

Chapter 6

Use of PE Samples

Project-specific PE samples are key tools for evaluating a laboratory's performance of sample analysis. PE samples are used to assess turnaround, customer service, and report content as well as data accuracy. Refer to EM 200-1-1, "Validation of Analytical Chemistry laboratories," for specifics regarding the USACE Laboratory Validation Program.

The uses of PE samples discussed in this chapter include:

- Pre-contract proficiency testing
- Post-contract performance monitoring
- Compliance and corrective actions

6.1. Pre-Contract Proficiency Testing.

6.1.1. Overview. The USACE laboratory validation process for HTRW environmental projects consists of five major sequential steps:

- (1) Review of qualification documents
- (2) Proficiency testing and/or evaluation of SOPs
- (3) On-site laboratory inspection
- (4) Resolution of inspection findings
- (5) Decision of validation status

The laboratory validation procedures described in this section relate directly to PE sample use and include:

- Initiation of laboratory validation
- Initial PE samples
- Analysis of PE samples
- Reporting of PE sample results
- Evaluation of PE sample results
- Tentatively Identified Compounds (TIC)
- Requested corrections
- Unavailable PE samples
- Remedial PE samples
- Multimedia validation

6.1.2. Initiation of Laboratory Validation. A written request for evaluation of laboratory performance from a customer to the Program Manager begins the process. Upon receipt of a

request, the Program Manager informs the laboratory of the forthcoming laboratory validation, sends an information package about the laboratory validation process and a questionnaire to the laboratory, and requests copies of laboratory's qualification documents. The qualification documents, such as QA Manual, SOPs, etc., shall provide pertinent information for the Program Manager to determine whether the laboratory is capable of meeting project requirements and whether project-specific PE samples should be sent.

6.1.3. Initial PE Samples. PE samples shall be prepared and sent out by designated PE Sample Providers through overnight delivery service. All PE samples shall be preserved and shipped according to USACE, USEPA, and DOT regulations or guidelines. A full chain-of-custody (COC) shall be maintained for each shipment of PE samples. Sample-specific instructions for individual PE samples are included in the shipment. (General guidelines for analysis and reporting are sent in the initial package from the Program Manager.)

6.1.4. Analysis of PE Samples. The following sections describe selection of PE samples, metal PE samples, analytical methods, modification and approval requirements of analytical methods, and laboratory analysis.

6.1.4.1. Selection of PE Samples. PE samples designed for project-required methods will be prepared and shipped to participating laboratories. If no PE sample for project-required method is available from the USACE in a timely manner, the Program Manager may consider a replacement PE sample. The replacement of PE samples is allowed only if both analyses are similar in technical nature, and the laboratory performs both analyses in-house on a routine basis.

6.1.4.2. Metal PE Samples. For metal analysis, the laboratory validation is granted based on a combination of the analytical methods used and the number of metal elements in the PE samples passed. The analytical methods are usually classified as FLAA, GHAA, CVAA, GFAA, ICP-AES, or ICP-MS. The metal elements are grouped into the following four categories.

- Category I: Eight Resource Conservation and Recovery Act (RCRA) metal elements including arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.
- Category II: Barium plus thirteen Priority Pollutant (PP) metal elements including antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc.
- Category III: Twenty-three USEPA Contract Laboratory Program (CLP) Target Analyte List (TAL) metal elements including aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver, sodium, thallium, vanadium, and zinc.
- Category IV: Any other combinations of metal elements.

Based on project requirements for metal analysis, one of the above categories of metal PE samples in combination with the analytical method(s) will be selected for proficiency testing. A laboratory may volunteer for any one of the four categories of metal PE samples provided the minimum project-required metals are analyzed.

6.1.4.3. Analytical Methods. Standard analytical methods from the following sources are usually required for USACE's HTRW environmental projects and hence for the analysis of PE samples.

- *Test Methods for Evaluating Solid Waste*, USEPA SW-846.
- *Methods for Chemical Analysis of Water and Wastes*, USEPA-600/4-79-020.
- *Methods for the Determination of Organic Compounds in Drinking Water*, USEPA-600/4-88/039.
- *Statements of Work for Organics Analysis, Inorganics Analysis, and Dioxin Analysis*, USEPA Contract Laboratory Program.
- Other published, standard methods of the most recent versions from USEPA, American Society for Testing and Materials, American Public Health Association, American Water Works Association, Water Environment Federation, United States Geological Survey, National Institute for Occupational Safety and Health, Department of Energy, and other equally qualified agencies or organizations.

