Battelle
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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Test/Quality Assurance Plan for Verification of Isotopic Carbon Dioxide Analyzers for Carbon Sequestration Monitoring

ETV ETV ETV

TEST/QUALITY ASSURANCE PLAN

for

Verification of
Isotopic Carbon Dioxide Analyzers
for Carbon Sequestration Monitoring

Version 1.0

July 1, 2010

Prepared by

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SECTION A

PROJECT MANAGEMENT

A1 VENDOR APPROVAL PAGE

ETV Advanced Monitoring Systems Center

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July 1, 2010
APPROVAL:

Name ________________________________

Company ______________________________

Date _________________________________

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A3 LIST OF ACRONYMS AND ABBREVIATIONS

%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
ABT	ambient breeze tunnel
ADQ	audit of data quality
AMS	Advanced Monitoring Systems
cfm	cubic feet per minute
CO_2	carbon dioxide
COA	certificates of analysis
CRDS	cavity ring down spectroscopy
DQIs	data quality indicators
EPA	U.S. Environmental Protection Agency
QMP	Quality Management Plan
ETV	Environmental Technology Verification
GCS	geologic carbon sequestration
IRMS	isotope ratio mass spectrometry
Lpm	liter per minute
LRB	laboratory record book
ppm	parts per million by volume
PDB	Pee Dee Belemnite
PE	performance evaluation
PO	project officer
QA	quality assurance
QC	quality control
QCL	quantum cascade laser
QMP	Quality Management Plan
RMO	Records Management Office
TQAP	test/quality assurance plan
TSA	technical systems audit

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A5 VERIFICATION TEST ORGANIZATION

The verification test described in this document will be conducted under the Environmental Technology Verification (ETV) Program. It will be performed by Battelle, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with the U.S. Environmental Protection Agency (EPA). The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil.

This verification test will be coordinated and directed by Battelle in cooperation with the EPA, with the support of staff at a geologic carbon sequestration (GCS) site. Laboratory and field testing will be conducted over a five-week period at three testing locations: a Battelle laboratory in Columbus, Ohio; a Battelle testing facility in West Jefferson, Ohio; and a coal-fired power plant where carbon dioxide (CO_2) captured from the flue gas is being geologically sequestered. The testing will involve the evaluation of commercial isotopic CO_2 analyzers, which may include cavity ring down spectroscopy (CRDS) and pulsed quantum cascade laser (QCL) spectroscopy monitoring systems specifically for the measurement of stable carbon isotope ratios ($^{13}C/^{12}C$) and CO_2 concentration ($^{12}CO_2 + ^{13}CO_2$). Battelle staff at the sequestration site will provide on-site support during the verification test.

The vendors of the CO_2 analyzers being tested will install, operate, and repair or maintain one of their systems during the verification test.

Quality assurance (QA) oversight will be provided by the Battelle AMS Center Quality Manager, and by the EPA AMS Center QA Manager at her discretion. The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals associated with the verification test. Roles and responsibilities are defined further below.

A5.1 Battelle

Dr. Ann Louise Sumner is the AMS Center Verification Test Coordinator for this test. In this role, Dr. Sumner will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, she will:

- Assemble a team of qualified technical staff to conduct the verification test.

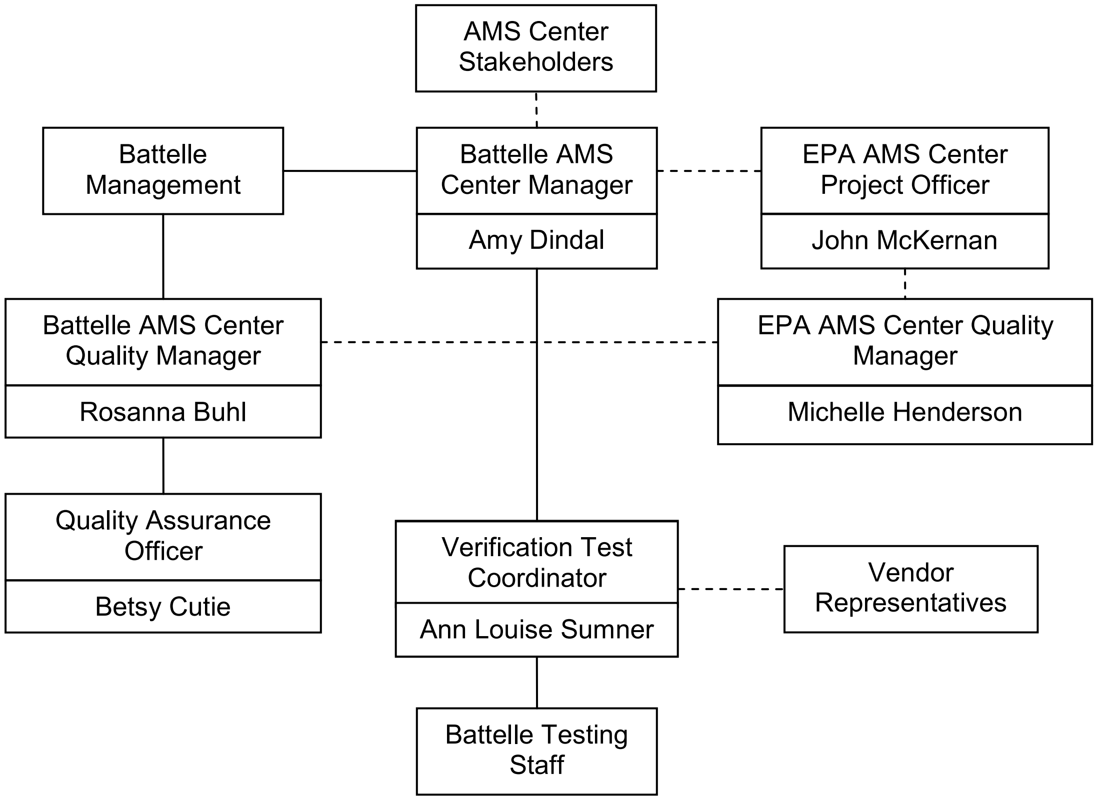

Figure 1. Organizational Chart

- Hold a kick-off meeting approximately one week prior to the start of the verification test to review the critical logistical, technical, and administrative aspects of the verification test. Responsibility for each aspect of the verification test will be confirmed.
- Direct the team (Battelle testing staff and vendor) in performing the verification test in accordance with this test/QA plan (TQAP).
- Ensure that all quality procedures specified in the TQAP and in the AMS Center Quality Management Plan[1] (QMP) are followed.
- Maintain real-time communication with the Battelle AMS Center Manager and EPA AMS Center Project Officer and Quality Assurance Manager on any potential or actual deviations from the TQAP.
- Coordinate with Battelle Testing Staff to ensure that the planned testing will not interfere with the carbon sequestration site operations.

- Provide test data, including data from the first day of testing, to the Battelle AMS Center Manager and EPA AMS Center Project Officer and Quality Assurance Manager
- Prepare the draft and final TQAP, verification report(s), and verification statement(s).
- Conduct a technical review of all test data. Designate an appropriate Battelle technical staff member to review data generated by the Verification Test Coordinator.
- Revise the draft TQAP, verification report(s), and verification statement(s) in response to reviewers' comments.
- Compile data from the first day of the verification test and provide the data to EPA for review.
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.
- Serve as the primary point of contact for vendor representatives and collaborators.
- Coordinate distribution of the final TQAP, verification report(s), and statement(s).
- Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.

Ms. Amy Dindal is Battelle's manager for the AMS Center. Ms. Dindal will:

- Review the draft and final TQAP.
- Review the draft and final verification report(s) and verification statement(s).
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.
- Ensure that confidentiality of sensitive vendor information is maintained.
- Maintain communication with EPA's AMS Center Project Officer and Quality Manager.
- Facilitate a stop work order if Battelle or EPA QA staff discover adverse findings that will compromise data quality or test results.

Battelle Testing Staff will conduct portions of the testing of the CO_2 analyzers at each of the three sites and will be in weekly communication with the Verification Test Coordinator, and with technology vendors as needed. The responsibilities of the field testing staff will be to:

- Coordinate with the test site to ensure that Battelle testing staff, vendors, EPA, and subcontractors have appropriate access to the test site.
- Coordinate with test site to ensure suitable space and electrical power to perform the necessary testing activities at the test site.
- Coordinate the operation of the test site for the purposes of ETV testing.
- Coordinate the installation of vendors' equipment at the test sites.
- Communicate needs for safety and other training of staff working at the test site.
- Perform the verification test as described in the TQAP.
- Record qualitative observations about the maintenance and operation of the CO_2 analyzers during testing.
- Ensure that the data from the CO_2 analyzers are immediately checked, and on at least a weekly basis, compiled, recorded, and transmitted to the Verification Test Coordinator.
- Provide input in responding to any issues raised in assessment reports and audits related to facility operations.
- Perform analysis of the collected data to carry out the statistical evaluations in Section B1.2.
- Provide input on test procedures, technology operation and maintenance, and field conditions for the draft verification reports.
- Review draft verification reports and statements as needed.

Ms. Rosanna Buhl is Battelle's Quality Manager for the AMS Center. Ms. Buhl will:

- Review the draft and final TQAP.
- Assign a Quality Assurance Officer (QAO) for this verification test.
- Delegate to other Battelle quality staff any QAO responsibilities assigned below as needed to meet project schedules.
- Review any audit checklists prepared by the QAO for completeness and detail.

