THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM

U.S. Environmental Protection Agency

TECHNOLOGY TYPE:	**ISOTOPIC CARBON DIOXIDE ANALYZERS**	
APPLICATION:	**CARBON SEQUESTRATION MONITORING**	
TECHNOLOGY NAME:	**Cavity Ring-Down Spectroscopy Analyzer for Isotopic CO_2 Model G1101-*i***	
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ETV Joint Verification Statement

The U.S. Environmental Protection Agency (EPA) has established the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies. Information and ETV documents are available at www.epa.gov/etv.

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

The Advanced Monitoring Systems (AMS) Center, one of six verification centers under ETV, is operated by Battelle in cooperation with EPA's National Risk Management Research Laboratory. The AMS Center evaluated the performance of isotopic carbon dioxide analyzers for carbon sequestration monitoring. This verification statement provides a summary of the test results for Picarro, Inc.'s Cavity Ring-Down Spectroscopy Analyzer for Isotopic Carbon Dioxide - Model G1101-*i*.

VERIFICATION TEST DESCRIPTION

This verification test of the Model G1101-*i* was conducted from July 9 through August 17, 2010 at Battelle laboratories in Columbus, OH, Battelle's Ambient Breeze Tunnel (ABT) in West Jefferson, OH, and a geological carbon sequestration site located at a coal-fired power plant in West Virginia. Performance of the Model

G1101−*i* was verified for carbon dioxide (CO_2) concentration and the stable isotope ratio of carbon in CO_2. 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 1 and expressed in per mil (‰), or part per thousand.

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

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‰ and fossil fuels are typically in the range of −28‰. Reference analyses of CO_2 concentration and $\delta^{13}C$ by nondispersive infrared (NDIR) analysis and isotope ratio mass spectrometry (IRMS), respectively, were performed between August 11 and August 20, 2010 by the National Oceanic and Atmospheric Administration (NOAA) and the Stable Isotope Lab (SIL) at the Institute for Arctic and Alpine Research (INSTAAR) in Boulder, CO.

One of the goals of this verification test was to provide information on the potential use of the Model G1101-*i* for monitoring at or near facilities utilizing geologic carbon sequestration (CS) for captured CO_2. Since the $\delta^{13}C$ of CO_2 from fossil fuels can be distinguished from ambient air, technologies that detect $\delta^{13}C$ in addition to CO_2 concentration may be able to identify leakage more quickly than by monitoring for CO_2 concentration alone and therefore are likely to be of interest to CS site operators and regulators. To accomplish this monitoring goal, the experimental design included 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 to provide performance data under a variety of simulated and real-world conditions. The Model G1101-*i* was evaluated in terms of:

- Accuracy and bias – comparison of analyzer CO_2 concentration and $\delta^{13}C$ response to dilutions from certified gas standards to nominal levels and at variable temperature and relative humidity (RH) conditions
- Linearity – linear regression analysis of analyzer CO_2 concentration and $\delta^{13}C$ response to dilutions from certified gas standards versus nominal levels
- Precision – average analyzer response to triplicate challenges at each of 11 CO_2 concentrations
- Response time – 95% rise and fall times calculated from transitions between CO_2 gas standard dilutions of increasing and decreasing concentration, respectively
- Minimum detectable leak rate – the minimum flow rate of $^{12}CO_2$ detected by the Model G1101-*i* above ambient $\delta^{13}C$ variability under controlled field conditions
- Comparability – analyzer CO_2 concentration and $\delta^{13}C$ response to ambient air compared to NDIR and IRMS methods, respectively
- Data completeness – assessment of data return by the Model G1101-*i* during the verification test
- Operational factors – such as general operation, data acquisition, set up, and consumables.

The Model G1101-*i* was installed and operated according the vendor's instructions and manual by Battelle staff; the vendor representative was available to answer questions and provide support, but no formal training was conducted. Phase 1 of this verification test was conducted in Battelle laboratories in Columbus, OH to evaluate the analytical performance of the Model G1101-*i* under controlled laboratory conditions from July 9 through July 23 and August 11 through August 17, 2010. The Model G1101-*i* was challenged with gas standards of known isotopic composition and concentration to generate test samples over a range of CO_2 concentrations and isotopic compositions. CO_2 concentration and $\delta^{13}C$ data were first corrected for an error in the factory-set calibration and for water vapor interference then used to calculate accuracy, bias, linearity, precision, and response time, where appropriate. Bias with respect to ambient temperature and relative humidity (RH) was also assessed.

The ability of the Model G1101-*i* to detect CO_2 leaks was evaluated during Phase 2 of this verification test, which was conducted at Battelle's Ambient Breeze Tunnel (ABT) facility in West Jefferson, OH. The ABT was used to simulate leaks of ^{13}C-depleted CO_2 (i.e., $^{12}CO_2$) in ambient air under simulated field conditions. The Model G1101-*i* was installed inside the ABT, where ambient air was drawn through the tunnel at approximately 4 miles per hour (mph) and a stream of pure $^{12}CO_2$ at a fixed flow rate was periodically introduced. By varying the $^{12}CO_2$ flow rate, the minimum detectable CO_2 leak rate was determined. In addition, ambient air reference samples were collected to determine the comparability of the Model G1101-*i* to CO_2 concentration and $\delta^{13}C$ reference methods. Testing for Phase 2 was conducted from July 28 through July 30, 2010.

