

VERIFICATION TEST DESCRIPTION

The performance of the TitraSip™ was assessed in terms of its accuracy, response to injected contaminants, inter-unit reproducibility, ease of use, and data acquisition. The verification test was conducted between August 9 and October 28, 2004, and consisted of three stages, each designed to evaluate a particular performance characteristic of the TitraSip™. All three stages of the test were conducted using a recirculating pipe loop at the U.S. EPA's Test and Evaluation Facility in Cincinnati, Ohio.

In the first stage of this verification test, the accuracy of the measurements made by the TitraSip™ units was evaluated during nine, 4-hour periods of stable water quality conditions by comparing each TitraSip™ unit measurement to a grab sample result generated each hour using a standard laboratory reference method and then calculating the percent difference (%D). The second stage of the verification test involved evaluating the response of the TitraSip™ units to changes in water quality parameters by injecting contaminants (nicotine, arsenic trioxide, and aldicarb) into the pipe loop. Two injections of three contaminants were made into the recirculating pipe loop containing finished Cincinnati drinking water. The response of each water quality parameter, whether it was an increase, decrease, or no change, was documented and is reported here. In the first phase of Stage 3 of the verification test, the performance of the TitraSip™ units was evaluated during 52 days of continuous operation, throughout which reference samples were collected once daily. The final phase of Stage 3 (which immediately followed the first phase of Stage 3 and lasted approximately one week) consisted of a two-step evaluation of the TitraSip™ performance to determine whether this length of operation would negatively impact the results from the TitraSip™. First, as during Stage 1, a reference grab sample was collected every hour during a 4-hour analysis period and analyzed using the standard reference methods. Again, this was done to define a formal time period of stable water quality conditions over which the accuracy of the TitraSip™ could be evaluated. Second, to evaluate the response of the TitraSip™ to contaminant injection after the extended deployment, the duplicate injection of aldicarb, which was also included in the Stage 2 testing, was repeated. In addition, a pure *E. coli* culture, including the *E. coli* and the growth medium, was included as a second injected contaminant during Stage 3. Inter-unit reproducibility was assessed by comparing the results of two identical units operating simultaneously. Ease of use was documented by technicians who operated and maintained the units, as well as the Battelle Verification Test Coordinator.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 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 all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the TitraSip™ was provided by the vendor and does not represent verified information.

The TitraSip™ is designed for multi-parameter water quality testing. The system used for this verification test analyzed pH (following EPA Method 150.1, including calibration buffers with pHs of 4, 7, and 10), conductivity (following Standard Method [SM] 2510, which used a 1,413 microSiemens per centimeter standard for calibration), total alkalinity (following SM 2320B), total chlorine (following SM 4500-Cl B, with a potentiometric rather than a color, endpoint), temperature (following EPA Method 170.1), and turbidity (following SM 2130B, including calibration solutions of 0, 10, and 100 nephelometric turbidity unit polymer standards). Additional water quality parameters and modules (i.e., autosampler) may be added. TitraSip™ collects a sample from a free-flowing source (e.g., overflow cup) into the TitraSip™ Analysis Vessel and automatically completes analysis cycles at set time intervals (in this case, once every 30 minutes) to complete the analysis for all six water quality parameters without user intervention. The system includes a personal computer, software, interface, burets, turbidity module, pump/valve system for adding calibrants and standards, electrodes, overflow sample cup, and TitraSip™ Analysis Vessel. The system used for this verification test was positioned on a table top equipped with shelving for the sampling and analysis equipment. The total system was 30 inches high and 36 inches wide, excluding the personal

computer. Data are automatically collected at the conclusion of each cycle of sample analysis. The PC-Titrate software controls all aspects of TitraSip™ operation. Data may be viewed directly on the personal computer as they are acquired or they may be exported as a database or spreadsheet file. The cost of the TitraSip™ used for the verification test was approximately \$30,000. In addition, the calibration reagents cost approximately \$220 per month, preventive maintenance costs approximately \$2,797 (parts only) per year, and electrode replacement costs approximately \$1,220 per year, assuming that new electrodes are needed every six months.