- Review draft and final audit reports prior to release to the VTC and/or EPA for clarity and appropriate assessment of findings.
- Review audit responses for appropriateness.
- Review and approve TQAPs and deviations.
- Review draft and final verification report(s) and verification statement(s).
- Maintain real-time communication with the QAO on QA activities, audit results, and concerns.
- Work with the QAO, VTC, and Battelle's AMS Center Manager to resolve data quality concerns and disputes.
- Recommend a stop work order if audits indicate that data quality or safety is being compromised.

Ms. Betsy Cutie is Battelle's QAO for this test. Ms. Cutie will:

- Attend the verification test kick-off meeting and lead the discussion of the QA elements of the kick-off meeting checklist.
- Prior to the start of verification testing, verify the presence of applicable training records, including any vendor training on test equipment.
- Conduct a technical systems audit at least once near the beginning of the verification test.
- Conduct audits to verify data quality.
- Prepare and distribute an audit report for each audit.
- Verify that audit responses for each audit finding and observation are appropriate and that corrective action has been implemented effectively.
- Communicate to the VTC and/or technical staff the need for immediate corrective action if an audit identifies TQAP deviations or practices that threaten data quality.
- Provide a summary of the QA/QC activities and results for the verification reports.
- Review the draft and final verification report(s) and verification statement(s).
- Maintain real-time communication with the Battelle Quality Manager on QA activities, audit results, and concerns, including potential schedule and budget problems.

- Communicate data quality concerns to the VTC and/or Battelle's AMS Center Quality Manager; recommend the need for a stop work order if audits indicate that data quality or safety is being compromised.

A5.2 Vendors

The responsibilities of the CO_2 analyzer vendors are as follows:

- Review and provide comments on the draft TQAP.
- Approve the final TQAP prior to test initiation.
- Provide a complete CO_2 analyzer for evaluation during the verification test.
- Provide all other equipment/supplies/reagents/consumables needed to operate their monitoring system for the duration of the verification test.
- Supply a representative to install and maintain their technology, and to operate it in portions of the test specified in this TQAP, or provide written consent and instructions for Battelle staff to carry out these activities.
- Provide the data from the monitoring system to the Battelle field testing staff within one week of collection.
- Provide training to site operator(s) and others associated with supervising and/or maintaining system operation including during the verification testing period.
- Provide written instructions for routine operation of their technologies, including a daily checklist of diagnostic and/or maintenance activities.
- Review and provide comments on the draft verification report and statement for their monitoring system.

A5.3 EPA

EPA's responsibilities are based on the requirements stated in the "Environmental Technology Verification Program Quality Management Plan"[2] (ETV QMP). The roles of specific EPA testing staff are as follows:

Ms. Michelle Henderson is EPA's AMS Center QA Manager. Ms. Henderson will:

- Review the draft TQAP.
- Review the first day of data from the verification test and provide immediate comments if concerns are identified.
- Perform at her option one external technical systems audit and/or audit of data quality during the verification test.
- Notify the EPA AMS Center Manager of the need for a stop work order if the external audit indicates that data quality or safety is being compromised.
- Prepare and distribute an assessment report summarizing results of the external audit.
- Review the draft verification report(s) and statement(s).

Dr. John McKernan is EPA's Project Officer for the AMS Center. Dr. McKernan will:

- Review the draft TQAP.
- Approve the final TQAP.
- Review and approve deviations to the approved final TQAP.
- Appoint a delegate to review and approve deviations to the approved final TQAP in his absence, so that testing progress will not be delayed. Review the first day of data from the verification test and provide immediate comments if concerns are identified.
- Review the draft verification report(s) and statement(s).
- Oversee the EPA review process for the verification report(s) and statement(s).
- Coordinate the submission of verification report(s) and statement(s) for final EPA approval.

A5.5. Verification Test Stakeholders

This TQAP and the verification report(s) and verification statement(s) based on testing described in this document will be reviewed by experts in the fields related to carbon sequestration and/or analytical instrumentation. The following experts have been providing input to this TQAP and have agreed to provide a peer review:

- Sally M. Benson, Stanford University, Global Climate and Energy Project Director
- Chuck Dene, Electric Power Research Institute

- Dominic C. DiGiulio, US EPA
- Bruce J. Kobelski, US EPA
- Eben Thoma, US EPA

The responsibilities of verification test stakeholders include:

- Participate in technical panel discussions (when available) to provide input to the test design.
- Review and provide input to the TQAP
- Review and provide input to the verification report(s)/verification statement(s).

In addition, the TQAP in general was reviewed with the broader AMS Center Stakeholder Committee as a presentation during regular stakeholder teleconferences, including the November 5, 2009 meeting, and input from the committee was solicited.

A6 BACKGROUND

A6.1 Technology Need

The ETV Program's AMS Center conducts third-party performance testing of commercially-available technologies that detect or monitor natural species or contaminants in air, water, and soil. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Among the technology categories recommended for testing are isotopic CO_2 analyzers. In particular, the use of isotopic CO_2 analyzers for the monitoring of carbon sequestration sites for possible leakage was identified as an area of interest for technology verification.

Research on carbon storage in geologic reservoirs such as saline formations, coal seams, and depleted oil and gas fields, has gained momentum in recent years as interest in mitigation of greenhouse gases, such as CO_2, has increased and a number of pilot-studies have recently been brought online. Capture and geologic sequestration of CO_2 involves capturing emissions at a power plant or other large source, separating the emissions to isolate CO_2, and compressing the gas. The compressed CO_2 is injected into a deep underground rock formation. Potential sites are carefully evaluated for adequacy of containment layers, seismic stability, and other factors. As pilot- and full-scale geologic sequestration programs continue to be implemented, so do the needs to monitor leakage. GCS sites are expected to have several types of monitoring needs, as presented in Table 1.

Table 1. Anticipated Monitoring Needs for the GCS Sites

Location	Hazard	Monitoring Needs	Practical Considerations
High risk areas (transmissions lines, wells, etc.)	Subsurface emissions Above surface equipment leaks	• May result in high CO_2 in adjacent area (depending on magnitude of leak) • CO_2 source easily identified • Portable single-point analyzer for conducting surveys • Remote survey tool	• Ability to detect subsurface leak above ground • High sensitivity analyzers provide early detection • Ability to pinpoint leak location • Variability in ambient CO_2 concentrations
Sensitive ecosystems/ population centers near sequestration site	Intrusion from nearby well or geologic feature	• Sensitive ambient monitoring • Ability to identify or characterize CO_2 source	• Ability to detect leaks in ambient air • Variability in ambient CO_2 concentrations • High sensitivity analyzers provide early detection
Sequestration field	Quantify total emissions	• Survey tools • Open path systems • Flux chambers	• Ability to quantify emissions over large geographic area • Trace mapped emissions to source

Stable isotope analysis can be used in environmental forensics, for example to aid in determining the source of carbon dioxide. Deviations in the ratio of ^{13}C to ^{12}C ($^{13}C/^{12}C$) in atmospheric CO_2 relative to that in ambient air can be used to identify input from other carbon sources, such as fossil fuel combustion, since atmospheric, carbonate, and plant-derived carbon differ in their $^{13}C/^{12}C$ relative to the Pee Dee Belemnite (PDB) standard. The relative difference in stable carbon isotope from the PDB standard, referred to as $\delta^{13}C$, is calculated as shown in Equation A-1 and expressed in per mil (‰), or part per thousand.

$$\delta^{13}C_{Sample} = \left(\frac{^{13}C/\,^{12}C_{Sample}}{^{13}C/\,^{12}C_{PDB}} - 1\right) \times 1000 \qquad \text{(A-1)}$$

Since the PDB standard was highly enriched in ^{13}C, most naturally occurring carbon sources have a negative $\delta^{13}C$ value. For example, ambient air CO_2 has a global average $\delta^{13}C$ close to −8 per mil (i.e., parts per thousand) (cf., ref 3) and the global mean value from a 1991 inventory of fossil fuel types was −28.5 per mil.[4,5] Stable isotope measurements are traditionally conducted on discrete samples, such as air collected in canisters, in the laboratory using isotope ratio mass spectrometry (IRMS), but recent advances in spectroscopic monitoring technology have made it possible to conduct in situ measurements of stable isotope ratios with high frequency and precision. [6,7]

The use of isotopic CO_2 analyzers for ambient air monitoring in areas near GCS sites, for example, could be used to identify intrusion of non-ambient CO_2 and provide information about its source. Large-scale leaks in high risk areas where the source is well-understood can be detected by conventional CO_2 analyzers. Fast-response, portable analyzers, including infrared "cameras," could be useful as a survey tool to quickly assess larger geographic areas for large-scale leaks. The high sensitivity and fast response of isotopic CO_2 analyzers have the potential to detect smaller leaks and identify larger subsurface leaks before exceeding the detection limits of less sensitive techniques. Spectroscopic isotopic CO_2 analyzers have been proposed as a potentially viable technology for monitoring GCS sites, nearby communities, and sensitive ecosystems for CO_2 leaks, where analyzers would need to have sufficient accuracy and precision to detect background ambient air concentrations (~350 ppm) and $\delta^{13}C$ values (~ −8 per mil) and capture daily/seasonal variability.

