina. The accuracy of the monitoring technologies 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 semi-continuous monitoring was determined from comparisons of paired data from 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 field testing staff. Target performance goals were established by EPA to demonstrate if these monitoring systems are suitable for use in CASTNET. These specifications are referred to as “target performance goals” in this report and were used to evaluate data generated by the MARGA and reference methods. 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 verified during a field test conducted from October 1 to October 31, 2008. Testing was conducted at the Burdens Creek Air Monitoring Site in RTP, NC. The monitoring systems were operated and maintained by the vendor throughout the field period. Duplicate, integrated denuder/filter pack reference samples were collected over 12-hour sampling intervals throughout the testing period, from 6:00 am to 6:00 pm and from 6:00 pm to 6:00 am daily. The denuder/filter pack samples were collected and analyzed by North Carolina State University (NCSU). Additionally, the MARGA units were collocated with separate continuous gas analyzers for SO_2 and ammonia (NH_3), which were operated and maintained by EPA staff throughout the testing period.

In the test reported here, the 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. In addition, data completeness was evaluated for Cl^-, Ca^{2+}, and Na^+ in the particle phase.

3.2 Test Procedures

During testing, duplicate semi-continuous ambient air monitoring systems were installed inside an environmentally controlled shelter at the Burdens Creek Air Monitoring Site. The monitoring systems were operated and maintained by the vendor, and intended to operate continuously over the 30-day testing period. Maintenance performed on the monitoring systems was conducted by the vendor, documented by Battelle, and is reported in Section 6.4 of this report. Data from the monitoring systems was retrieved by the vendor and provided to Battelle within 24 hours of collection.

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 phosphorus 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 H_3PO_3 coated denuder "chaser" for the collection of volatilized particulate ammonium. The denuder/filter pack samplers were installed on the roof of the trailer housing the monitoring systems being tested and collected ambient air samples at a flow rate of 10 liters per minute (L/min). Figure 3-1 shows the sampling shelter with denuders and filter packs set up on the roof.

Figure 3-1. Sampling Shelter with Denuder/Filter Packs Deployed

Each reference sampler manifold contained eight measurement channels, which were used for seven denuder/filter pack sample trains and one blank train. Thus, when fully loaded the reference samplers could carry out three and one-half days of routine sampling (i.e., seven successive 12-hour samples). Consequently, changeout of collected reference samples and reloading of the samplers was conducted twice each week. The denuder/filter pack samples were retrieved and returned to the analytical laboratory for disassembly, extraction, and analysis. Figure 3-2 shows the retrieval process for the denuder/filter packs. After disassembly in the laboratory, the filters and denuders were extracted using deionized water and analyzed for target analytes. The denuder extracts were analyzed for SO_2 (as SO_4^{2-}), nitrous acid (HONO) (as nitrite (NO_2^-), HNO_3 (as NO_3^-), NH_3 (as NH_4^+), and HCl (as Cl^-). 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 denuder chaser extracts were analyzed for NH_4^+. Analysis for each 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]

Figure 3-2. Denuder/Filter Pack Retrieval

Specific sample handling procedures were implemented to minimize handling of the denuder/filter pack components and limit the number of transfers of the denuder/filter packs. When not in use, the denuders and assembled filter packs were sealed or capped, to prevent contamination. Clean lint-free gloves were used when handling the denuder/filter pack components. Clean forceps were used when handling filters. The denuders and filter packs were assembled in NCSU's analytical laboratory facilities and transferred by NCSU staff to the Burden's Creek Air Monitoring Site for sampling. Special care was taken to avoid breathing on components of the denuder/filter pack reference samples, to minimize ammonia contamination.

3.3 Field Site

The Burdens Creek Air Monitoring Site is near the EPA offices in RTP and is maintained by EPA staff. The site consists of 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 MARGAs evaluated during this verification were housed in an environmentally controlled shelter along with the continuous NH_3 instrument. The denuder/filter pack samplers were located on a platform on the roof of the trailer. Pumps for the denuder/filter packs were located in pump boxes adjacent to the trailer. Continuous SO_2 Federal Equivalent Method (FEM) measurements were collected in a separate trailer approximately 30 yards from the trailer housing the MARGAs.

3.4 Verification Schedule

The MARGA verification field effort took place from October 1 through October 31, 2008. Duplicate MARGA units had been installed by the vendor and were operating at the Burdens Creek site for several weeks prior to the start of the verification test. The vendor performed routine maintenance on both units to prepare them for the start of the verification test. The continuous SO2 and NH3 analyzers used for reference measurements were also installed and operating at the site before the start of the MARGA evaluation.

Denuder/filter pack reference measurements began on October 1 at 6:00 am and ran in 12-hour integrated samples through October 31 at 6:00 pm. However, each week two of the denuder/filter pack samples were collected on a time period shorter than 12 hours. The sample that should have started on Tuesdays at 6:00 am was started three hours later to allow for changeout of the denuder/filter packs. This sample was started on the hour after the changeout was completed to allow for comparison with hourly MARGA data. Similarly, the sample that should have finished sampling on Fridays at 6:00 pm was stopped at 3:00 pm to allow for changeout of the denuder/filter packs. All start and stop times were recorded by NCSU staff as part of the deployment/collection process.

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[8] except where noted below. QA/QC procedures and results are described below.

4.1 Deviations

There was one documented deviation from the test/QA plan during this verification test. The deviation involved the use of IC rather than inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the analysis of the metal cations (Na^+ and Ca^{2+}) from the collected reference method samples. IC was chosen as the preferred method since IC allowed for reanalysis of samples if needed. These cation data were used only for determination of data completeness, and the change in analytical methods did not negatively impact data quality

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 duplicate denuder/filter pack reference measurements. Quality control activities for the filter pack sampling included flow rate checks performed on the sampling trains and the collection of field blank samples. Prior to each sampling event, each sampling train was checked for leaks to ensure proper operation.

On each of the duplicate denuder/filter pack reference sample manifolds, one of the eight channels was reserved for the collection of field blank samples. The field blanks were collected by installing the sampling media (i.e., denuder and filters) in the sampling train but without drawing any air through the train. The field blank samples remained installed until the denuder/filter pack reference samples collected at the same time were retrieved. The field blank media were then recovered along with the other samples, and were handled and analyzed like normal samples. Additionally, travel blank samples were collected for the Na_2CO_3 and H_3PO_3 coated denuders. Table 4-1 presents a summary of the denuder/filter blank analyses, including the detection limit for each species and the number of blanks with results above the detection limit. The results of the field blank analyses were subsequently subtracted from the corresponding denuder/filter pack reference samples that were collected at the same time as the field blank samples. When the result of the field blank analysis was below the detection limit, the detection limit value was subtracted from the corresponding denuder/filter pack reference sample result.

Table 4-1. Summary of Field Blank Analyses

Medium	Analyte	Blank Type	Det. Limit (µg)	# of Blank Samples	# above D.L.	Average (µg) (St. Dev.)[1]
Teflon filter	NH_4^+	Field blank	0.25[2]	26	4	1.41 (0.55)
	NO_3^-	Field blank	0.1[2]	26	12	1.25 (1.22)
	SO_4^{2-}	Field blank	0.25	26	2	1.1 (1.1)
Nylon filter	NH_4^+	Field blank	0.05[2]	26	20	0.34 (0.34)
	NO_3^-	Field blank	0.15[2]	26	7	0.29 (0.12)
Na_2CO_3 denuder	NO_3^-	Field blank	0.2[2]	26	3	1.07 (0.71)
		Travel blank	0.2[2]	30	0	--
	SO_4^{2-}	Field blank	1.0	26	25	2.19 (0.61)
		Travel blank	1.0	30	26	2.03 (0.52)
H_3PO_3 denuder	NH_4^+	Field blank	0.1[2]	26	26	0.57 (0.42)
		Travel blank	0.1[2]	30	16	0.21 (0.03)
H_3PO_3 chaser	NH_4^+	Field Blank	0.1[2]	26	18	0.28 (0.12)

[1] – Average and standard deviation of the results above the detection limit.

[2] – Detection limit for nitrogen compounds is the mass of nitrogen only, not the mass of the compound.

4.2.2 Denuder/Filter Pack Analysis

The analysis of the denuder/filter pack samples was conducted by IC based on EPA Method 300.0[6] and by AC based on EPA Method 350.1.[7] Analysis of these samples was subject to the data quality criteria of the respective methods, which included the analysis of duplicate samples, blanks, and calibration check standards with every batch of samples analyzed by the different analytical methods. For each duplicate analysis the absolute relative percent difference (ARPD) between the measured results was calculated. Table 4-2 summarizes the results of the analysis of the duplicate samples for the collected denuder/filter pack reference samples. Only those samples for which both duplicate results are above twice the detection limit are included in this summary. The duplicate analysis exceeded the acceptance criterion of 20% ARPD established in the test/QA plan[4] a total of seven times. The ARPD exceeded 20% in one instance for the analysis of SO_4^{2-} from the Teflon filters, in three instances for the analysis of NH_4^+ from nylon filters, in one instance for the analysis of NO_3^- from nylon filters, and in two instances for the analysis of NH_4^+ from the H_3PO_3 denuders. In most cases, the exceedances were a result of limitations in the reporting precision of the analytical equipment because the ambient concentrations of the target analytes were very low. The causes for the other exceedances were not apparent.