VERIFICATION OF PERFORMANCE

| Evaluation Parameter | | Total Chlorine | Temperature | Conductivity | pH | Total Alkalinity | Turbidity | |
|---|---|---------------------|----------------------|------------------------------------|--------------------|---------------------|------------------------|----------------|
| Stage 1— Accuracy | Units 1 and 2, range of %D (median) | -13.2 to 20.6 (7.5) | -9.1 to 52.5 (-0.04) | 37.9 to 94.3 (57.5) ^(a) | -2.2 to 5.4 (0.6) | 3.2 to 30.4 (11.5) | -65.2 to 0.6 (-45.2) | |
| Stage 2— Response to Injected Contaminants | Nicotine | Reference | - | NC | NC | NC | ^(b) | |
| | | TitraSip™ | - | NC | NC | NC | ^(b) | |
| | Arsenic trioxide | Reference | - | NC | + | + | + | ^(b) |
| | | TitraSip™ | - | NC | + ^(c) | + | + | ^(b) |
| | Aldicarb | Reference | - | NC | NC | NC | NC | ^(b) |
| | | TitraSip™ | - | NC | NC | NC | NC | ^(b) |
| Stage 3— Accuracy During Extended Deployment | Units 1 and 2, range of %D (median) | -18.0 to 30.0 (2.7) | -15.7 to 3.7 (-3.1) | -2.8 to 5.2 (0.7) | -4.4 to 0.7 (-1.1) | -16.5 to 14.4 (5.7) | -96.7 to 155.3 (-37.3) | |
| Stage 3— Accuracy After Extended Deployment | Unit 1, %D | 1.0 | -2.2 | 0.3 | -1.0 | -0.4 | 35.3 | |
| | Unit 2, %D | 0.0 | -1.9 | 1.1 | -2.1 | 4.5 | 41.2 | |
| Stage 3— Response to Injected Contaminants | <i>E. coli</i> | Reference | - | NC | + | - | + | + |
| | | TitraSip™ | - | NC | + | - | + | ^(c) |
| | Aldicarb | Reference | - | NC | NC | - | - | + |
| | | TitraSip™ | - | NC | NC | - | - | ^(c) |
| Injection Summary | For a reason that is not clear, aldicarb and total alkalinity altered the pH, as measured by the reference method, during the Stage 3 injections, but not during the Stage 2 injections. | | | | | | | |
| Inter-unit Reproducibility (Unit 2 vs. Unit 1) | Slope (intercept) | 1.06 (0.03) | 1.06 (-1.22) | 1.16 (-38.1) | 0.94 (0.545) | 0.79 (18.1) | 0.67 (0.104) | |
| | r ² | 0.958 | 0.942 | 0.896 | 0.981 | 0.873 | 0.683 | |
| | p-value | 0.481 | 0.915 | 0.110 | 0.851 | 0.149 | 0.449 | |
| All sensors generated results that were similar and repeatable between the units. | | | | | | | | |
| Ease of Use and Data Acquisition | The TitraSip™ units required daily calibration, which involved operator intervention. Initially, the sample cell on Unit 1 did not drain completely between pH calibration solutions, but once the drain problem was resolved, both units functioned properly. Monitor results were recorded once every 30 minutes, which is the maximum data collection frequency. | | | | | | | |

^(a) Calibration procedure for the conductivity meter was changed after Stage 1, resulting in much lower percent differences throughout the remainder of the verification test.

^(b) Relatively large uncertainties in the reference and continuous measurements made it difficult to determine a significant change.

^(c) Duplicate injection results did not agree.

+/- = Parameter measurement increased/decreased upon injection.

NC = No obvious change was noted through a visual inspection of the data.