A.6.2 Technology Description

One technique for isotopic CO_2 detection is cavity ring down spectroscopy (CRDS), in which sensitivity to target analytes is enhanced through the use of multi-pass optical cells that vastly increase the effective pathlength of the absorbing radiation over typical absorption techniques.[8,9] In CRDS, the beam from a laser enters a cavity defined by two or more highly reflective mirrors. As the light in the cavity reflects back and forth between the mirrors, a small portion of the light exits the cavity since the mirrors are not completely reflective. The amount of light exiting the cavity is directly proportional to the intensity in the cavity. Thus, by monitoring the intensity of light exiting the cavity, the intensity of the light in the chamber can be deduced.

In the absence of an absorbing species in the cavity, once the laser is turned off the light intensity inside the cavity will steadily leak out and decay (or "ring down") to zero in an exponential fashion. If a gas species that absorbs the laser light is introduced into the cavity, a portion of the light will be absorbed and the ring-down time will shorten compared to that in a cavity without any additional absorption due to a targeted gas species. Measurement of the respective ring-down times thus allows for an accurate determination of the concentration of the absorbing gas, in this case, both the ^{13}C and ^{12}C isotopes of CO_2 in the cavity.

A7 VERIFICATION TEST DESCRIPTION AND SCHEDULE

The purpose of this verification test is to generate performance data on isotopic CO_2 analyzers with a particular focus on applications relevant to GCS monitoring applications, specifically for the sequestration of CO_2 from a coal-fired power plant. The data generated from this verification test are intended to provide organizations and users interested in GCS monitoring with information on the potential use of these analyzers for that application and on their performance under such conditions.

A7.1 Verification Test Description

Battelle testing staff will conduct the test over a period of approximately 5 weeks, which will involve three distinct activities, or phases, as summarized in Table 2. In Phase 1, the analytical performance of the CO_2 analyzers will be evaluated under controlled laboratory conditions with respect to CO_2 isotopic composition and CO_2 concentration. Gas standards of known isotopic composition and concentration will be used to generate test samples over a range of CO_2 concentrations and a minimum of two isotopic compositions. During Phase 2, the CO_2 analyzers will be installed in a chamber in which CO_2 leaks will be simulated in ambient air under controlled conditions and the minimum detectable leak rate will be determined for ^{13}C-depleted CO_2. Phase 3 will include mobile surveys of the GCS site transmission lines and infrastructure and continuous monitoring at the GCS site. If feasible within test site operating requirements, captured CO_2 will intentionally be released to simulate an above-ground leak in a high-risk area. The CO_2 analyzers will be evaluated on the following performance parameters:

- Accuracy and bias
- Linearity
- Precision
- Response time
- Minimum detectable leak rate

Table 2. Planned Verification Test Activities

Phase	Location	Testing Activities
1	Battelle Laboratories Columbus, OH	Installation Analyzer operation training Gas standard challenges
2	ABT Battelle West Jefferson, OH	Controlled leak simulations
3	GCS site WV	Mobile surveys Intentional CO_2 release Continuous ambient monitoring Remove CO_2 analyzers from test site

- Data completeness
- Operational factors.

When possible, parameters will be assessed with respect to CO_2 concentration and isotopic composition. Accuracy and bias will be assessed for the CO_2 analyzers being verified by determining the degree of agreement with known concentrations and isotopic ratios of CO_2 from compressed gas standards. Precision will be assessed in terms of the repeatability of the CO_2 concentration and isotopic ratio measurements under stable test conditions using CO_2 compressed gas standards. Linearity and response time will also be assessed using commercial compressed gas standards of CO_2. Minimum detectable leak rate will be assessed by simulating CO_2 leaks under controlled and ambient conditions. Data completeness will be determined from a review of the valid data collected during the verification testing period and evaluated separately for mobile/survey data collection efforts. Operational performance parameters such as maintenance requirements, ease of use, and field portability will be determined from observations by the Battelle testing staff. Information on costs will be provided by the technology vendor. This test is not intended to simulate long-term performance of these technologies at a monitoring site, but rather assess the feasibility of their use for various GCS monitoring scenarios, such as those suggested by the GEO-SEQ Project Team,[8] who recommend that monitoring plans be tailored to address the specific conditions and risks for a given site.

Subsequent to the verification test, Battelle will draft a separate verification report for each analyzer tested. The reports will be reviewed by the respective technology vendor and by peer reviewers, revised, and submitted to EPA for final approval. In performing the verification test, Battelle will follow the technical and QA procedures specified in this TQAP and will comply with the data quality requirements in the AMS Center QMP.[1]

A7.2 Proposed Testing Schedule

Table 3 shows the planned schedule of testing and data analysis/reporting activities to be conducted in this verification. The verification process is planned to begin in June 2010 and be completed in July 2010. Each phase of the test is expected to span approximately one to three weeks.

Table 3. Planned Verification Test Schedule

Phase	Approximate Date(s),	Location	Testing Activities	Data Analysis and Reporting
1	July 6 –16	Battelle Columbus, OH	Installation Analyzer operation training Gas standard challenges	Begin preparation of report template Review and summarize testing staff observations Compile data from CO_2 analyzer(s)
2	July 19 – 22	ABT Battelle West Jefferson, OH	Controlled leak simulations	Review and summarize testing staff observations Compile data from CO_2 analyzer Begin data analysis
3	July 27 – 30	GCS site WV	Mobile surveys Intentional CO_2 release Continuous ambient monitoring Remove CO_2 analyzers from test site	Review and summarize testing staff observations Compile data from CO_2 analyzer Perform data analysis Begin draft report(s)
	August 13			Complete draft report(s)
	August 27			Complete peer review of draft report(s)
	September 10			Revise draft report(s) Submit final report for EPA approval

A7.3 Battelle Laboratory Testing Facilities

Phase 1 testing will be conducted in Battelle laboratories in Columbus, Ohio. Battelle staff will conduct testing in laboratories that are fully equipped for the production and delivery of CO_2 in test atmospheres of controlled temperature and humidity.

A7.4 Ambient Breeze Tunnel

The Ambient Breeze Tunnel (ABT) facility is located at the Battelle West Jefferson campus. It will be used to generate and deliver CO_2 leaks in ambient air for the purpose of characterizing the minimum detectable leak rate of the CO_2 analyzers. The ABT has physical dimensions of approximately 150 × 20 × 20 feet (L × W × H), while the entire facility area measures approximately 190 × 60 feet. Included in the facility are test trailers that can be used to conduct tests, analyze test data, and provide storage. The area is secured by a gated fence to offer a protected location for test equipment and related materials. The site provides a secure location to set up and conduct tests or perform maintenance, while allowing operators access to all the amenities of the facility (storage, power, air compressor, internet access, etc.).

As shown in Figure 2, the ABT itself is divided into five major sections. Although it will be used for this test to release CO_2 as a controlled leak, the facility was designed to generate aerosol. The aerosol generation section is the segment of the test system where the challenge aerosol is generated, but in this case where the CO_2 gas will be released. The baffles in the mixing section of the ABT enhance mixing of the CO_2 gas with the ambient air by creating mixing inducing vortices. Whereas the inlet baffle upstream of the aerosol generation section creates relatively large mixing vortices, the "checkerboard" baffle plane generates smaller mixing vortices. The result is a series of mixing vortices starting out relatively large at the ABT inlet and growing increasingly smaller through the length of the ABT mixing section. In the

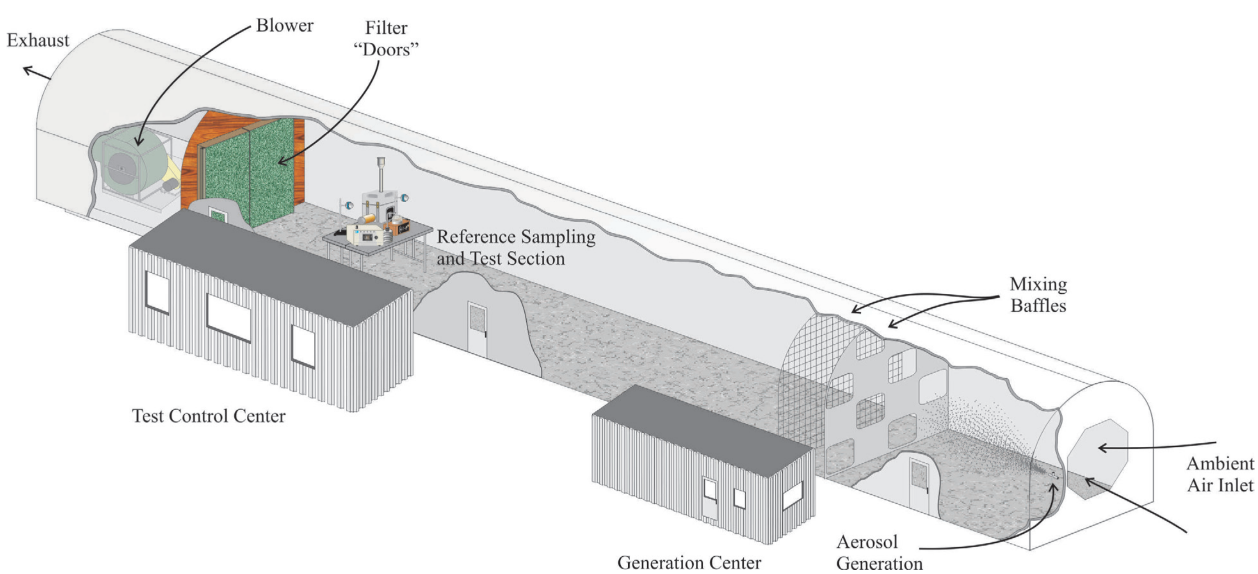

Figure 2. Schematic Diagram of the ABT

transition section, the flow velocity across the cross section is fairly consistent, and the air continues to mix with the intentionally generated material due to turbulence. The sampling section is the portion of the ABT where sampling instrumentation, including the systems being tested and those instruments used to characterize the challenge, are located. The exhaust section of the ABT contains the large blower that pulls air through the test system at volumetric flow rates of up to about 120,000 cubic feet per minute (cfm). The blower is contained within a wooden structure called the blower house, which is essentially a large room with a cement floor, wooden ceiling and walls, and two large "filter doors" designed to hold a total of 56 filters (28 filters per door) with standard nominal dimensions of 2 × 2 feet. During testing, the amount of CO_2 released is expected to increase the CO_2 concentration in the ABT by only a small amount (i.e., 1 ppm). A photograph of the ABT is shown in Figure 3.