The utility of the Model G1101-*i* for monitoring at GCS sites was evaluated during Phase 3, which was conducted at a coal-fired power plant in West Virginia. The analyzer was installed in a shed near the sequestration wells and sampled ambient air drawn from near the main wellhead over a one-week period from August 2 through August 6, 2010. During that period, ambient air reference samples were collected to determine the comparability of the Model G1101-*i* to CO_2 concentration and $\delta^{13}C$ reference methods. The Model G1101-*i* was also installed in a hybrid sedan vehicle and operated using battery power to conduct mobile surveys of GCS site transmission lines and infrastructure. Finally, CO_2 from the sequestration operation was intentionally released to simulate a high-risk area above-ground leak, and the leak-rate response time was determined.

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

TECHNOLOGY DESCRIPTION

The following is a description of the technology, based on information provided by the vendor. The information provided below was not verified in this test.

The Model G1101-*i* is a low-drift, high-precision analyzer designed to measure the stable isotope ratio of carbon in CO_2 and CO_2 concentration. This analyzer is based on cavity ring-down spectroscopy (CRDS), which is a technique in which a gas sample is introduced into a high-finesse optical cavity, and the optical absorbance of the sample is determined, thus providing concentration or isotopic ratio measurements of a particular gas species of interest.

The analyzer continuously scans a laser through a sample, and determines individual carbon dioxide rovibrational resonant absorption lines for $^{12}CO_2$ and $^{13}CO_2$. Each spectrum is comprised of absorption loss as a function of optical frequency. The concentration is proportional to the area under each measured spectral feature. Concentration measurements are provided approximately every second, corresponding to a total of 100 ring-down and wavelength monitor measurements, and the isotope ratio ($^{13}C/^{12}C$) is derived from the ratio of the $^{13}CO_2$ and $^{12}CO_2$ concentrations in the sample volume.

The Model G1101-*i* weighs 26 kg (58 lbs), has dimensions of 43 × 25 × 59 cm (17" × 9.75" × 23") including the feet, and can be rack mounted or operated on a bench top. The approximate purchase price of the Model G1101-*i* is U.S. $60,500.

VERIFICATION RESULTS

The verification of the Model G1101-*i* is summarized below. The estimate of uncertainty in the nominal CO_2 concentrations for dilutions used to evaluate the Model G1101-*i* was approximately 7%. It is not possible to determine from these measurements alone whether the observed inaccuracies and biases relative to gas standard challenges are due to errors in the instrument response or the gas preparation.

Concentration Accuracy, Bias, Precision, and Response Time. The accuracy of the Model G1101-*i* was assessed over the range of 100 ppm to 5,000 ppm in terms of %R, which ranged from 90 to 113%, with an average of 96%. Bias, or the average percent difference between the Model G1101-*i* response and the known value, was −4.0%. Precision of the Model G1101-*i* was determined from the average responses to triplicate challenges at each of 11 CO_2 concentrations. The relative standard deviation values ranged from 0.10% to 1.2%, with an average of 0.30%. The average 95% response time was 142 seconds for rise time and 152 seconds for fall time.

Concentration Linearity. Linearity was evaluated in terms of slope, intercept, and R^2. Over the 0 to 400 ppm range, the slope of the regression line was 0.935 (±0.036), with an intercept of 11.3 (±8.90) and R^2 value of 0.996. Over 0 to 5,000 ppm, the slope of the regression line was 0.938 (±0.006), with an intercept of -1.32 (±13.6) and R^2 value of 0.999. (The 95% confidence interval for the slope and the intercept of each line is shown in parenthesis.)

Isotope Ratio Accuracy, Bias, and Linearity. The accuracy of the Model G1101-*i* $\delta^{13}C$ response was assessed at −3.60 ‰, −10.4‰, and −40.8‰ at three concentration levels: 259 ppm, 370 ppm, and 740 ppm. Values for $\delta^{13}C$ differed from the expected value by between 1.1 to 2.7‰, with an average of 1.7‰. The lowest absolute differences were observed for the −40.8‰ standard and at the higher CO_2 concentrations. Isotope ratio linearity was assessed in terms of slope, intercept, and R^2 at −3.60‰, −10.4‰, and −40.8‰. The strongest correlation between concentration and measured isotope ratio was observed for the −3.60‰ standard, with an R^2 value of 0.947, a slope of −0.0025 and intercept of 3.24. (The 95% confidence interval for the slope and the intercept of each line is shown in parenthesis.)