Calibration curves were run after every set of 25 samples using aqueous solution calibration standards and method blanks. Table 4-3 presents the coefficient of variation (CV), defined as the standard deviation of the instrumental results divided by the mean of the results, for the individual standards used in the calibrations. Shown for each analyte is the concentration of the standard in µg/L, accompanied by the CV of all such standards (as a percent, in parentheses). The CV results are all ≤4.0% for SO_4^{2-}, ≤5.7% for NO_3^-, and ≤1.1% for NH_4^+.

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

Medium	Analyte	# of Samples	# above 2 x D.L.	Average ARPD	Max. ARPD
Teflon filter	NH_4^+	17	9	5.1%	18.9%
	NO_3^-	17	10	2.9%	8.7%
	SO_4^{2-}	17	8	7.3%	40.8%
Nylon filter	NH_4^+	16	11	9.7%	28.6%
	NO_3^-	16	14	2.3%	22.2%
Na_2CO_3 denuder	NO_3^-	22	10	1.7%	11.8%
	SO_4^{2-}	22	14	2.1%	7.5%
H_3PO_3 denuder/chaser	NH_4^+	35	30	4.4%	23.3%

Table 4-3. Calibration Standard Coefficients of Variation

Analyte		SO_4^{2-}	NO_3^-	NH_4^+
Standard Concentration (µg/L) (CV)	**Blank**	0[a]	0[a]	0[a]
	1	400 (3.6%)	90 (5.7%)	310 (0.6%)
	2	800 (4.0%)	160 (3.3%)	620 (1.1%)
	3	1600 (2.5%)	360 (2.0%)	1240 (0.7%)
	4	4000(1.8%)	900 (1.8%)	3100 (0.8%)

[a] CV results are not reported for blank samples since the mean result is set to zero.

4.2.3 Gas Analyzers

The continuous gas analyzers used for this verification test were already in operation at the Burdens Creek site and were included in routine QC activities at the site. Quality control activities associated with the SO_2 continuous gas analyzer included multipoint calibrations of the analyzer, routine zero/span checks, and biweekly precision checks. A multipoint calibration of the NH_3 continuous gas analyzer was performed before and after the verification test. The continuous NH_3 data were also corrected for water vapor interference based on an observed linear relationship between the Pranalytica baseline and atmospheric dewpoint. 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

PE audits of the denuder/filter pack reference method sampling procedures were performed by measuring the sample flow rate through the denuder/filter pack inlet during sampling. The flow rate was measured using a National Institute of Science and Technology (NIST)-traceable flow transfer standard. During the testing period, a total of 42 flow rate checks were performed. The results of those checks are summarized in Table 4-4.

Table 4-4 shows that in 30 of the 42 flow checks, the sampler flow rate was within the target ±5% tolerance of the nominal flow rate. In the 12 cases where the measured flow rate was outside that tolerance, the sampling trains were inspected for any apparent problems. In two cases, an obstruction that completely blocked the air pathway was found and removed. In the other cases the flow rate was only slightly outside the target tolerance with a range from +5.1% to -11.1%. No apparent cause for the discrepancy in flow rates was found and in those cases the measured (rather than nominal) flow rate was used in calculating the ambient concentrations.

Additionally, a PE audit of the analytical methods was performed by supplying the analytical laboratory with samples prepared from independent NIST-traceable standard solutions. The samples were analyzed and the results are summarized in Table 4-5. The target acceptance criteria for the PE audit results were 5% for the IC results and 10% for the AC results. In all but one case (NH_4^+ by AC at 1,000 µg/L), the results of the PE audit met the target acceptance criteria.

4.3.2 Technical Systems Audit

The Battelle Quality Manager performed a TSA of the testing procedures during the first week of the verification test. The purpose of this audit was to ensure that the verification test was being performed in accordance with the AMS Center QMP,[8] the test/QA plan for this verification test,[4] published reference methods,[5-7] and any SOPs used by the analytical laboratory. In this audit, the Battelle Quality Manager reviewed the reference methods used, compared the actual test procedures being performed to those specified or referenced the test/QA plan, and reviewed data acquisition and handling procedures. The TSA was performed at both the verification test site and the analytical laboratories at NCSU where the

Table 4-4 Summary of Denuder/Filter Pack Flow Rate Checks

Date	Train	Measured Flow (L/min)	%Difference from Nominal	Comment
10/1/2008	Train 1-3	9.33	-6.7%	No cause identified[a]
10/1/2008	Train 1-4	0.00	-100%	Flow obstruction
10/1/2008	Train 2-3	9.82	-1.8%	
10/1/2008	Train 2-4	10.00	0.0%	
10/2/2008	Train 1-5	9.70	-3.0%	
10/2/2008	Train 1-6	0.00	-100%	Flow obstruction
10/2/2008	Train 2-5	10.01	0.1%	
10/2/2008	Train 2-6	9.95	-0.5%	
10/7/2008	Train 1-1	9.52	-4.8%	
10/7/2008	Train 1-2	9.51	-4.9%	
10/7/2008	Train 2-1	9.88	-1.2%	
10/7/2008	Train 2-2	9.69	-3.1%	
10/10/2008	Train 1-7	9.90	-1.0%	
10/10/2008	Train 2-7	10.47	4.7%	
10/14/2008	Train 1-3	10.14	1.4%	
10/14/2008	Train 1-4	10.30	3.0%	
10/14/2008	Train 2-3	10.42	4.2%	
10/14/2008	Train 2-4	10.36	3.6%	
10/17/2008	Train 1-5	9.66	-3.4%	
10/17/2008	Train 1-6	9.52	-4.8%	
10/17/2008	Train 2-5	10.00	-0.04%	
10/17/2008	Train 2-6	9.51	-4.9%	
10/21/2008	Train 1-7	10.51	5.1%	No cause identified[a]
10/21/2008	Train 2-7	9.76	-2.5%	
10/24/2008	Train 1-1	9.97	-0.3%	
10/24/2008	Train 2-1	10.31	3.1%	
10/28/2008	Train 1-2	9.62	-3.8%	
10/28/2008	Train 2-2	9.51	-5.0%	
10/31/2008	Train 1-1	9.22	-7.8%	No cause identified[a]
10/31/2008	Train 1-2	9.33	-6.7%	No cause identified[a]
10/31/2008	Train 1-3	8.89	-11.1%	No cause identified[a]
10/31/2008	Train 1-4	9.35	-6.5%	No cause identified[a]
10/31/2008	Train 1-5	9.18	-8.2%	No cause identified[a]
10/31/2008	Train 1-6	9.37	-6.3%	No cause identified[a]
10/31/2008	Train 1-7	9.20	-8.1%	No cause identified[a]
10/31/2008	Train 2-1	9.99	-0.1%	
10/31/2008	Train 2-2	9.43	-5.7%	No cause identified[a]
10/31/2008	Train 2-3	10.09	0.9%	
10/31/2008	Train 2-4	10.04	0.4%	
10/31/2008	Train 2-5	9.98	-0.3%	
10/31/2008	Train 2-6	10.02	0.2%	
10/31/2008	Train 2-7	9.98	-0.3%	

a: Sampler operating normally, no cause was found for flow measurement outside of ±5% target tolerance. Measured flow rate used to calculate ambient concentrations.

Table 4-5 Summary of PE Audits of Analytical Methods

Analyte	Analytical Method	Standard Concentration (μg/L)	Measured Concentration (μg/L)	Percent Difference
NH_4^+	AC	1000	945	-5.5
NH_4^+	AC	100	95	-5.0
NH_4^+	AC	100	103	3.0
NO_3^-	AC	1000	997	-0.3
NO_3^-	IC	1000	1007	0.7
SO_4^{2-}	IC	1000	1050	5.0
NH_4^+	IC	100	107	7.0

reference method analyses were performed. During the TSA, the Battelle Quality Manager observed the reference method sampling and sample recovery; inspected documentation of reference sample chain of custody; and reviewed laboratory record books. He also checked data acquisition procedures, and conferred with the vendor, EPA, and NCSU testing staff.

As noted in Section 4.1, one deviation from the test/QA plan was identified as a result of the TSA. The deviation involved the use of IC rather than ICP-AES for the analysis of the metal cations (Na^+ and Ca^{2+}) from the collected reference method samples. IC was chosen as the preferred method since a significantly smaller volume of sample was required and thus IC allowed for reanalysis of samples if needed. These cation data were used only for determination of data completeness, and the change in analytical methods did not negatively impact data quality since the detection limits for the two methods are approximately equal.