Figure 3. Photograph of the ABT

A7.5 GCS Test Site

Field testing will be conducted at a coal-fired power plant in West Virginia, where CO_2 from the flue gas is being captured, separated, compressed, and stored in a geologic formation over 7,000 feet below the surface. Figure 4 shows a diagram of the GCS site (not to scale). When operational, approximately 100,000 metric tons per year (tonnes/year) (~274 tonnes/day) of captured and compressed CO_2 will be provided for injection into the two deep wells. The injection wells, monitoring wells, above-ground transmission pipeline, and other site features are accessible by vehicle for conducting mobile surveys and as sites for continuous monitoring. Battelle staff will position a shed near the main injection well to provide shelter for the CO_2 analyzers; power is available at the injection well site.

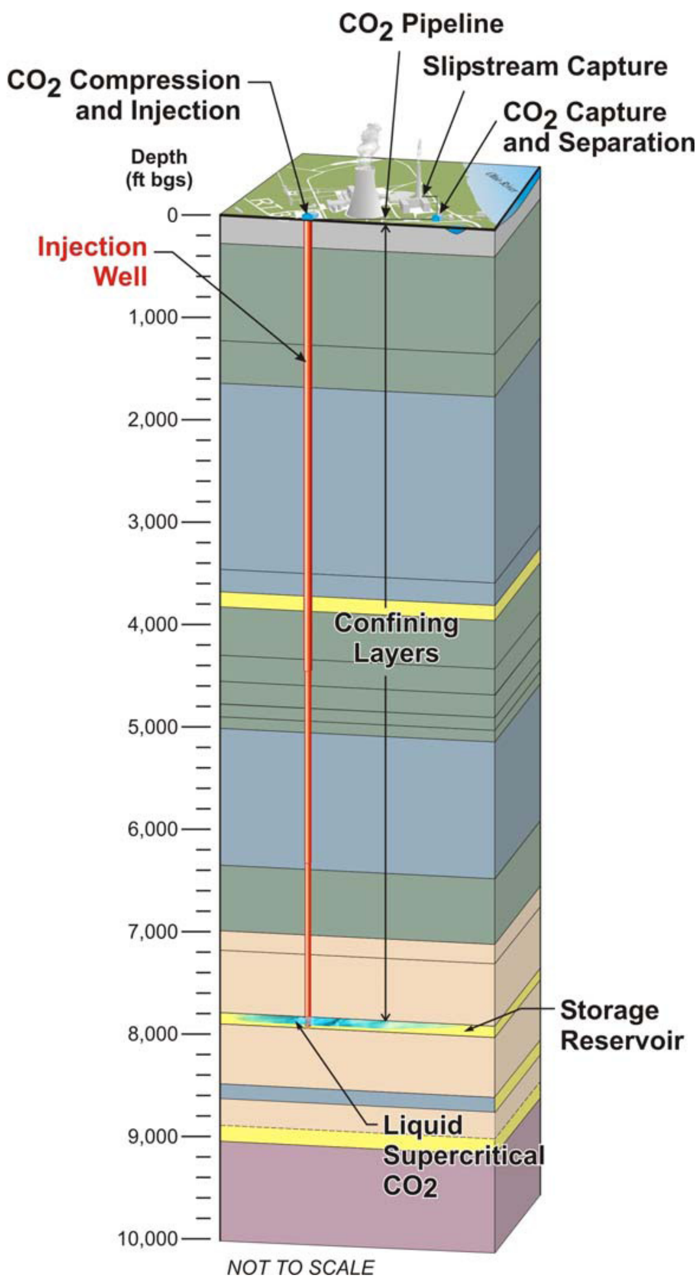

Figure 4. Diagram of GCS Site

A8 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The objective of this verification test is to evaluate the performance of the CO_2 analyzers under potential scenarios relevant to GCS monitoring. This evaluation will in part assess the capabilities of the CO_2 analyzers for determining the CO_2 concentration and isotope ratio in the ambient air and to detect leaks of CO_2 gas with isotope ratios different from ambient air. Additionally, this verification test will include instrument challenges using CO_2 gas standards to assess performance under controlled and repeatable test conditions. The verification test will also rely upon operator observations to assess other performance characteristics of the CO_2 analyzers being tested including data completeness, ease of use, and maintenance requirements.

DQIs indicate the minimum quality of data required to meet the objectives of the verification test and are different than the QA/QC requirements. To ensure that this verification test provides suitable data for a robust evaluation of performance, a data quality indicator (DQI) has been established for leak flow rate accuracy in Phase 2. The DQI was established to ensure that data used to support the quantitative performance evaluations of the CO_2 analyzers are of sufficient quality. The DQI for these supporting measurements is quantitatively defined in Table 4 along with the acceptance criteria. Quantitative performance parameters for vendor technology performance are discussed in Section B.

Table 4. DQI and Criteria for Critical Supporting Measurements

Phase	DQI	Method of Assessment	Frequency	Acceptance Criteria	Corrective Action
2	Leak flow rate accuracy	Comparison to independent flow transfer standard	Each simulated leak test	±10%	Investigate discrepancy. Inspect meter and replace meter box as needed.

During Phase 2, the accuracy of the leak flow rate will be verified using an independent flow transfer standard. If greater than 10% relative percent difference is found, Battelle will investigate the discrepancy and replace the flow transfer standard as needed. Additionally, the verification test relies in part on observations of the Battelle field testing staff for assessment of the performance of the CO_2 analyzers being tested. The requirements for these observations are described in the discussion of documentation requirements and data review, verification, and validation requirements for this verification test.

The Battelle QAO will perform a technical systems audit (TSA) of laboratory and field-based testing activities to augment these QA/QC requirements. A TSA of Phase 1 laboratory-based testing activities will be performed within the first week of the verification test. A TSA of field testing activities will be performed within the first week of the Phase 3 GCS field testing. The EPA Quality Manager also may conduct an independent TSA, at her discretion.

A9 SPECIAL TRAINING/CERTIFICATION

Documentation of training related to technology testing, field testing, data analysis, and reporting is maintained for all Battelle technical staff in training files at their respective locations. The Battelle Quality Manager may verify the presence of appropriate training records prior to the start of testing. Battelle technical staff supporting this verification test has a minimum of a bachelor's degree in science/engineering.

Portions of the verification test described in this TQAP will be performed at a GCS site. All participants in this verification test (i.e., Battelle, EPA, and vendor staff) will adhere to the health and safety requirements of the GCS site and in Battelle facilities. For example, personal CO_2 monitors will be used in locations where high CO_2 levels may be encountered. Vendor staff will operate only their CO_2 analyzers during parts of the verification test. They are not responsible for, nor permitted to, operate the test site equipment or perform any other verification activities identified in this TQAP.

Battelle testing staff will give a site-specific safety briefing to all staff visiting the test site or Battelle laboratories/facilities. This briefing will include a description of emergency operating procedures (i.e., in case of fire, tornado, laboratory accident), identification, location, and operation of safety equipment (e.g., fire alarms, fire extinguishers, eye washes, exits), and host site PPE requirements and site-specific procedures.

A10 DOCUMENTATION AND RECORDS

The documents and records for this verification test include the TQAP, certificates of analysis (COA), chain-of-custody forms, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), and the final verification report(s). All of these documents and records will be maintained in the Verification Test Coordinator's office during the test and will be transferred to permanent storage at Battelle's Records Management Office

(RMO) at the conclusion of the verification test. Documents and records generated at the ABT and GCS test site will be stored in a secure location until they can be transferred to the Verification Test Coordinator (within one week of generation). Electronic documents and records will also be uploaded to a SharePoint site designated for this test and will be provided to EPA upon request. All Battelle LRBs are stored indefinitely, either by the Verification Test Coordinator or Battelle's RMO. EPA will be notified before disposal of any files. Section B10 further details the data recording practices and responsibilities.

SECTION B

MEASUREMENT AND DATA ACQUISITION

B1 EXPERIMENTAL DESIGN

The verification test described in this TQAP will specifically address verification of isotopic CO_2 analyzers for GCS monitoring applications by evaluating the following performance factors:

- Accuracy and bias
- Linearity
- Precision
- Response time
- Minimum detectable leak rate
- Data completeness
- Operational factors.

