

US EPA ARCHIVE DOCUMENT

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



ETV Joint Verification Statement

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| TECHNOLOGY TYPE: | PORTABLE ANALYZER FOR DETECTION OF HEAVY METAL IONS | |
| APPLICATION: | ANALYSIS OF ARSENIC IN WATER | |
| TECHNOLOGY NAME: | PDV 6000 with VAS Version 2.1 Software | |
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The U.S. Environmental Protection Agency (EPA) supports 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.

ETV works in partnership with recognized standards and testing organizations; with stakeholder groups that consist of buyers, vendor organizations, and permittees; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (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 seven technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of portable analyzers for arsenic in water. This verification statement provides a summary of the test results for the Monitoring Technologies International Pty. Ltd. (MTI) PDV 6000 portable analyzer for measuring arsenic in water.

VERIFICATION TEST DESCRIPTION

The PDV 6000 is a portable analyzer designed for the on-site rapid analysis of heavy metal ions. For this test, the PDV 6000 and VAS Version 2.1 software were used to measure arsenic in water. The PDV 6000 was verified in terms of its performance on the following parameters: accuracy, precision, linearity, method detection limit (MDL), matrix interference effects, inter-unit reproducibility, and rate of false positives/false negatives. All preparation and analyses were performed according to the vendor's recommended procedures. Results from the PDV 6000 were compared to those from the reference method to assess accuracy, linearity, and detection limit. Multiple aliquots of performance test samples and environmental samples were analyzed to assess precision. Matrix interference effects were assessed by challenging the analyzer with performance test samples of known arsenic concentrations containing both low-level and high-level interferences. The test/QA plan specified that all analyses would be performed by a technical operator and a non-technical operator to evaluate operator bias; however, the operators were not able to successfully set up and operate the PDV 6000 using the materials and instructions provided by the vendor. Consequently, all samples were analyzed by an MTI representative and operator bias was not evaluated. All samples were analyzed using two PDV 6000 units to evaluate inter-unit reproducibility. False positives and negatives were evaluated relative to the 10-ppb maximum contaminant level for arsenic in drinking water. In addition to the analytical results, the time required for sample analysis and observations concerning the use of the test kit (e.g., frequency of calibration, ease of use, maintenance) were recorded.

Three types of samples were used in the verification test: quality control (QC) samples, performance test (PT) samples, and environmental water samples. The QC and PT samples were prepared from National Institute of Standards and Technology traceable purchased standards. The environmental water samples were collected from various drinking water and surface water sources. All samples were analyzed using the PDV 6000 and by a laboratory reference method.

QA oversight of verification testing was provided by Battelle. Battelle QA staff conducted a data quality audit of 10% of the test data, a performance evaluation audit, and a technical systems audit of the procedures used in this verification.

TECHNOLOGY DESCRIPTION

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

The PDV 6000 comprises a small analytical cell assembly and handheld controller used together as a portable tool for field screening for particular heavy metals. The PDV 6000 can be powered from a main power supply, a portable battery pack, or internal 9-vold batteries. When used in conjunction with VAS Version 2.1 software, a Windows application provided with the PDV 6000, the PDV 6000 is capable of more accurate metal ion analysis in the field as well as the laboratory. The performance of the PDV 6000 in conjunction with the VAS software was verified in this test.

The principal of analysis used by the PDV 6000 is anodic stripping voltammetry (ASV). A reducing potential is applied to the working electrode. When the electrode potential exceeds the ionization potential of the analyte metal ion in solution, it is reduced to the metal which plates onto the working electrode surface. The longer the potential is applied, the more metal is reduced and plated onto the electrode surface (also known as the "deposition" or "accumulation" step). When sufficient metal has been plated onto the working electrode, the metal is stripped (oxidized) off the electrode by increasing, at a constant rate, the potential applied to the working electrode. For a given electrolyte solution and electrode, each metal has a specific potential at which the oxidation reaction will occur. The electrons released by this process form a current, which is measured and may be plotted as a function of applied potential to give a "voltammogram." The current at the oxidation or stripping potential for the analyte metal is seen as a peak. To calculate the sample concentration, the peak height or area is measured and compared to that of a

known standard solution analyzed under the same conditions. The sample result is provided as a digital readout on the handheld controller, or if VAS software is being used, on the computer monitor screen. Sample results can be stored electronically using the VAS software. The vendor provides instructions for the analysis of water samples with arsenic concentrations ranging from five parts per billion (ppb) to 1,000 ppb.

VERIFICATION OF PERFORMANCE

Accuracy: The bias for the PDV 6000 ranged from -74% to 31%. Almost all biases were less than 25% except for the high- and low-level interferent samples, the Battelle drinking water laboratory-fortified matrix (LFM) sample, and the Ayer treated water LFM sample. The LFM sample results suggest that the Battelle drinking water and Ayer treated water samples had matrices that adversely affect the detection of arsenic by the PDV 6000.

Precision: Precision expressed as a relative standard deviation (RSD) ranged from 6% to 16% for unit #1 and from 3% to 15% for unit #2

Linearity: The linearity of response was evaluated by plotting the PDV 6000 results against the reference analysis results for the PT samples. PDV results were generally lower than the reference method results. The equation for the linear regressions that were performed to evaluate linearity are as follows, where x is the reference method concentration and y is the test kit concentration:

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| Unit #1 | $y = 0.77x + 1.22, R = 0.9934$ |
| Unit #2 | $y = 0.91x + 0.59, R = 0.9955$ |

Method Detection Limit: The MDLs calculated using precision data from seven replicates of a low-level spiked sample were 8.6 ppb for unit #1, and 5.8 ppb for unit #2.

Matrix Interference Effects: Low and high levels of interferents (iron and/or sulfide) adversely affected the detection of arsenic. Biases for these samples were higher than those calculated for PT samples containing arsenic only.

Inter-Unit Reproducibility: Unit #2 tended to return higher measurements than unit #1. A paired t-test indicated that the data for the two PDV 6000 units were significantly different at a 5% significance level; however, they were not significantly different if the 100 ppb arsenic PT samples were excluded from the analysis. The regression equation was as follows, where x is unit #1 and y unit #2:

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| PDV 6000 | $y = 1.17x - 1.56, R = 0.9954$ |
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Rate of False Positives/False Negatives: None of the PDV 6000 results demonstrated a false positive. The false negative rates were 42% for unit #1 and 38% for unit #2.

Other Factors: Instructions in the operation manual were difficult to follow and required moving back and forth between operation manual chapters and the accompanying Application Note for analysis of arsenic in water. Some of the test sample peaks were manually adjusted to obtain the final arsenic concentration, and some professional judgment was required when selecting the appropriate standard to use for test sample quantification. All of these factors indicate that level of experience in the operation of the PDV 6000 analyzer and VAS software is likely to influence the reliability of the results.

The PDV 6000 portable analyzer was readily transported to the storage shed where environmental samples were tested. The analyzer and associated equipment were easily stored in a durable carrying case. The PDV 6000 and laptop computer would require protection from rain and high winds during outdoor use. The instrument setup and calibration time prior to sample analysis was approximately one-half hour. The average total analysis time for each sample was about five minutes. The PDV 6000 operated reliably during the test except for the failure of a stir motor in one analyzer, and the malfunction of the VAS software on one occasion. The listed price for PDV 6000, including VAS software, software upgrades, batteries, charger, and carrying case is \$7,900.

signed by Gabor J.Kovacs 8/7/03
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Vice President
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Gary J. Foley Date
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