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.

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 TSA were submitted to the EPA.

4.5 Data Review

All data received from the Vendor from the two MARGA units, from the EPA for the SO_2 and NH_3 analyzers, and from NCSU for the denuder/filter pack reference measurements underwent 100% validation by Battelle technical staff before being used for any statistical calculations. Data were assessed technically and results that appeared anomalous, based on comparisons to other comparable data, were flagged and removed from additional statistical calculations. When possible, the cause of the anomalous data was investigated through analysis of other testing records (e.g., logbook entries) to assess if unusual events occurring during testing may have potentially affected the data in question.

Records generated in the verification test received a one-to-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. Qualitative observations were also used to evaluate verification test data.

5.1 Accuracy

The accuracy of the MARGA monitoring systems was evaluated in two ways 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

Firstly, the accuracy was determined from a linear least squares regression analysis of the measured concentrations of the target analytes determined from the MARGA systems and the corresponding reference methods. For comparison to the denuder/filter pack reference samples, average concentrations from each of the two MARGA systems were determined separately for each of the 12-hour sampling periods during the testing period, by averaging the 1-hour results over the corresponding sampling periods. For each of the duplicate MARGAs, 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 duplicate monitoring systems, and for each target analyte. For the continuous gas measurements (SO_2 and NH_3), 1-hour average concentration readings from each monitoring system were plotted against the corresponding 1-hour average reference measurements, excluding data below twice the instrument detection limit. 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.

5.1.2 MARPD Analysis

The accuracy of the MARGA systems in terms of median ARPD (MARPD) was calculated as the median value of the ARPD results determined using Equation 1:

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

where C_i and $\overline{C(ref)_i}$ are the average target analyte concentration measured by a MARGA system and the mean of the duplicate reference method concentrations, respectively, for the i^{th} reference sampling period.

The accuracy of the MARGA systems was determined for all periods for which concentrations determined by both the reference method samplers were greater than twice the detection limit.

5.2 Precision

5.2.1 Comparison of Paired Results

For this assessment of precision, the MARPD between the paired measurements from the duplicate MARGA monitoring systems was calculated as the median value of the ARPD values determined using Equation 2:

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

where $C(1)_i$ and $C(2)_i$ are the target analyte concentration measured by the first and second of the two duplicate monitoring systems. For this calculation, periods when measurement data for either of the MARGA systems was below twice the instrumental detection limit was excluded from the analysis.

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 MARPD to the 95th percentile of the pooled relative percent difference of the duplicate reference method measurements. For this calculation, periods when measurement data for either of the reference method samples were below twice the instrumental detection limit were excluded from the analysis.
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 system during the testing period. For each of the duplicate MARGA systems, this calculation used the total hours of apparently valid data reported by the monitoring systems and available within 24 hours, divided by the total hours of data in the entire field period. Also, the number of hours of valid monitoring system data was assessed relative to the number of hours in each reference method sampling period. The performance goals for both of these measures of data completeness were ≥ 80%. The causes of any substantial incompleteness of data return were established from operator observations or vendor records, 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 the monitoring systems operated in measurement mode over the duration of the test period. This assessment is reported independently for the two duplicate MARGA systems. Additionally, reliability was assessed in terms of the ability of the instruments to perform a controlled shut-down in the case of a power failure, followed by an automated return to measurement mode within four hours after power has 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 monitoring systems during and after the power outage.

5.5 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, repair requirements, etc., were evaluated based on observations recorded by Battelle and facility staff, and explained by the vendor as needed. Battelle staff were at the monitoring site whenever the vendor was present and recorded all activities performed on the monitoring systems. A laboratory record book was maintained at the test site, and was 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 monitoring systems; use or replacement of any consumables; the effort or cost associated with maintenance or repair; vendor effort (e.g., time on site) for repair or maintenance; the duration and causes of any down time or data acquisition failure; and Battelle testing staff observations about ease of use of the monitoring systems.

Chapter 6
Test Results

Figures 6-1 through 6-6 show time sequence plots of the duplicate MARGA data recorded on an hourly basis 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, where the vertical error bars on the reference measurements represent the range of the duplicate reference measurements, and the horizontal extent of the reference result indicates the time frame of sampling. Where no error bars are shown, only one reference measurement was above detection limit. The quality of the reference method results as a basis for assessing MARGA performance is discussed in subsequent sections of this chapter.

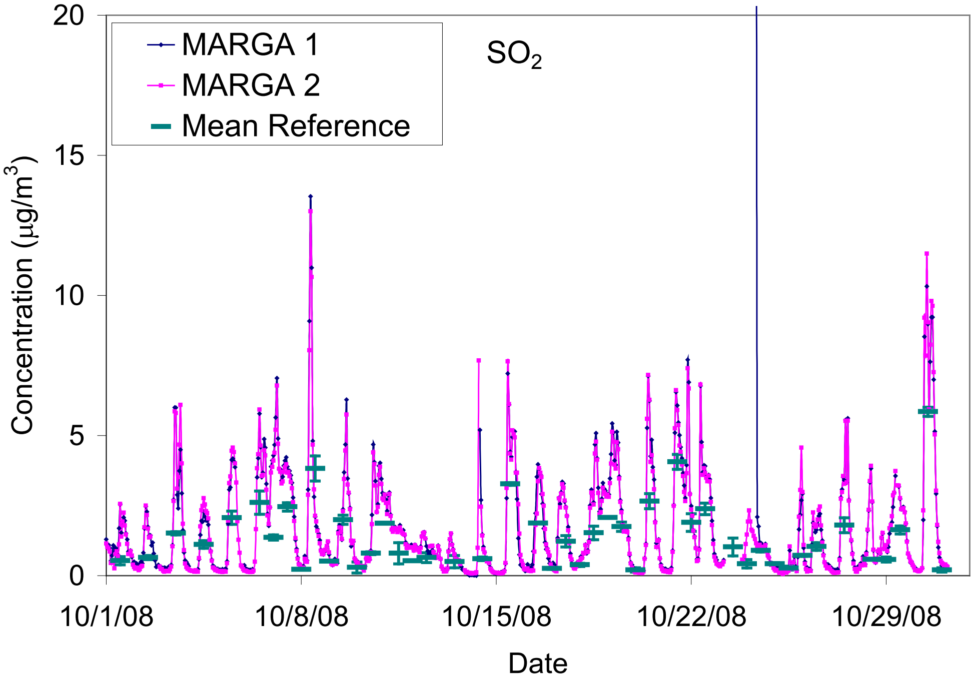

Figure 6-1. Time sequence plot of SO_2 measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

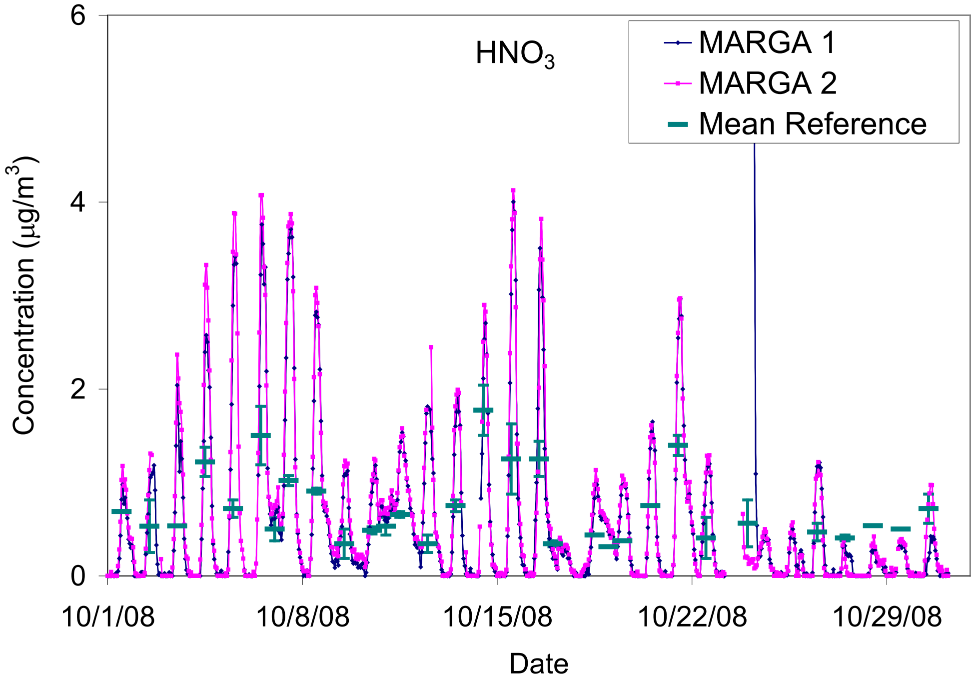

Figure 6-2. Time sequence plot of HNO$_3$ measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