The verification test will be conducted over a period of approximately 5 weeks. A window of approximately one week prior to testing will be available for installing the CO_2 analyzers at the facility, and conducting a trial run of the CO_2 analyzers before the verification test begins. The installation and training period is scheduled to begin in late June, 2010. The analyzers undergoing verification will report total CO_2 concentrations ($^{12}CO_2 + {}^{13}CO_2$) and isotopic composition ($\delta^{13}C$) for all testing activities. The verification testing will involve a combination of controlled gas challenges in an indoor laboratory environment and a sheltered ambient breeze tunnel, survey measurements for above-ground leak detection, and continuous ambient monitoring, conducted in three distinct phases:

- Phase 1 – Battelle will evaluate the analytical performance of the CO_2 analyzers under controlled laboratory conditions. The CO_2 analyzers will be challenged with gas standards of known isotopic composition and concentration to generate test samples over a range of CO_2 concentrations and isotopic compositions. Bias with respect to ambient temperature and relative humidity (RH) will also be assessed.
- Phase 2 –Battelle will evaluate the minimum detectable CO_2 leak rate for ^{13}C-depleted CO_2. Battelle will install the CO_2 analyzers in the ABT where CO_2 leaks will be simulated in ambient air under controlled conditions by releasing pure $^{12}CO_2$.

- Phase 3 – Battelle will evaluate the ability of the CO_2 analyzers to survey GCS site transmission lines and infrastructure for leaks and be used for continuous monitoring at the GCS site. If feasible within test site operating requirements, captured CO_2 will intentionally be released to simulate a high risk area, above ground leak.

The CO_2 analyzer readings during Phase 1 will be compared to the delivered concentrations and isotopic ratios as calculated based on dilution ratios and concentration and isotopic ratio of the certified gas standards used for testing. For Phases 2 and 3, the CO_2 analyzers will be evaluated based on a determination of the minimum detectable CO_2 leak, where the leak source gas is pure (99.95%) $^{12}CO_2$. The leak rate at a range of $\delta^{13}C$ values between ambient air (approximately −8 per mil) and those expected for fossil fuel combustion (approximately −30 per mil) will be calculated based on the results of the minimum detectable leak determination from Phase 1 and the actual concentration of $^{12}CO_2$ in the gas standard. If an intentional release of captured CO_2 is conducted, the time elapsed before the leak is detected by the CO_2 analyzers will be reported.

Table 5 presents a summary of the tests to be performed. The time durations specified in the following sections were set assuming the CO_2 analyzers are operated with 1-minute time resolution. If higher time resolution settings are used, the test durations may be shortened provided that a minimum of five CO_2 analyzer measurements could be reported during a given test condition. The Verification Test Coordinator will determine what time resolution will be used during the verification test to balance practical considerations against the requirements described in this TQAP, with input from the technology vendor.

Throughout the verification test, each CO_2 analyzer undergoing testing will be operated by the vendor's own staff or by Battelle staff trained by the vendor. However, the intent of the testing is for the CO_2 analyzers to operate in a manner simulating use by GCS site operators to monitor and/or survey a facility on a continuous basis or to monitor ambient air nearby a GCS site with little user intervention. As a result, once the verification test has begun, no adjustment or recalibration will be performed, other than what would be conducted automatically by the CO_2 analyzer in normal unattended operation. Repair or maintenance procedures may be carried out at any time, but testing may not be interrupted, and data completeness will be reduced if such activities prevent collection of CO_2 analyzer data required for verification.

Table 5. Summary of Tests and Testing Frequency

Phase	Performance Parameter	Objective	Comparison Based On	Testing Frequency	Number of Data Points
1	Accuracy and Bias	Determine degree of quantitative agreement with compressed gas standard	Challenges with CO_2 gas standards of known $\delta^{13}C$ at 3 RH levels and 3 temperatures	-3 runs at each of 12 nominal concentrations (one $\delta^{13}C$ value) -1 run at each of 15 combinations of RH, temperature, and CO_2 concentration (one $\delta^{13}C$ value) -3 runs at each of 9 combinations of CO_2 concentration and $\delta^{13}C$)	78
1	Linearity	Determine linearity of response over a range of CO_2 concentrations	Dynamic spiking with gas standards	-3 runs at each of 12 nominal concentrations (one $\delta^{13}C$ value) -3 runs at each of 9 combinations of CO_2 concentration and $\delta^{13}C$)	36
1	Precision	Determine repeatability of successive measurements at fixed CO_2 levels	Repetitive measurements under constant facility conditions measured	-3 runs at each of 12 nominal concentrations (one $\delta^{13}C$ value)	36
1	Response Time	Determine 95% rise and fall time	Recording successive readings at start and end of sampling CO_2 gas standard	Once during each day of dynamic spiking testing	3
2	Minimum Detectable Leak Rate	Determine the minimum detectable CO_2 leak rate under controlled and ambient conditions	Repetitive measurements of a low-level $^{12}CO_2$ leak	Once	1
3	Leak Response Rate	Determine the amount of time between an intentional release of captured CO_2 and detection of the leak by the CO_2 analyzers	Recording the elapsed time between start of release and positive detection	Once (optional)	1

B1.1 Test Procedures

The CO_2 analyzers undergoing verification will be installed at an appropriately sheltered location at each test site and/or on a mobile platform for conducting surveys. For gas standard challenges, the inlet port for the CO_2 analyzers will be connected to a manifold to which gas standards will be delivered and that is equipped with an ambient pressure vent. Excess CO_2 and instrument exhaust will be vented to a hood or outside inhabited areas. A broad range of concentrations will be tested at a single $\delta^{13}C$ to establish basic concentration-based performance of the CO_2 analyzers; however, fewer concentrations will be tested for bias tests involving different $\delta^{13}C$ values due to schedule and resource limitations.

B1.1.1 CO_2 Concentration Accuracy, Bias, Precision, and Linearity

During Phase 1, each of the CO_2 analyzers will be challenged with a series of compressed CO_2 gas standards diluted in CO_2-free zero air to achieve measurements in the range of expected ambient air concentrations (i.e., 350 ppm) and also at higher concentrations (up to 5000 ppm CO_2) to simulate concentrations that could be observed in high hazard areas. Three non-consecutive measurements will be recorded at each of twelve different nominal concentration levels at one $\delta^{13}C$ value. Each concentration will be supplied to the analyzers for at least twenty minutes. A calibrated programmable dilution system may be used to automatically supply the diluted gas standards to the CO_2 analyzers. Table 6 shows the approximate CO_2 concentration values to be supplied to the analyzers being tested, and the order in which the concentrations will be supplied. As Table 6 indicates, the CO_2 concentrations will first be supplied to the analyzers in increasing order, then in random order, and finally in decreasing order. Dilutions will be prepared from a certified compressed mixture of 11% CO_2 in air (Air Liquide Acublend Master Class, 11.0% ±1%). These tests will be conducted at room temperature without added humidity. The room temperature will be recorded daily using a calibrated thermometer.

Table 6. Approximate CO_2 Concentrations for Multi-point Challenges

Nominal CO_2 Concentration (ppm)	Measurement Number		
0	1	16	36
100	2	22	35
200	3	18	34
300	4	14	33
400	5	23	32
500	6	20	31
750	7	15	30
1600	8	17	29
2450	9	21	28
3300	10	19	27
4150	11	24	26
5000	12	13	25

B1.1.2 Isotopic Ratio Bias

During Phase 1, the analyzer response to the series of CO_2 gas standards will be used to evaluate accuracy, bias, precision, and linearity with respect to CO_2 concentration. Section B1.2 presents the statistical procedures that will be used. Accuracy will be calculated at each concentration and for each replicate relative to the nominal CO_2 concentration. Bias will be calculated for each series of multi-point CO_2 challenges. The analyzer precision will be demonstrated by the reproducibility of the analyzer response at each nominal CO_2 concentration after a stable reading is achieved. Linearity will be assessed by establishing a multi-point calibration curve from the analyzer response.

Analyzer bias with respect to the $\delta^{13}C$ value will be assessed by challenging the analyzers with dilutions from three CO_2 isotope mixtures [SMU Stable Isotope Laboratory, through Oztech Trading Corporation, -3.61; -10.41; and -40.80 per mil (0.01 standard deviation)], each at three CO_2 concentrations (see Table 7). Bias will be calculated for each $\delta^{13}C$ value. Each CO_2 concentration/$\delta^{13}C$ pair will be delivered to the analyzers three times for a total of 27 data points.

Table 7. Approximate CO_2 Concentrations and Isotope Ratios for Bias Tests

Approximate $\delta^{13}C$ (per mil)	Nominal CO_2 Concentrations (ppm)
-3.61 ± 0.01[(a)]	350
	500
	1000
-10.41 ± 0.01	350
	500
	1000
-40.8 ± 0.01	350
	500
	1000

(a) Uncertainties are standard deviations reported on COAs for each gas standard.