Temperature and Relative Humidity Bias. Temperature and RH bias were assessed by comparing the Model G1101-*i* CO_2 concentration and $\delta^{13}C$ response to dilutions from a certified CO_2 standard at five temperature/RH conditions to its response at 20°C and 0% RH. During this evaluation, the Model G1101-*i* was installed in a temperature/RH-controlled chamber; humidified zero air was added to the CO_2 gas standard dilution to achieve the desired RH. The following test conditions were evaluated: 20°C/50% RH; 20°C/90% RH; 32°C/50% RH; 32°C/90% RH; 4°C/50% RH. In general, variability in ambient temperature and RH conditions resulted in bias values of 3.0% or less for the Model G1101-*i* concentration measurements and 0.70‰ or less for isotope ratio. The maximum concentration bias value, 3.0%, was observed for CO_2 concentration at 4°C/50% RH. The largest isotope ratio average difference of 0.7‰ was observed for 32°C/90% RH.

Minimum Detectable Leak Rate. The ability of the Model G1101-*i* to identify CO_2 leaks above ambient air variability was evaluated by simulating leaks under controlled field conditions in the Ambient Breeze Tunnel. Pure $^{12}CO_2$ was periodically released into a constant flow of ambient air and the flow rate adjusted until the Model G1101-*i* difference in the $\delta^{13}C$ response during the "leak" compared to ambient air was greater than 2 times the ambient air $\delta^{13}C$ variability. Under conditions that simulated 1.8 m/s winds, the minimum detectable leak rate was 0.423 LPM $^{12}CO_2$, which resulted in a 0.90‰ decrease, on average, in the Model G1101-*i* $\delta^{13}C$ readings compared to ambient air (approximately -6.4). This result was extrapolated to determine the equivalent leak rates for CO_2 sources of with $\delta^{13}C$ values -35‰, -20‰, and -3.5‰. The equivalent leak rates were 14.62 LPM, 31.84 LPM, and 198.2 LPM, respectively.

Ambient Air Monitoring. The Model G1101-*i* monitored ambient air at the GS site between August 2 and August 6, 2010. During this period, the average ambient CO_2 concentration was 411 ppm, with a range of 365 to 488 ppm. The average measured stable isotope ratio was −6.42 and values ranged from −9.50 to −4.28. The relationship between CO_2 concentration and $\delta^{13}C$ was investigated by producing a Keeling Plot. The value of the intercept, which represents the $\delta^{13}C$ of the CO_2 source, is −23.1‰ and is consistent with the value for captured CO_2 at this site. An intentional release of captured CO_2 was detected by the Model G1101-*i* in less than 60 seconds. A Keeling Plot of the data from the intentional release period had an R_2 value of 0.939 and an intercept of −24.0 (± 0.2)‰, that is similar to the intercept found for ambient measurement data and is consistent with the isotope ratio of the CO_2 injected at the site.

Mobile Surveys.

During Phase 3, the Model G1101-*i* was transported to road-accessible features of the GS, such as transmission lines and monitoring wells, to evaluate the ease of use and operational factors of the analyzers during use in a mobile survey mode. The Model G1101-*i* surveyed 16 features at the GS while installed in the back seat of a Nissan Altima hybrid sedan and operating on power from a marine deep cycle/RV battery and power inverter. Once the first installation in the vehicle had been completed, it generally took approximately 15 minutes with two testing staff to shut down the analyzer, move all the components into the vehicle, and conduct data collection on battery power. Some additional time was then needed for the analyzer response to stabilize. At least one hour of monitoring data could be collected on a single battery.

Comparability to Reference Methods. Comparability was determined as the accuracy (%R) and bias (average percent difference) of the Model G1101-*i* response compared to CO_2 concentration (NDIR) and $\delta^{13}C$ (IRMS) reference method results for 10 duplicate grab samples of ambient air. The average accuracy for CO_2 concentration was 98% with a range of 94% to 101%. For $\delta^{13}C$, the average difference was −3.0% and values ranged from −3.5% to −2.1%. Bias was calculated separately for each site. At the ABT and GS site, concentration bias was −0.20% and −2.5%, respectively.

Data Completeness. The Model G1101-i operated for 100% of the available time during Phase 1 and Phase 2 of the verification test. During Phase 3, internal calibrations took place during 7.0% of the available testing time (6 hours) and the analyzer was shut down for 2.6 hours because ambient temperatures in the shed where the analyzer was operated exceeded operating limits identified by the vendor. The internal calibrations and temperature-related downtime resulted in a 91% data return during Phase 3 of this verification test. When supplied with the necessary power (i.e., a fully charged battery), the Model G1101-*i* data return during mobile survey testing was 100%.

Operational Factors. The Model G1101-*i* was installed in the laboratory and at both field sites by Battelle testing staff; the installation was completed in less than one hour; no formal training by the vendor was necessary. Instructions in the user manual for the installation were clear and easy to follow. A checklist was provided by the vendor representative to establish whether the analyzer was in proper working order during the test. No maintenance was performed on the analyzer. Data were downloaded on a daily basis to a USB memory stick or expansion drive. In general, the Model G1101-*i* software was easy to use. Battelle staff found the zoom and other features on the graphical display to be somewhat cumbersome and not especially intuitive. Ease of use of the software improved with practice. Batteries used to operate the Model 1101-*i* during mobile surveys were reusable and rechargeable. The Model G1101-*i* did not generate any waste or use consumable supplies.

Signed by Tracy Stenner June 15, 2011
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