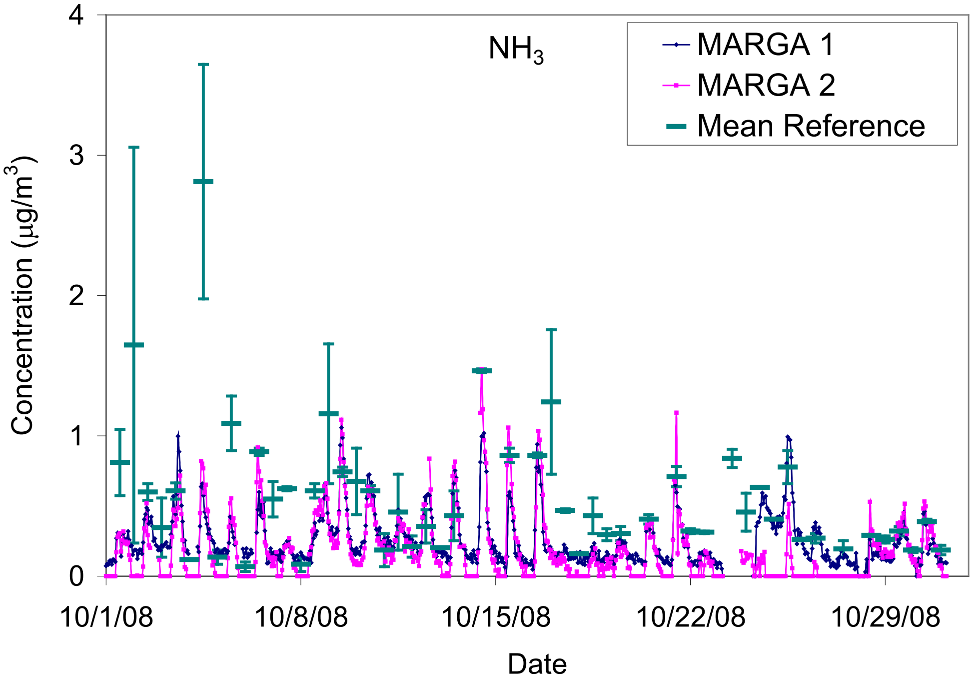

Figure 6-3. Time sequence plot of NH$_3$ measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements. (No apparent cause was identified for the outlier reference data shown in this figure.)

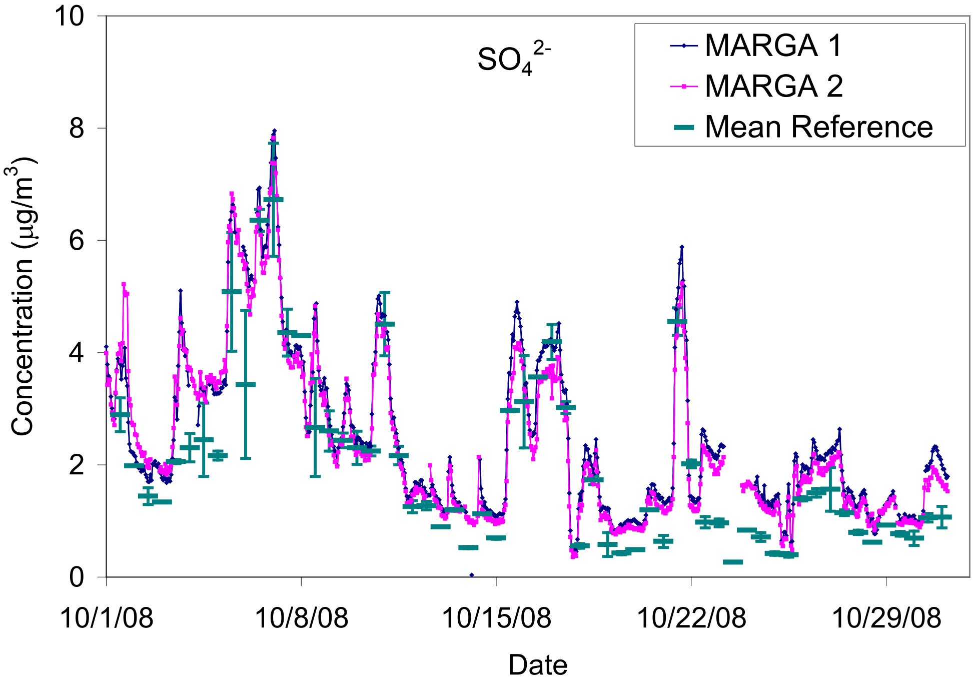

Figure 6-4. Time sequence plot of SO_4^{2-} measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements.

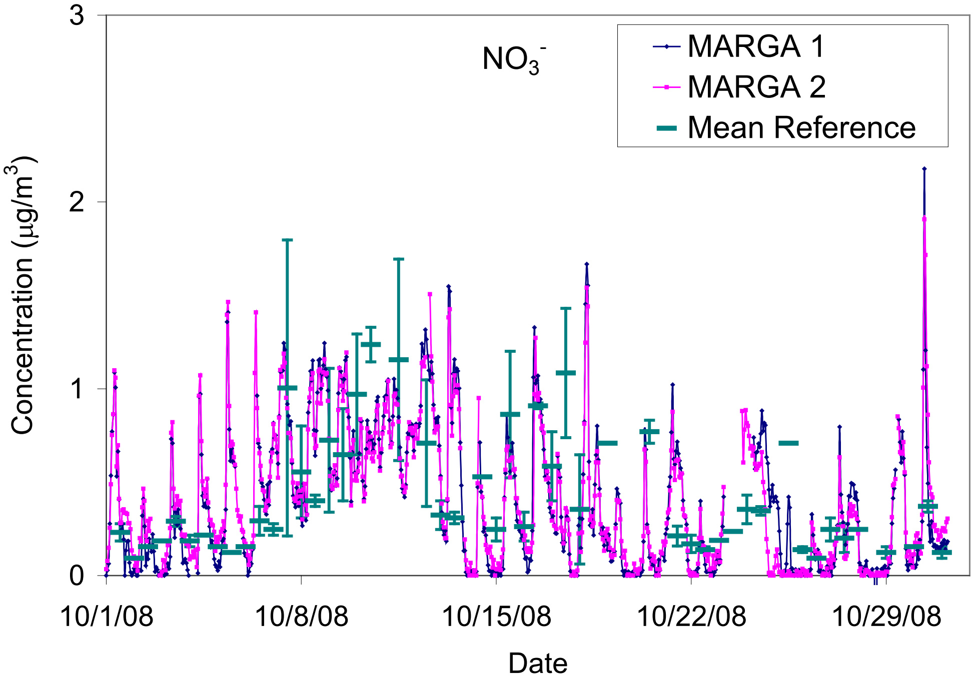

Figure 6-5. Time sequence plot of NO_3^- measurement results from duplicate MARGA and mean denuder/filter pack reference method measurements. (A total of five outlier reference measurements were excluded from the dataset.)

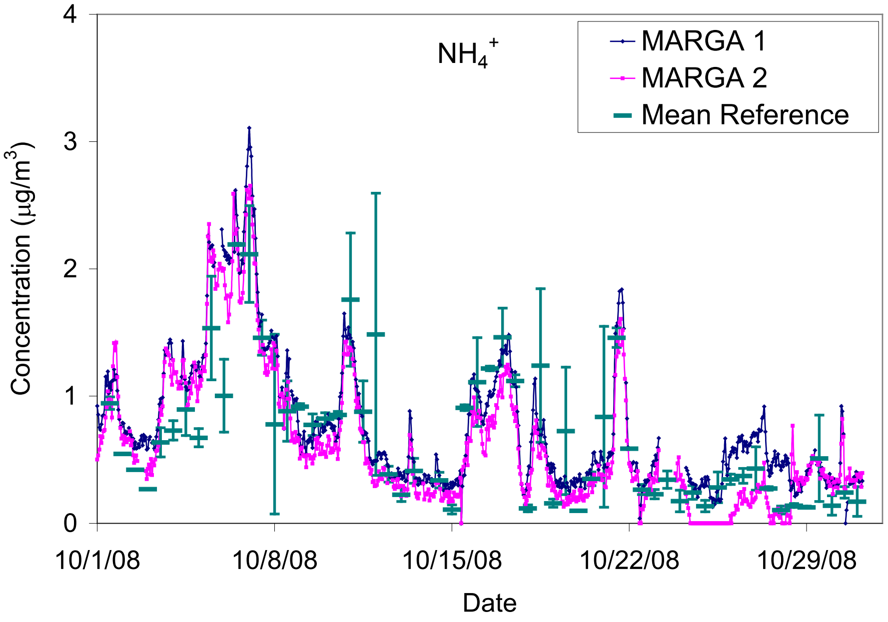

Figure 6-6. Time sequence plot of NH$_4^+$ measurement results from duplicate MARGA and mean denuder filter pack reference method measurements.