B1.1.3 Temperature and RH Bias

Assessments of bias due to the ambient and sample temperature and RH will be assessed during Phase 1 by installing the analyzers in a temperature and RH-controlled chamber and delivering dilutions of a CO_2 gas standard to the chamber at three concentrations under varying temperature and RH conditions. The CO_2 gas dilutions will pass through a coil placed within the chamber so the sample temperature will match ambient temperatures. Battelle staff will adjust the RH of the CO_2 gas dilutions by humidifying all or a portion of the gas stream using water bubblers or similar apparatus. The RH of the sample will be verified using an independent calibrated sensor. The specific target conditions are listed in Table 8. If possible, a high RH/high temperature (i.e., >90% RH and >30°C) condition will also be included. The analyzers will be subjected to each condition once for a minimum of twenty minutes. One $\delta^{13}C$ value will be used for these tests. Bias will be calculated as described in Section B1.2.

Table 8. Approximate Conditions for Temperature and RH Bias Tests

Approximate RH (%)	Approximate Temperature (°C)	Nominal CO_2 Concentration (ppm)
0 ±10%	20 ± 2°C	350
		500
		1000
50 ±10%	4 ± 2°C	350
		500
		1000
	20 ± 2°C	350
		500
		1000
	32 ± 2°C	350
		500
		1000
90 ±10%	20 ± 2°C	350
		500
		1000
	32 ± 2°C (optional)	350
		500
		1000

B1.1.4 Response Time

The data collected for the multi-point CO_2 challenges (Section B1.1.2) during Phase 1 will also be used to determine the analyzer response time. The 95% rise time and 95% fall times will be calculated for the consecutive concentration steps (Table 6, measurements 1-12 and 25-36). Calculations for response time are described in Section B1.2.6.

B1.1.4 Minimum Detectable Leak Rate

The minimum leak rate that can be detected above ambient variability and the precision of the CO_2 analyzers will be determined under controlled conditions during Phase 2. The analyzers will be installed in the Reference Sampling and Test Section of the ABT. A leak will be considered to be successfully identified if an increase or decrease in the measured $\delta^{13}C$, greater than 2 times the variability in ambient $\delta^{13}C$, is measured by the CO_2 analyzer for at least three consecutive measurement points. The ambient air $\delta^{13}C$ variability will be determined from one hour of ambient air CO_2 analyzer data measured on the day of testing. Injection of pure (99.95%) $^{12}CO_2$ into the ambient air diluent being drawn into the ABT will be used to simulate a low-level leak of ^{13}C-depleted CO_2. This approach assumes that a low-level leak would be wellmixed in the ambient air diluent before reaching the CO_2 analyzers undergoing verification, which is expected for a flow rate of approximately 30,000 cfm (approximately 5 miles per hour velocity). The equivalent leak rate as a function of source $\delta^{13}C$ will be back-calculated for several relevant $\delta^{13}C$ values, including the expected value for the GCS field site. This calculation will assume that the magnitude of the measured changes in $\delta^{13}C$ values from ambient levels will be the same for the pure (99.95%) $^{12}CO_2$ and for the calculated leak levels for ^{13}C-depleted CO_2. This assumption allows the calculation of CO_2 release rate necessary to achieve the overall $\delta^{13}C$ change for a given $\delta^{13}C$ source value, knowing the ambient $\delta^{13}C$ value and the flow rate of air through the ABT. It should be noted that the use of a pure ^{12}C source for leakage (i.e., -1000 per mil) maximizes instrument sensitivity to $\delta^{13}C$, although not to total CO_2 concentration; thus, conditions during an actual leak would be different with respect to both $\delta^{13}C$ and total CO_2 concentration. Although it would be preferable to simulate leaks using a mixture of $^{13}CO_2$ and $^{12}CO_2$ at a ratio that would be realistic for fossil fuel combustion, a substantial quantity of CO_2 source gas would be needed to meet the low-level leak conditions described above and falls outside the limitations of this verification test.

The initial $^{12}CO_2$ leak rate will be set at a nominally detectable level that is twice the standard deviation (s) in $\delta^{13}C$ measured by the analyzer for a period of at least one hour on the day of testing or the vendor's reported $\delta^{13}C$ precision, whichever is greater. Leaks at that rate will be introduced three times for approximately 20 minutes with at least 15 minutes of ambient air flow between simulated leaks. If all three leaks are successfully detected, the leak rate will be reduced at the discretion of the testing staff. At each leak rate, the CO_2 analyzer will report at least 4 data points during each of three trials, for a minimum of 12 data points. Once a leak rate that is not identified for each of the three trials has been reached, the rate will be increased to a level where all three replicates are successfully identified. This leak rate is the minimum detectable limit for the technology under the test conditions. If time permits, this process may be repeated during the Phase 2 test period. A conventional CO_2 analyzer will be used to monitor the CO_2 concentration in the ambient air diluent to assist in identifying changes in air mass or nearby CO_2 sources that could impact the CO_2 concentration or $\delta^{13}C$. Keeling plots may also be used to evaluate the CO_2 analyzer's ability to detect CO_2 leaks. Specifically, uncertainty in the intercept of the Keeling plot will be determined.

B1.1.5 Ambient Air Monitoring

In the evenings and when the CO_2 analyzers are not undergoing testing during Phase 3, they will be installed in a shelter near the GCS wellhead and set up to monitor ambient air. The purpose of this activity is to evaluate data completeness and operational factors during deployment for ambient monitoring. The ambient air measurements (CO_2 concentration and $\delta^{13}C$) and meteorological conditions will be reported with summary statistics (average and standard deviation). While the analyzers are installed at the wellhead, a planned release of captured CO_2 will be conducted if feasible within plant operations. The leak rate response time, the time between initiation of the release and when the leak is detected by the CO_2 analyzers as described in Section B1.1.4, will be determined.

B1.1.6 Mobile Surveys

During Phase 3, the CO_2 analyzers will be transported to road-accessible features of the GCS, such as transmission lines, monitoring wells, and abandoned wells. The purpose of these tests is to evaluate the ease of use and operational factors of the analyzers during use in a mobile survey mode. Analyzers will be installed on a mobile platform, such as a pick-up truck, and set up to sample continuously as the analyzers are moved to and between target features. In addition to the above-ground transmission lines, a minimum of three groundwater monitoring wells and 6 soil gas monitoring wells will be surveyed. Features will be selected at the discretion of testing staff based on access, atmospheric/meteorological conditions, and potential of specific features to leak captured or sequestered CO_2. The feature locations will be documented in a manner that will not identify the GCS site location, but provide descriptive information about the type of feature and its role in carbon capture or sequestration. Ambient air CO_2 concentrations and $\delta^{13}C$ values will be recorded as the feature is approached, while in the immediate vicinity of the feature, and as the analyzer is moved away from the feature. Approximate survey location and speed data will be collected using a common GPS devices (e.g., GPS equipped cellular telephone); GPS coordinates will not be reported. Since meteorology can influence the level of detection, meteorological conditions near each feature will be recorded and reported. During testing, the vehicle speed will be recorded and maintained as constant as possible and care will be taken to ensure that exhaust from the vehicle transporting the analyzers does not contribute to the measured CO_2 signal. A sampling line will be used to supply the analyzers with ambient air.

To the extent possible, the vehicle will be driven such that the exhaust is downwind of the sampling line. Measurements recorded during the mobile surveys, particularly while the vehicle is idling, will be closely investigated to assess if there is any potential interference from the vehicle exhaust. If evidence of interference is suspected, the suspect data will be flagged and reported accompanied by an explanation.

B1.1.7 Data Completeness

No additional test procedures will be carried out specifically to address data completeness. This parameter will be assessed based on the overall data return achieved by each analyzer.

B1.1.8 Operational Factors

Operational factors such as maintenance needs, calibration frequency, data output, consumables used, ease of use, repair requirements, and sample throughput will be evaluated based on operator observations. Battelle testing staff will document observations in a laboratory record book (LRB) or data sheets. Examples of information to be recorded include the daily status of diagnostic indicators for the technology, 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 technology down time or data acquisition failure, operator observations about technology startup, ease of use, clarity of the vendor's instruction manual, user-friendliness of any needed software, overall convenience of the technologies and accessories/consumables, or the number of samples that could be processed per hour or per day. Battelle will summarize these observations to aid in describing the technology performance in the verification report on each technology.

B1.2 Statistical Evaluation

The statistical methods and calculations used for evaluation of the quantitative performance parameters are described in the following sections.

B1.2.1 Accuracy

Accuracy of the CO_2 analyzers with respect to the individual CO_2 gas standards will be assessed as the percent recovery (%R), using Equation B-1:

$$\%R = \left[1 + \left(\frac{Y - X}{X}\right)\right] \times 100 \quad \text{(B-1)}$$

where Y is the average measured CO_2 analyzer value and X is the nominal CO_2 gas standard concentration. The average, minimum, and maximum %R values will be reported for each series of multi-level CO_2 challenges. The accuracy of the analytical standards, as certified by the manufacturer, will also be reported. Similarly, the accuracy of the CO_2 analyzers with respect to isotope ratio will be determined where Y is the average measured CO_2 analyzer $\delta^{13}C$ value and X is the nominal $\delta^{13}C$ value.