In addition to the denuder/filter pack reference samples, separate continuous gas analyzers were used to monitor SO_2 and NH_3. Figures 6-7 and 6-8 show time sequence plots of the measurements from these gas analyzers with the corresponding MARGA measurements.

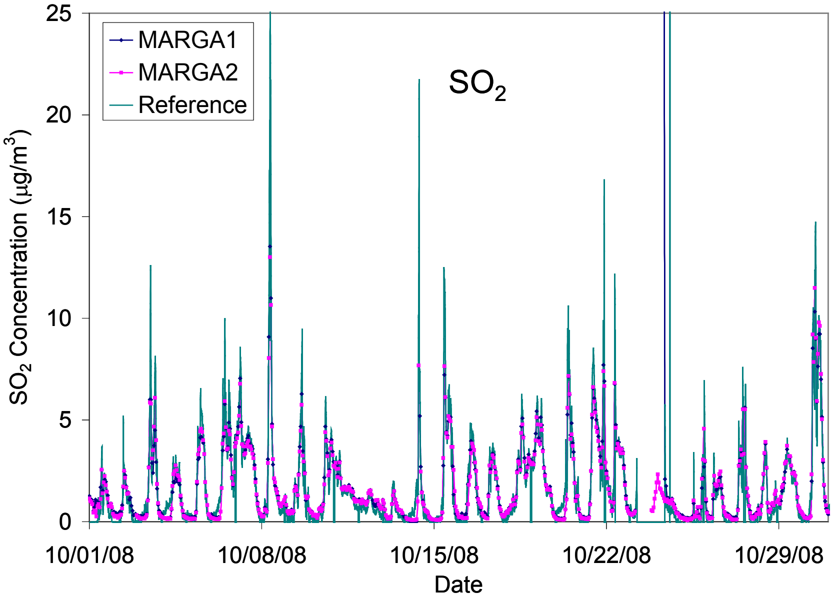

Figure 6-7. Time sequence plot of SO_2 measurement results from duplicate MARGA and Continuous SO_2 Reference Monitor.

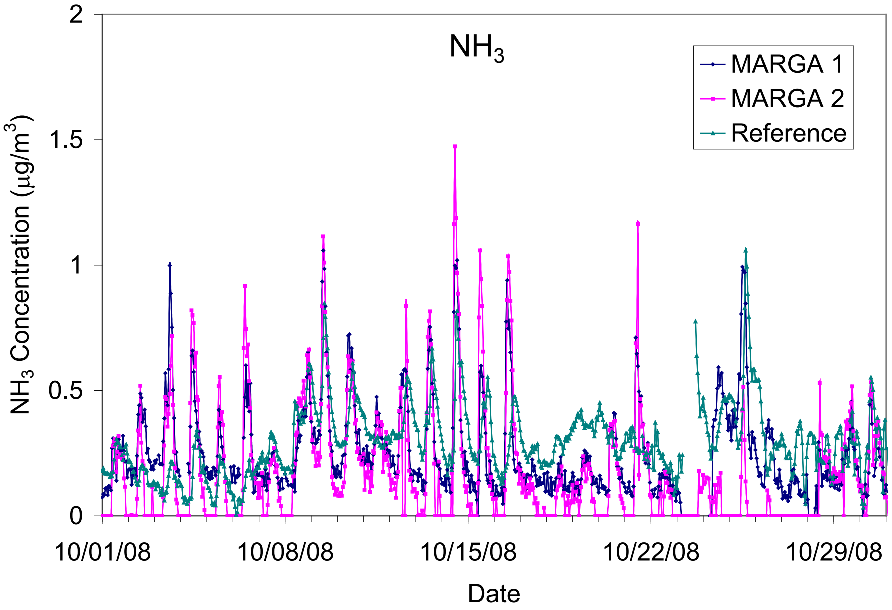

Figure 6-8. Time sequence plot of NH_3 measurement results from duplicate MARGA and the Mean of the Continuous NH_3 Reference Monitors.

As discussed in Chapter 4, a number of QA/QC activities were performed to assure the quality of the reference method data. Figure 6-9 shows scatter plots of the duplicate denuder/filter pack reference trains (Train 2 vs. Train 1) for each of the target analytes. The reference method data failed to meet some of the target performance goals established by EPA in consideration of the monitoring needs for CASTNET and are not always of sufficient quality to allow a definitive assessment of the MARGA in terms of these target performance goals. Nonetheless, the results of the verification tests of the MARGA semi-continuous ambient air monitoring system are presented below for each of the performance parameters. Where appropriate, the performance of the reference method relative to the target performance goals is shown to indicate the relative utility of the reference method results as an appropriate standard for testing against the target performance goals.

6.1 Accuracy

The accuracy of the MARGA systems 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 from each of the two MARGA monitoring unit and 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 for all sampling periods in which the measured reference concentrations were greater than twice the detection limit, as described in Section 5.1.2. The results of these analyses are presented below.

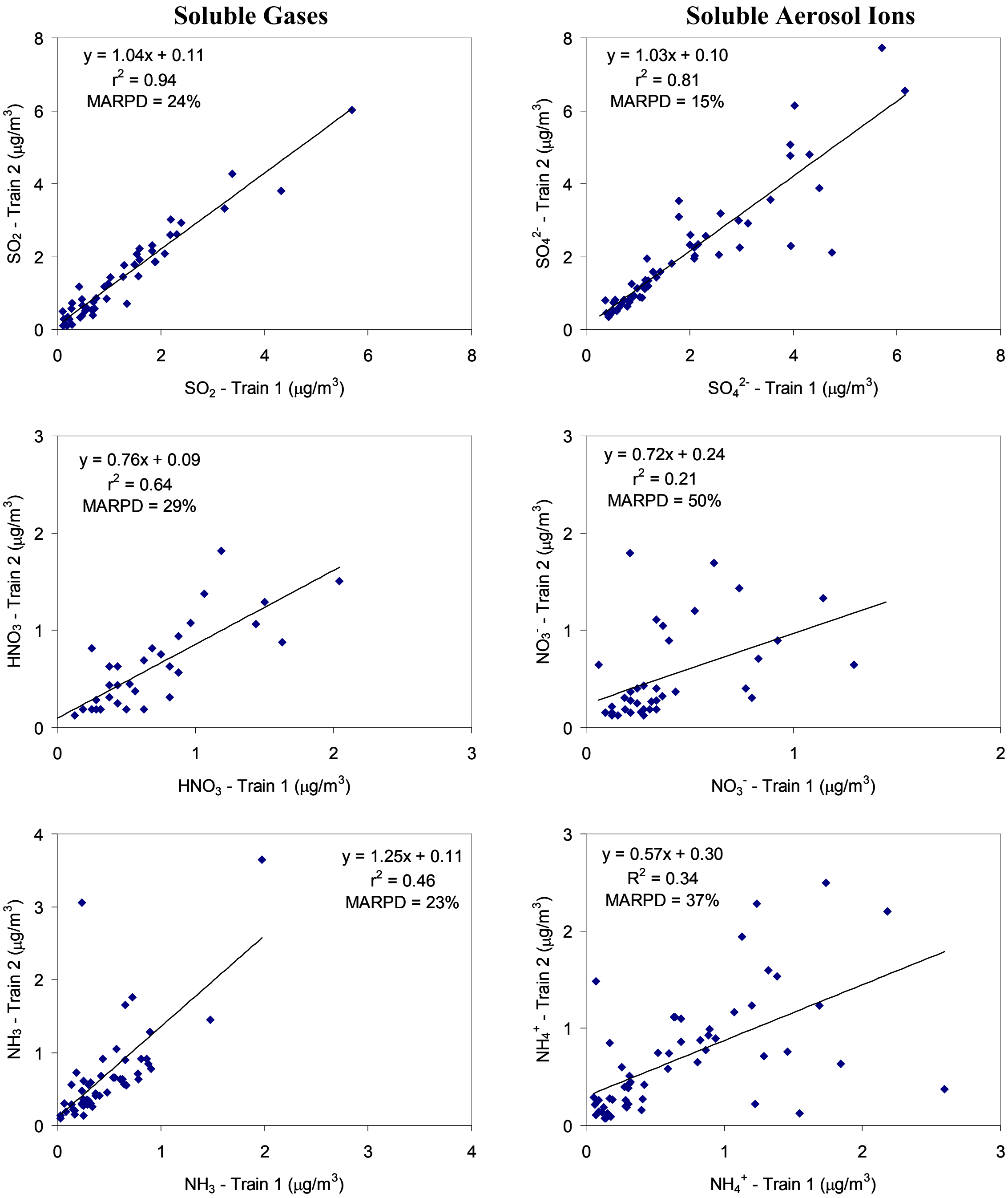

Figure 6-9. Scatter Plots Comparing Reference Data from Duplicate Trains for Target Analytes.