B1.2.2 Bias

Bias of the CO_2 analyzers is defined as a systematic error in measurement that results in measured error that is consistently positive or negative compared to the true value. The bias will be calculated as the average percent difference (%D) of the CO_2 analyzer compared to the nominal CO_2 gas standard value (with respect to concentration and isotope ratio) and will be calculated for each series of multi-point CO_2 challenges and isotope ratio bias tests, using Equation B-2:

$$\%D = \frac{1}{k}\sum_{j=1}^{k}\left(\frac{Y - X}{X}\right)_j \times 100 \quad \text{(B-2)}$$

where k is the number of valid comparisons, and Y and X are the same as stated in B1.2.1. For temperature and RH bias, the basis of comparison for isotope ratio will be the ratio measured by the CO_2 analyzer at room temperature without added water vapor (dry conditions).

B1.2.3 Precision

The precision of the CO_2 analyzers will be evaluated from the triplicate responses to each CO_2 gas standard supplied during the multi-point challenges (outlined in Table 6). The precision will be defined as the percent relative standard deviation (%RSD) of the triplicate measurements and calculated for each CO_2 concentration and isotope ratio listed in Table 6, using Equation B-3:

$$\%RSD_i = \frac{s}{\overline{Y}_i} \times 100 \qquad \text{(B-3)}$$

where $\overline{Y}_i$ is the average analyzer response at CO_2 concentration or isotope ratio *i*, and s the standard deviation of the analyzer responses at that concentration. The overall average %RSD will also be calculated for each series of multi-point CO_2 challenges (with respect to CO_2 concentration) and for each gas standard (with respect to CO_2 $\delta^{13}C$) and will include the %RSD for all CO_2 concentrations tested for each gas source.

B1.2.4 Linearity

Linearity with respect to concentration and isotopic ratio will be assessed by a linear regression analysis of the gas challenge data using the calculated CO_2 concentrations or $\delta^{13}C$ as the independent variable and the CO_2 analyzer results as the dependent variable. The results of the gas challenge tests will be plotted and linearity will be expressed in terms of slope, intercept, and coefficient of determination (R^2).

B1.2.5 Minimum Detectable Leak Rate

The minimum detectable leak rate that represents the minimum level successfully identified by each of three trials will be determined experimentally; all trial results will be reported. The equivalent leak rate at several $\delta^{13}C$ values of interest, such as −30 per mil, will be calculated based on the flow rate of −30 per mil CO_2 that would be needed to give the same change in measured $\delta^{13}C$ with respect to ambient air (−8 per mil). For example, a leak rate of 0.9 Lpm of 99.95% $^{12}CO_2$ would result in a $\delta^{13}C$ of −11.0 per mil under expected conditions at the ABT. The equivalent final $\delta^{13}C$ could be achieved with a leak rate of 46.9 Lpm for a −30 per mil CO_2 source. (Note that the change in total CO_2 concentration would not be equivalent for the two CO_2 sources.) In addition, the isotopic ratios measured by the CO_2 analyzers will be plotted versus the inverse of the CO_2 concentration (i.e., in Keeling plots) and the uncertainty in the intercept determined. The intercept will represent the isotopic ratio of the leak source. When the Keeling plot intercept for a given leak rate is equal to the known value of the leak, within the uncertainty of the intercept, the leak rate would be considered to be "detectable." Keeling plots will also be developed for intentional releases at the GCS site, if conducted.

B1.2.6 Response Time

Response time will be assessed in terms of both the rise and fall times (with respect to CO_2 concentration) of each CO_2 analyzer when sampling CO_2 gas standards. Rise time (i.e., 0% - 95% response time) will be determined by recording all CO_2 analyzer readings as the gas supplied to the analyzers is switched between increasing concentration CO_2 standards. Once a stable response has been achieved with the gas standard, the fall time (i.e., the 100% to 5% response time) will be determined in a similar way, by recording all CO_2 analyzer readings as the CO_2 concentration in the gas supplied is reduced in concentration. For CO_2 analyzers which provide periodic rather than continuous readings, determination of rise and fall times may involve interpolation between readings. Rise and fall times will each be determined once during multi-point gas challenges. Rise and fall times will be reported in units of seconds.

B1.2.7 Data Completeness

Data completeness will be assessed based on the overall data return achieved by each CO_2 analyzer during the testing period. For each of the CO_2 analyzers, this calculation will use the total number of apparently valid data points reported by the analyzers divided by the total number of data points potentially available in the entire field period. The causes of any incompleteness of data return will be established from operator observations or vendor records, and noted in the discussion of data completeness results.

B1.3 Reporting

The statistical comparisons described above will be conducted separately for each CO_2 analyzer being tested, and information on the operational performance will be compiled and reported. A verification report will be prepared for each CO_2 analyzer tested, that presents the test procedures and test data, as well as the results of the statistical evaluation of those data.

Operational aspects of the monitoring systems will be recorded by Battelle testing staff at the time of observation during the field test, and summarized in the verification report. For example, descriptions of the data acquisition procedures, use of vendor-supplied proprietary software, consumables used, repairs and maintenance needed, and the nature of any problems will be presented in the report. The verification report will briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. The results of the verification test regarding CO_2 analyzer performance will be stated quantitatively. Each draft verification report will be subjected to review by the vendor, EPA, and other peer reviewers. The resulting review comments will be addressed in a subsequent revision of the report, and the peer review comments and responses will be tabulated to document the peer review process and submitted to EPA. The reporting and review process will be conducted according to the requirements of the ETV/AMS Center QMP.[1]

B2 SAMPLING METHOD REQUIREMENTS

Reference samples will not be collected during this test.

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Reference samples will not be collected during this test.

B4 ANALYTICAL METHOD REQUIREMENTS

No analytical methods are needed for this test.

B5 QUALITY CONTROL REQUIREMENTS

Reference measurements will not be collected as part of this verification test.

B6 INSTRUMENT/ EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

When Battelle staff operate and maintain the CO_2 analyzers undergoing testing, those activities will be performed as directed by the vendor. Otherwise, operation and maintenance of the analyzers will be the responsibility of the analyzer vendors.

B7 INSTRUMENT CALIBRATION AND FREQUENCY

The calibration of instrumentation used in this verification test, such as dilution systems and flow controllers, will be verified immediately prior to use in this verification test. A minimum of three flow rates for each flow controller or flow reader will be verified with an independent factory-calibrated flow meter. Calibration of the meteorological station will have been performed within 1 year of the verification test.

The CO_2 analyzers undergoing testing will be calibrated initially by the respective analyzer vendors at the time of installation, at the vendor's discretion. Calibration gases will not be provided for vendors' use; instrument calibration gases must be independent of those used for testing activities. In the event that recalibration is deemed necessary, that recalibration will be carried out by the analyzer vendor, or by Battelle staff under the direction of the vendor. All calibrations performed will be documented by Battelle staff in the LRB dedicated to the respective analyzer.

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Upon receipt of any supplies or consumables used for the gas challenges, Battelle will visually inspect and ensure that the materials received are those that were ordered and that there are no visual signs of damage that could compromise the suitability of the materials. If damaged or inappropriate goods are received they will be returned or disposed of and arrangements will be made to receive replacement materials. Certificates of analysis (COA) or other documentation of analytical purity will be checked for all gases, reagents, and standards to ensure suitability for this verification test. Unsuitable materials will be returned or disposed of and arrangements for the receipt of replacement materials will be made.

The air used for diluting CO_2 standards for delivery to the CO_2 analyzers will be commercial ultra-high purity (UHP, i.e., minimum 99.999% purity). Compressed gas standards containing CO_2 will be obtained for use in the laboratory-based gas standard challenges, for example 11% CO_2 in air, and obtained from Air Liquide America Specialty Gases LLC (formerly Scott Specialty Gases). Certified mixtures of $^{13}CO_2/^{12}CO_2$ will be obtained for the isotope bias testing from Oztech Trading Corporation. Pure $^{12}CO_2$ (99.95%) will be obtained for leak rate determination testing from Cambridge Isotopes. All cylinders will include a COA specifying analytical purity and the cylinder calibration expiration date.

B9 NON-DIRECT MEASUREMENTS

No non-direct measurements will be used during this verification test.

B10 DATA MANAGEMENT

Various types of data will be acquired and recorded electronically or manually by Battelle and vendor staff during this verification test. All manually-recorded data will be recorded in permanent ink. Corrections to records will be made by drawing a single line through the entry to be corrected and providing a simple explanation for the correction, along with a date and the initials of the person making the correction. Table 9 summarizes the types of data to be recorded. All maintenance activities, repairs, calibrations, and operator observations relevant to the operation of the monitoring systems being tested will be documented by Battelle or vendor staff in the LRB. Report formats will include all necessary data to allow traceability from the raw data to final results.

Records received by or generated by any Battelle or subcontractor staff during the verification test will be reviewed by a Battelle staff member within five days of receipt or generation, respectively, before the records are used to calculate, evaluate, or report verification results. If a Battelle staff member generated the record, this review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member who originally received or generated the record. The review will be documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, any calculations performed by Battelle will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this TQAP.

Table 9. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
Dates, times, and details of test events	ETV LRBs, field sampling records	Start/end of test event	Battelle staff	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
CO_2 analyzer calibration information, maintenance, down time, etc.	ETV LRBs, or electronically	When performed	Vendor and Battelle staff	Incorporated in verification report as necessary
CO_2 analyzer readings	Recorded electronically by each monitor and then downloaded to computer daily	Recorded continuously by each monitoring system	Vendor staff for transfer to Battelle	Converted to spreadsheet for statistical analysis and comparisons
Supplemental CO_2 concentration and meteorological parameter measurement results	Electronically from continuous gas analyzers and meteorological station	Recorded continuously by analyzers	Battelle staff	Converted to spreadsheets for statistical analysis and comparisons

Battelle will provide technology test data and associated reference data (including records; data sheets; notebook records) from the first day of testing within one day of receipt to EPA for simultaneous review. The goal of this data delivery schedule is prompt identification and resolution of any data collection or recording issues. These data will labeled as preliminary and will not have had a QA review before their release.