6.1.1 Regression Analysis

Figure 6-10 shows regression plots of the results from the duplicate MARGA instruments versus the denuder/filter pack reference results for each of the target analytes. Figure 6-11

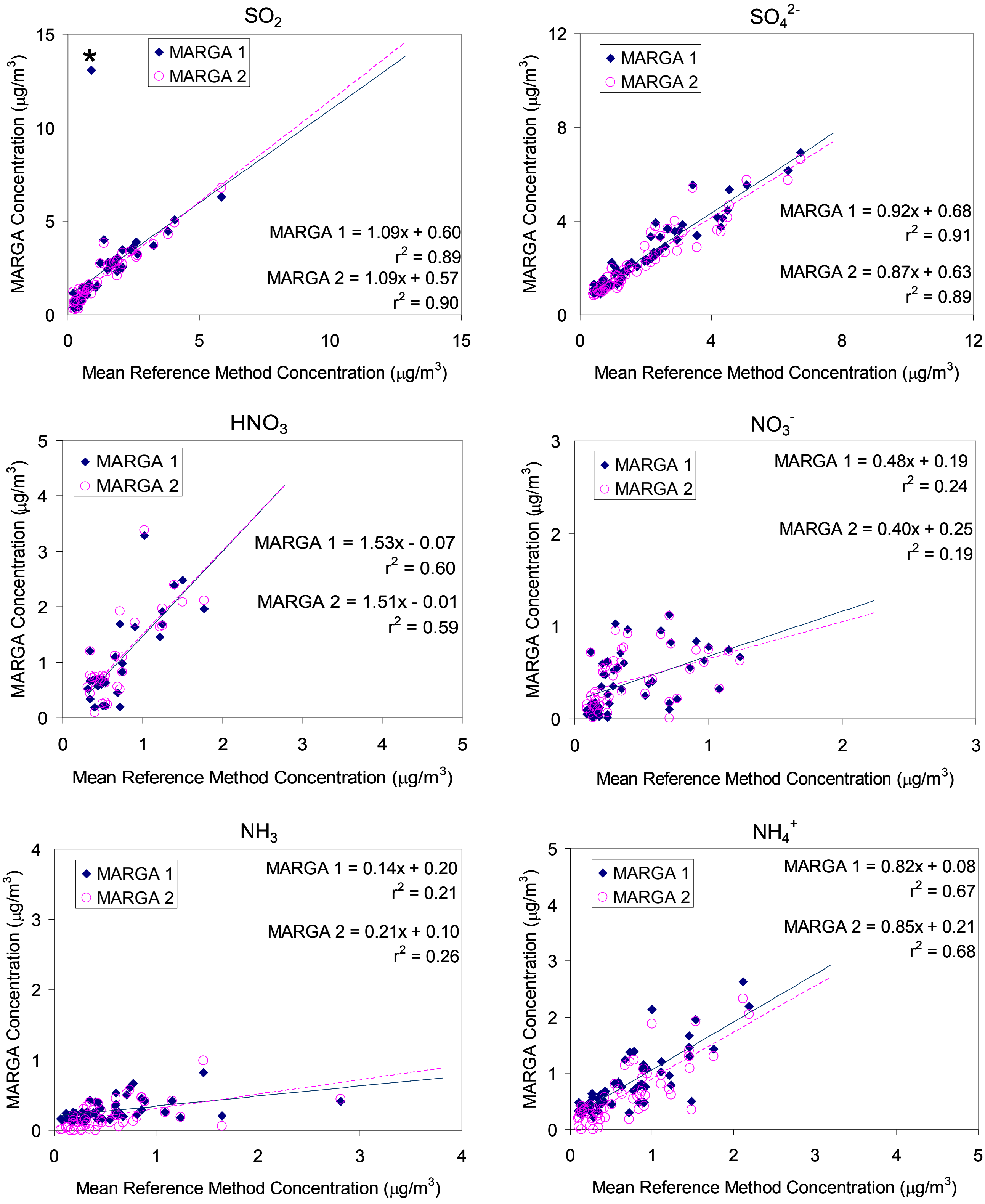

Figure 6-10. Regression Plots of MARGA data versus mean reference method data for SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and NH_4^+.(*One outlier excluded from the SO_2 regression for MARGA 1. This was the first data point recorded by the MARGA after a 15 hour power outage. With this point included slope is 1.00, intercept is 1.0, and r^2 is 0.31 for MARGA 1.)

shows scatter plots of the hourly MARGA readings versus hourly average readings from the reference continuous gas monitors.

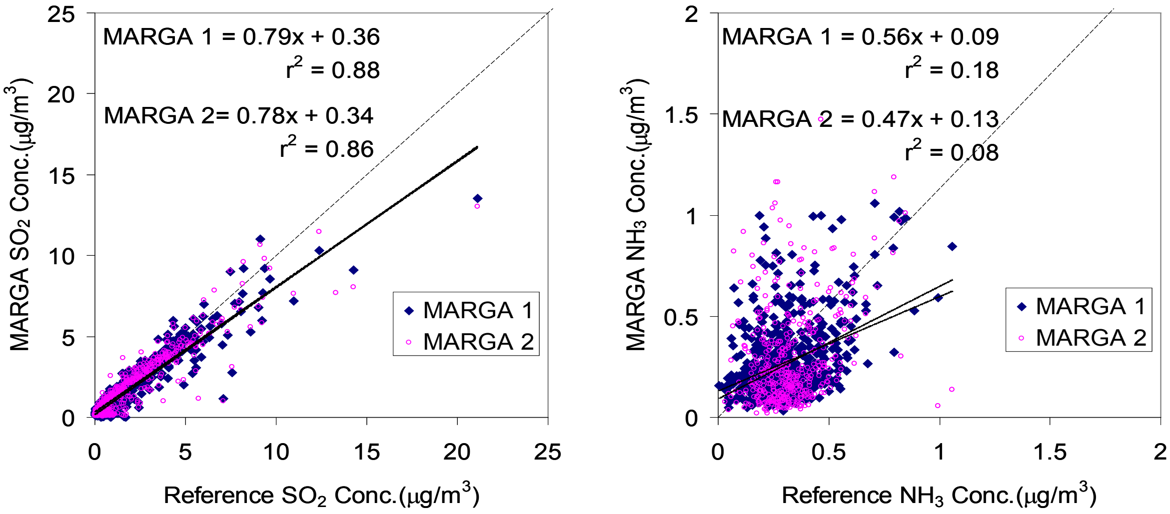

Figure 6-11. Regression Plots of MARGA data versus reference data from the continuous gas monitors for SO_2 and NH_3.

Table 6-1 presents a summary of the linear regression analysis of these data for each target analyte. Asterisks in this table indicate that the reference method measurements did not meet the target performance goals and should not be used as a basis for evaluating the performance of the MARGA.

Table 6-1. Summary of Regression Analysis Results for the MARGA Systems Relative to Reference Method Results.

Target Analyte (reference method)	MARGA 1			MARGA 2		
	Slope	Intercept µg/m^3	r^2	Slope	Intercept µg/m^3	r^2
SO_2 (12-hour)[a]	1.00 (1.09[b])	1.00 (0.60[b])	0.31 (0.89[b])	1.09	0.57	0.90
SO_2 (1-hour)[c]	0.79	0.36	0.88	0.78	0.34	0.86
HNO_3	1.53*	-0.07*	0.60*	1.51*	-0.01*	0.59*
NH_3 (12-hour)[a]	0.14	0.20	0.21	0.21	0.10	0.26
NH_3 (1-hour)[c]	0.56	0.09	0.18	0.47	0.13	0.08
SO_4^{2-}	0.92	0.68	0.91	0.87	0.63	0.89
NO_3^-	0.48*	0.19*	0.24*	0.40*	0.25*	0.19*
NH_4^+	0.82*	0.08*	0.67*	0.85*	0.21*	0.68*

a–Based on comparisons to 12-hour denuder/filter pack reference measurements.
b–Values for slope, intercept, and r^2 with removal of one outlier that occurred immediately after a power failure.
c–Based on comparisons to 1-hour continuous gas analyzer measurements.
* Duplicate denuder/filter pack reference method results do not meet target performance goals.

The target performance goals for semi-continuous ambient air monitoring systems call for a slope of the regression analysis between 0.80 and 1.20, and an intercept between 0 ± 10 parts per billion (ppb) for each analyte. Table 6-2 summarizes the performance of the duplicate MARGAs relative to these goals for each target analyte (note that the intercept values in Figure 6-10 and Table 6-1 were converted from μg/m^3 to ppb for comparison to the target performance goals). This table also considers the regression results from the duplicate reference method results as shown in Figure 6-9. A check mark in Table 6-2 means that the indicated method met the target performance goal for the indicated target analyte. Table 6-2 shows that whereas all target goals for regression intercept were met by both the reference methods and the MARGAs, the goals for regression slope were met by both reference and MARGA results only for SO_2 and SO_4^{2-}. In addition, the denuder/filter pack results met the slope goal for NH_3, and the MARGAs met the slope goal for NH_4^+. When the reference method results do not meet the performance goals, it is not appropriate to use them as a basis of comparison for the MARGA.

Table 6-2. Summary of Denuder/Filter Pack Reference Method and MARGA Regression Analysis Results versus Target Performance Goals

Target Analyte	Slope			Intercept		
	Reference	MARGA 1	MARGA 2	Reference	MARGA 1	MARGA 2
SO_2	✓	✓	✓	✓	✓	✓
HNO_3	○	○	○	✓	✓	✓
NH_3	✓	○	○	✓	✓	✓
SO_4^{2-}	✓	✓	✓	✓	✓	✓
NO_3^-	○	○	○	✓	✓	✓
NH_4^+	○	✓	✓	✓	✓	✓

NA – Not applicable. Only a single continuous analyzer was used.
✓ indicates that target performance goal was met.
○ indicates that target performance goal was not met.

6.1.2 MARPD Analysis

Table 6-3 presents a summary of the calculated MARPD results and whether the results meet the target accuracy goals for each target analyte for each of the duplicate MARGA systems. The MARPD of the paired denuder/filter pack reference data has been included to show the precision of the reference data. In all cases except for SO_4^{2-}, the duplicate reference method measurements failed to meet the precision DQO of ≤ 20%. In most cases this was likely because of the very low and narrow range of concentrations of the target analytes during the testing period. Because the reference method failed to meet the testing DQO, comparisons of the MARGA data to the reference data should not be considered as conclusive evidence of MARGA performance. Nonetheless, in the one instance where the reference data did meet the DQO, both MARGA units met the target accuracy goal (for SO_4^{2-}). Both MARGA units also met the target goals in one other case where the reference method failed to meet the testing DQO (for NH_4^+).

Table 6-3. Summary of Calculated MARPD Results for Reference Data and MARGA Systems

Target Analyte	Reference Method*	MARGA 1		MARGA 2	
	MARPD (DQO ≤ 20%)	MARPD	Target Goal	MARPD	Target Goal
SO_2	21%	59%	○	53%	○
HNO_3	22%	42%	○	43%	○
NH_3	21%	41%	○	64%	○
SO_4^{2-}	15%	35%	✓	35%	✓
NO_3^-	56%	66%	○	69%	○
NH_4^+	32%	24%	✓	29%	✓

✓ indicates that target performance goal was met.
○ indicates that target performance goal was not met.
* Reference method data (other than SO_4^{2-}) did not meet the data quality objectives (DQOs) set forth for this evaluation (MARPD < 20%). Comparisons of reference method data to MARGA data are presented, but it should be noted that the reference data did not meet the DQOs.

6.2 Precision

Precision was assessed in two ways as described in Section 5.2. Firstly, the MARPD of paired 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 resulting MARPD results for the duplicate MARGAs. This table also presents a summary of the number of data points for each analyte where both MARGA results exceeded twice the detection limit as well as the number of points below twice the detection limit for each MARGA. For all analytes, the duplicate MARGAs met the target precision goal of MARPD ≤ 25%, with the MARPD values ranging from 5% for SO_2 to 20% for NH_4^+.

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

Target Analyte	MARPD (Goal ≤ 25%)	Number of Data Points with Both Monitors above 2 x DL	Number of Data Points below 2 x DL	
			MARGA 1	MARGA 2
SO_2	5%	552	59	113
HNO_3	12%	341	314	296
NH_3	18%	239	237	413
SO_4^{2-}	9%	651	1	0
NO_3^-	8%	368	279	253
NH_4^+	20%	575	13	112

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 target performance goal for this measure of precision is for the MARPD of the MARGAs to be less than the corresponding 95th percentile of the reference data. The MARGAs met this performance goal for all target analytes, exhibiting better duplicate precision than did the reference measurements.

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

Target Analyte	RPD_{95}	MARPD (%)	Met Target Goal
SO_2	76%	5%	✓
HNO_3	51%	10%	✓
NH_3	121%	26%	✓
SO_4^{2-}	57%	10%	✓
NO_3^-	168%	6%	✓
NH_4^+	137%	23%	✓

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 average percentage of valid data collected per day and as the average percentage of valid data collected during each reference period when detectable levels were observed in both reference method samples. Data validity, as reported by the MARGA systems, was used to evaluate data completeness; no external validation procedure was used. Completeness was calculated independently for each MARGA and for each target analyte. Included in this calculation were the MARGA analytes Na^+, Ca^{2+}, and Cl^-, which were not included in evaluations for other performance parameters. Table 6-6 summarizes the results of the data completeness calculations. All of the completeness results in Table 6-7 exceed the target value of $\geq$80%, except for the valid data per reference period result for Cl^- for MARGA 1.

6.4 Reliability

Instrument reliability was assessed in three ways. First, 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. The target goal for this metric is $\geq$90%. Second, reliability was assessed in terms of the ability of the instruments to perform a controlled shut-down in the case of a power failure, followed by an automated return to measurement mode within four hours after power was restored. For this assessment, the testing staff imposed a temporary power outage at the test site and monitored the performance of one of the monitoring systems during and after the power outage. Additionally, the average number of site visits per week

Table 6-6. Summary of Data Completeness for MARGAs

Target Analyte	Average % of Valid Data per Day (e.g., per 24 hours)		Average % of Valid Data per Reference Sampling Period (e.g., per 12 hours)	
	MARGA 1	MARGA 2	MARGA 1	MARGA 2
SO_2	91%	90%	94%	98%
HNO_3	91%	90%	85%	98%
NH_3	90%	90%	93%	97%
SO_4^{2-}	90%	90%	94%	98%
NO_3^-	91%	90%	95%	99%
NH_4^+	90%	90%	93%	98%
Na^+	90%	90%	94%	96%
Ca^{2+}	90%	90%	NA	NA
Cl^-	91%	90%	40%	90%

NA – not available, as Ca^{2+} was never detected in both reference method samples for a given sampling period.

that were required to keep the MARGA units operating was recorded; the target goal is ≤2 visits per week. These assessments are reported independently for the duplicate monitoring systems in Table 6-7, which shows that the MARGA units met all reliability goals. Note that MARGA startup after a power outage can occur in less than one hour, provided the outage occurs early enough in the instrument's hourly sampling/analysis cycle. However, even if the outage occurs very late in the current hourly cycle the startup will occur by the end of the subsequent hour. As a result, the time to startup shown in Table 6-7 (< 2 hours) covers all outage conditions.

Table 6-7. Summary of MARGA Reliability Assessments

	% of Time in Operating Mode	Time to Start-up after Power Interruption	Average Site Visits (per week)
MARGA 1	95%	NA	1.6
MARGA 2	96%	< 2 hours	1.6

NA: Not applicable, power interruption test only conducted for MARGA 2.

6.5 Operational Factors

Table 6-8 presents a summary of the maintenance activities performed on the MARGA systems during the verification test.

6.5.1 Ease of Use

The MARGA systems were installed by a single representative of Applikon BV prior to testing. No documentation of the time required for the installation was available, however, the representative of Applikon BV indicated that the installation was completed over the course of 3-4 days. The MARGA systems operated primarily unattended during the verification test, and all maintenance activities performed on the MARGA systems were performed by a representative of Applikon BV.