SECTION C

ASSESSMENT AND OVERSIGHT

C1 ASSESSMENTS AND RESPONSE ACTIONS

Every effort will be made in this verification test to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of this TQAP is to establish mechanisms necessary to ensure this. Internal quality control measures described in this TQAP, which is peer reviewed by a panel of outside experts, implemented by the technical staff and monitored by the Verification Test Coordinator, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the Verification Test Coordinator, who will contact the Battelle AMS Center Manager, Battelle AMS Center Quality Manager, EPA AMS Center Project Officer, and EPA AMS Center Quality Manager if any deviations from the TQAP are observed. The Verification Test Coordinator will describe the deviation in a teleconference or by email, and once a path forward is determined and agreed upon with EPA, the deviation form will be completed. Technical staff has the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the Verification Test Coordinator, who will work with the Battelle Quality Manager to resolve any issues. Action will be taken by the Verification Test Coordinator and Battelle testing staff to identify and appropriately address the issue, and minimize losses and correct data, where possible. Independent of any EPA QA activities, Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

C1.1 Performance Evaluation Audit

Since no reference measurements will be conducted, no performance evaluation (PE) audits are planned for this verification test. The certified $^{13}CO_2/^{12}CO_2$ gas mixtures to be used in this verification test have COAs and a calibrated dilution system will be used to ensure that test reference gas concentrations are accurate.

C1.2 Technical Systems Audits

The Battelle QAO will perform a TSA during performance of laboratory and field-testing activities. The purpose of these audits is to ensure that the verification test is being performed in accordance with the AMS Center QMP[1] and this TQAP. In this TSA, the Battelle QAO may compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. The Battelle QAO will prepare a project-specific checklist based on the TQAP requirements to guide the TSA, which will include a review of the test location and general testing conditions; observe the testing activities; and review laboratory record books. She will also check gas standard certifications and data acquisition procedures, and may confer with the vendor staff. The Battelle QAO will prepare an initial TSA report and will submit the report to the EPA Quality Manager (with no corrective actions documented) and Verification Test Coordinator within 10 business days after completion of the audit. A copy of each final TSA report (with corrective actions documented) will be provided to the EPA AMS Center Project Officer and Quality Manager within 20 business days after completion of the audit. At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to technical staff at the time of the audit and documented in a TSA report.

C1.3 Data Quality Audits

The Battelle QAO, or designee, will audit at least 10% of the sample results data acquired in the verification test and 100% of the calibration and QC data versus the TQAP requirements. Four ADQs will be conducted for this project: The first batch of data will be audited within 10 business days of receipt and assessed using a project-specific checklist. Additional ADQs will be audited within 10 business days of receipt of all Phase 1, 2, and 3 data. During these audits, the Battelle QAO, or designee, will trace the data from initial acquisition (as received from the vendor's technology), through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the ADQ will be checked. Data must undergo a 100% validation and verification by technical staff (i.e. Verification Test Coordinator, or designee) before it will be assessed as part of the data quality audit. All QC data and all calculations performed on the data undergoing the audit will be checked by the Battelle QAO. Results of each ADQ will be documented using the checklist and reported to the Verification

Test Coordinator and EPA within 10 business days after completion of the audit. A final ADQ that assesses overall data quality, including accuracy and completeness of the technical report, will be prepared as a narrative and distributed to the Verification Test Coordinator and EPA within 10 business days of completion of the audit.

C1.4 QA/QC Reporting

Each assessment and audit will be documented in accordance with Section 3.3.4 of the AMS Center QMP.[1] The results of all audits will be submitted to EPA within 10 business days as noted above. Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Recommendations for resolving problems. (If the QA audit identifies a technical issue, the Verification Test Coordinator or Battelle AMS Center Manager will be consulted to determine the appropriate corrective action.
- Confirmation that solutions have been implemented and are effective
- Citation of any noteworthy practices that may be of use to others.

C2 REPORTS TO MANAGEMENT

During the field and laboratory evaluation, any TQAP deviations will be reported immediately to EPA. The Battelle Quality Manager and/or Verification Test Coordinator, during the course of any assessment or audit, will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. A summary of the required assessments and audits, including a listing of responsibilities and reporting timeframes, is included in Table 10. If serious quality problems exist, the Battelle Quality Manager will notify the AMS Center Manager, who is authorized to stop work. Once the assessment reports have been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken. The TQAP and final report are reviewed by the EPA AMS Center Quality Manager and the EPA AMS Center Project Officer. Upon final review and approval, both documents will then be posted on the ETV website (www.epa.gov/etv).

Table 10. Summary of Assessment Reports[1]

Assessment	Prepared By	Report Submission Timeframe	Submitted To
Each TSA (Initial)	Battelle	10 business days after TSA is complete	EPA ETV AMS Center
Each TSA (Final)	Battelle	TSA response is due to QAO within 10 business days of receipt from QAO TSA responses will be verified by the QAO and provided within 20 business days	EPA ETV AMS Center
ADQ (Initial)	Battelle	ADQ will be completed within 10 business days after receipt of first data set	EPA ETV AMS Center
ADQ (Phases 1, 2, and 3)	Battelle	ADQ will be completed within 10 business days after all data for a phase is submitted	EPA ETV AMS Center
ADQ (Final)	Battelle	10 business days after completion of the verification report review	EPA ETV AMS Center

[1] Any QA checklists prepared to guide audits will be provided with the audit report.

SECTION D

DATA VALIDATION AND USABILITY

D1 DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

The key data review and data verification requirements for this test are stated in Section B10 of this TQAP. In general, the data review requirements specify that data generated during this test will be reviewed by a Battelle technical staff member within two weeks of generation of the data. The reviewer will be familiar with the technical aspects of the verification test but will not be the person who generated the data. This process will serve both as the data review and the data verification, and will ensure that the data have been recorded, transmitted and processed properly. Furthermore, this process will ensure that the monitoring systems data were collected under appropriate testing.

The data validation requirements for this test involve an assessment of the quality of the data relative to the DQI for this test referenced in Table 4. Any deficiencies in these data will be flagged and excluded from any statistical comparisons to the CO2 analyzers being tested, unless these deviations are accompanied by descriptions of their potential impacts on the data quality.

D2 VERIFICATION AND VALIDATION METHODS

Data verification is conducted as part of the data review as described in Section B10 of this TQAP. A visual inspection of handwritten data will be conducted to ensure that all entries were properly recorded or transcribed, and that any erroneous entries were properly noted (i.e., single line through the entry, with an error code, such as “wn” for wrong number, and the initials of the recorder and date of entry). Electronic data from the CO2 analyzers, continuous gas analyzers, and analytical equipment used during the test will be inspected to ensure proper transfer from the datalogging system. All calculations used to transform the data will be reviewed to ensure the accuracy and the appropriateness of the calculations. Calculations performed manually will be reviewed and repeated using a handheld calculator or commercial software (e.g., Excel). Calculations performed using standard commercial office software (e.g., Excel) will be reviewed by inspection of the equations used for the calculations and verification of selected calculations by handheld calculator. Calculations performed using specialized commercial software (i.e., for analytical instrumentation) will be reviewed by inspection and, when feasible, verified by handheld calculator, or standard commercial office software.

To ensure that the data generated from this test meet the goals of the test, a number of data validation procedures will be performed. Sections B and C of this TQAP provide a description of the validation safeguards employed for this verification test. Data validation efforts include the completion of QC activities, and the performance of a TSA audit as described in Section C. The data from this test will be evaluated relative to the measurement DQIs described in Section A7 of this TQAP. Data failing to meet these criteria will be flagged in the data set and not used for evaluation of the CO2 analyzers, unless these deviations are accompanied by descriptions of their potential impacts on the data quality.

An audit of data quality will be conducted by the Battelle Quality Manager to ensure that data review, verification, and validation procedures were completed, and to assure the overall quality of the data.

D3 RECONCILIATION WITH USER REQUIREMENTS

This purpose of this verification test is to evaluate the performance of isotopic CO2 analyzers for use in GCS monitoring. In part, this evaluation will include demonstrations of the monitoring ability of CO2 analyzers to detect various kinds of leaks from GCS sites. To meet the requirements of the user community, input on the tests described in this TQAP has been provided by external experts. Additional performance data regarding operational characteristics of the CO2 analyzers will be collected by verification test personnel. To meet the requirements of the user community, these data will include thorough documentation of the performance of the monitoring systems during the verification test. The data review, verification, and validation procedures described above will assure that data meeting these requirements are accurately presented in the verification reports generated from this test, and will assure that data not meeting these requirements will be appropriately flagged and discussed in the verification reports.

This TQAP and the resulting ETV verification report(s) will be subjected to review by the vendor, EPA, and expert peer reviewers. The reviews of this TQAP will help to improve the design of the verification test and the resulting report(s) such that they better meet the needs of potential users of these monitoring systems.

SECTION E

REFERENCES

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