Table 6-8. Summary of Maintenance Activities Performed on MARGAs During Verification Testing

Date	Duration	Activity	Down Time
10/03/08	2.5 hours	Replacement of wetted rotating denuder on MARGA1, alignment screw adjustment, tubing length on new denuder shortened.	None
10/06/08	1.5 hours	Check syringe pump operation on MARGA1.	3 hours
10/07/08	10 minutes	Add solution to anion eluent, cation eluent, and absorbing solution reservoirs. Empty waste container.	None
10/08/08	5 minutes	Filter exchange on MARGA1 and MARGA2.	None
10/14/08	10 minutes	Add solution to anion eluent, cation eluent, and absorbing solution reservoirs. Empty waste container.	None
10/15/08	5 minutes	Filter exchange on MARGA1 and MARGA2.	None
10/21/08	10 minutes	Add solution to anion eluent, cation eluent, and absorbing solution reservoirs. Empty waste container.	None
10/22/08	5 minutes	Filter exchange on MARGA1 and MARGA2	None
10/23/08	10 minutes	Instruments put back in measurement mode after a power outage at the site.	15 hours
10/24/08	20 minutes	Remove air from denuder syringe pumps on MARGA1.	11 hours
10/28/08	5 minutes	Add absorbing solution to MARGA1.	None
10/29/08	10 minutes	Reboot both computers to restart data writing to files.	None
10/30/08	10 minutes	Add solution to anion eluent, cation eluent, suppressor regenerant, and absorbing solution reservoirs. Empty waste container. Filter exchange on MARGA1 and MARGA2.	None

6.5.2 Maintenance

Routine maintenance consisted of preparation and changeout of cation and anion IC eluents, absorbing solution, internal standard, and suppressor regenerant. Cation eluent, anion eluent, and absorbing solution were refilled on a weekly basis. The suppressor regenerant and internal standard were prepared once at the beginning of the study and lasted for the entire 30 day duration. Additionally, particle filters downstream of the aerosol collection device were changed on a weekly basis. The Applikon BV representative chose to change these particle filters on a different day than the solution changeouts, but those activities would generally be performed in one site visit. Other maintenance activities included replacement of the wetted rotating denuder, syringe pump maintenance, reboot of instrument software, and maintenance related to an unplanned power failure during the study.

6.5.3 Consumables/Waste Generation

During the verification test, the MARGA systems required the use of several standard consumable materials. The consumables that were used included absorbing solution (deionized water), internal lithium bromide standard, suppressor regenerant (sulfuric acid), cation eluent (sodium carbonate and sodium bicarbonate solution), anion eluent (nitric acid) and particle filters. The eluents were consumed at a rate of approximately 5 L per week for each instrument. Absorbing solution was consumed at a rate of approximately 15 L per week for each instrument. Internal standard and suppressor regenerant were consumed at approximately 1 L per week for each instrument. Approximately 20 L of waste were generated by each instrument in one week. Waste was emptied once per week. All wastes are considered non-hazardous and do not require any special treatment for disposal.

Chapter 7
Performance Summary

Table 7-1 presents a summary of the results of the verification of the MARGA systems during this verification test. It is important to note that the reference method data for this verification test failed to meet some of the target performance goals specified by EPA in consideration of the monitoring needs for CASTNET. Specifically, the reference data for HNO_3, NO_3^-, and NH_4^+ failed to meet the target performance goals for accuracy based on a regression analysis. Also, the duplicate reference method data failed to meet the data quality objectives of this verification test for MARPD for all target analytes except SO_4^{2-}. In those cases, the data are annotated in Table 7-1 and should not be considered to be of sufficient quality to allow a definitive assessment of the MARGA. Bolded entries indicate that the target performance goal was met.

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

Parameter Evaluated	Method of Evaluation	Results				
		Analyte	**MARGA 1**		**MARGA 2**	
			Slope	**Intercept ($\mu g/m^3$)**	**Slope**	**Intercept ($\mu g/m^3$)**
Accuracy	Regression analysis comparison to reference samples	SO_2	**1.00 (1.09[a])**	**1.00 (0.60[a])**	**1.09**	**0.57**
		HNO_3	1.53*	**-0.07***	1.51*	**-0.01***
		NH_3	0.14	**0.20**	0.21	**0.10**
		SO_4^{2-}	**0.92**	**0.68**	**0.87**	**0.63**
		NO_3^-	0.48*	**0.19***	0.40*	**0.25***
		NH_4^+	**0.82***	**0.08***	**0.85***	**0.21***
		Analyte	**MARPD**			
			MARGA 1		**MARGA 2**	
Accuracy	Calculation of MARPD between MARGA results and reference method results	SO_2 **	59%		53%	
		HNO_3 **	42%		43%	
		NH_3 **	41%		64%	
		SO_4^{2-}	**35%**		**35%**	
		NO_3^- **	66%		69%	
		NH_4^+ **	**24%**		**29%**	

Table 7-1. (Continued)

<table>
<tr><th>Parameter Evaluated</th><th>Method of Evaluation</th><th colspan="5">Results</th></tr>
<tr><td rowspan="7">Precision</td><td rowspan="7">Comparison of results from duplicate monitoring systems</td><th colspan="3">Analyte</th><th colspan="2">1-Hour MARPD</th></tr>
<tr><td colspan="3">SO_2</td><td colspan="2">5%</td></tr>
<tr><td colspan="3">HNO_3</td><td colspan="2">12%</td></tr>
<tr><td colspan="3">NH_3</td><td colspan="2">18%</td></tr>
<tr><td colspan="3">SO_4^{2-}</td><td colspan="2">9%</td></tr>
<tr><td colspan="3">NO_3^-</td><td colspan="2">8%</td></tr>
<tr><td colspan="3">NH_4^+</td><td colspan="2">20%</td></tr>
<tr><td rowspan="7">Precision</td><td rowspan="7">Comparison of MARPD of 12-hour average MARGA data and 95th percentile of pooled RPD results from reference measurements (RPD_{95})</td><th colspan="2">Analyte</th><th>Ref. Method RPD_{95}</th><th colspan="2">MARGA 12-Hour MARPD</th></tr>
<tr><td colspan="2">SO_2</td><td>76%</td><td colspan="2">5%</td></tr>
<tr><td colspan="2">HNO_3</td><td>51%</td><td colspan="2">10%</td></tr>
<tr><td colspan="2">NH_3</td><td>121%</td><td colspan="2">26%</td></tr>
<tr><td colspan="2">SO_4^{2-}</td><td>57%</td><td colspan="2">10%</td></tr>
<tr><td colspan="2">NO_3^-</td><td>168%</td><td colspan="2">6%</td></tr>
<tr><td colspan="2">NH_4^+</td><td>137%</td><td colspan="2">23%</td></tr>
<tr><td rowspan="11">Data completeness</td><td rowspan="11">Ratio of number of samples successfully collected to number of potential samples that could have been collected</td><th rowspan="2">Target Analyte</th><th colspan="2">Average % of Valid Data per Day (e.g., per 24 hours)</th><th colspan="2">Average % of Valid Data per Reference Sampling Period (e.g., per 12 hours)</th></tr>
<tr><th>MARGA 1</th><th>MARGA 2</th><th>MARGA 1</th><th>MARGA 2</th></tr>
<tr><td>SO_2</td><td>91%</td><td>90%</td><td>94%</td><td>98%</td></tr>
<tr><td>HNO_3</td><td>91%</td><td>90%</td><td>85%</td><td>98%</td></tr>
<tr><td>NH_3</td><td>90%</td><td>90%</td><td>93%</td><td>97%</td></tr>
<tr><td>SO_4^{2-}</td><td>90%</td><td>90%</td><td>94%</td><td>98%</td></tr>
<tr><td>NO_3^-</td><td>91%</td><td>90%</td><td>95%</td><td>99%</td></tr>
<tr><td>NH_4^+</td><td>90%</td><td>90%</td><td>93%</td><td>98%</td></tr>
<tr><td>Na^+</td><td>90%</td><td>90%</td><td>94%</td><td>96%</td></tr>
<tr><td>Ca^{2+}</td><td>90%</td><td>90%</td><td>NA</td><td>NA</td></tr>
<tr><td>Cl^-</td><td>91%</td><td>90%</td><td>40%</td><td>90%</td></tr>
<tr><td>Reliability</td><td>Percentage of time in operating mode</td><td colspan="5">MARGA 1: 95% MARGA 2: 96%</td></tr>
<tr><td>Reliability</td><td>Time to start-up after power interruption</td><td colspan="5">MARGA 1: Not tested MARGA 2: < 2 hours</td></tr>
<tr><td>Reliability</td><td>Number of site visits per week</td><td colspan="5">MARGA 1: 1.6 MARGA 2: 1.6</td></tr>
</table>

Table 7-1. (Continued)

Ease of use	Operator observations	• Routine operations of the instrument were generally easy with the only regularly scheduled tasks being solution preparation and changing, and filter replacement • Installation performed by Applikon over 3-4 days (not independently observed as part of this verification)
Maintenance	Operator observations	• Routine maintenance consists of preparing and changing/refilling solutions and replacement of particle filters • Non-routine maintenance observed included wet rotating denuder replacement, syringe pump maintenance, and PC reboot to restart data acquisition
Consumables/waste generated	Operator observations	• Cation and anion eluents, and absorbing solution refilled weekly • Supressor regenerant and internal standard refilled monthly • Internal filters replaced weekly • Waste emptied weekly

* Duplicate denuder/filter pack reference method results do not meet target performance goals for the MARGA and should not be used for performance evaluation.

** Reference method data (other than SO_4^{2-}) did not meet the data quality objectives (DQOs) set forth for this evaluation (MARPD < 20%). Comparisons of reference method data to MARGA data are presented, but it should be noted that the reference data did not meet the DQOs.

[a] Values for slope and intercept with removal of one outlier that occurred immediately after a power failure.

Chapter 8
References

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