6.1.4.4. Modification of Analytical Methods. A laboratory must analyze PE samples using the preparation and analytical methods specified on the chain-of-custody form enclosed in the sample shipping container. Any changes or modifications in preparation or analytical methods of PE samples must be approved by the Program Manager. Use of nonstandard or modified standard methods without preapproval from the Program Manager may result in failure of PE sample analysis.

6.1.4.5. Approval for Modified Analytical Methods. Because the acceptance limits of PE samples are developed for specific combinations of sample preparation and analytical methods, the acceptance limits may not be applicable if methods are modified. If a laboratory plans to use modified standard methods, it must submit its in-house method SOPs and method validation data (including MDL, initial performance demonstration, QC limits on precision and bias, chromatograms, etc.) to the Program Manager for approval prior to proficiency testing. For technical and/or cost reasons, PE samples for nonstandard or modified standard methods may not be available in a timely manner.

6.1.4.6. Laboratory Analysis. A laboratory shall treat PE samples as regular field samples and follow the specified methods and any sample-specific instructions to analyze and report PE samples. A laboratory shall also perform all method-required QC analyses that normally include, but are not limited to, analysis of blanks, spikes, duplicates, and QA samples. If the amount of a

PE sample provided is not enough for all QC analyses, the QC analyses shall be performed on spiked reagent water or clean solid matrices.

6.1.5. Reporting of PE Sample Results. Guidelines for reporting PE samples including QC and raw data, format and contents, and time requirements are described in this section.

6.1.5.1. General Reporting Requirements. A laboratory shall report the concentrations of all target analytes, specified by the PE Sample Providers, including estimated values, MDL, Method Quantitation Limits (MQL), Method Reporting Limits (MRL), and dilution factors. (Refer to EM 200-1-3 for the definition and use of MDL, MQL and MRL.) All data for soil/sediment PE samples shall be reported on a dry-weight basis along with percent moisture on an as-received basis, or per sample-specific instruction. No data shall be corrected for spike recoveries or blank contaminations.

6.1.5.2. QC and Raw Data. All batch-associated QC data including blank analysis, replicate analysis, spike recovery, etc., that are required by the analytical methods shall also be reported. Raw data, including sample preparation and run logs, instrument calibrations, chromatograms, calculations, etc., are generally not required but should be available if requested for review by the Program Manager. The data package of PE sample analysis shall be received by the Program Manager within 20 calendar days after receipt of the PE samples, unless otherwise instructed. For projects requiring quick turnarounds, the turnaround times of the PE samples shall also be reduced accordingly. Failure to analyze the PE samples correctly or within the required time frame may result in termination of the validation process.

6.1.5.3. Format and Contents. A laboratory may use its standard data package to report PE sample results, but the data package must be paginated and contain, at a minimum, the following information:

- A cover sheet containing the report's title and date and the laboratory's name and location.
- Table of contents.
- A case narrative including problems with PE sample analysis.
- Sample preparation information including the date and method of digestion, extraction, and cleanup procedures.
- Analytical results including the date and method of analysis, analyte concentrations, MDL, MQL, MRL, and dilution factors.
- Summary of the batch-associated QC data and acceptance limits to demonstrate data quality (precision and bias).
- Phone conversation records on major issues related to PE sample analysis.
- A chain-of-custody report.

6.1.5.4. Time Requirements. Failure to submit required information within the required time frame may result in termination of the validation process. It is the responsibility of the laboratory to keep the Program Manager informed early of any problems with PE sample analyses that would affect the return of results within a required time frame.

6.1.6. Evaluation of PE Sample Results. Acceptance limits and evaluation criteria of PE samples are discussed below.

6.1.6.1. Evaluation Report. Within ten calendar days after receipt of PE sample results, the PE Sample Provider shall prepare and send a written evaluation report to the Program Manager for review. The report shall contain the following information:

- Laboratory name, location (city and state), point of contact, phone and facsimile numbers, and e-mail address if available.
- Dates that PE samples were shipped and results were received.
- PE sample name, control number, and preparation and certification methods.
- Laboratory results, reference values, and warning and control limits of each target analyte.
- Narratives about special problems or issues.
- Follow-ups on failed parameters.
- A line-item summary report to present the status of proficiency testing. The summary report shall include the name of each PE sample, names of target analytes correctly identified but quantitated outside control limits, and the number of false positives and/or negatives reported for each PE sample without disclosure of their identities. More details on the format and contents of evaluation reports can be found in EM 200-1-1.

6.1.6.2. Status of Proficiency Testing. The Program Manager will review the evaluation report and determine the pass/fail status of each PE sample based on the statistically established acceptance limits of each PE sample and the method-specified acceptance criteria of the internal QC samples. The acceptance limits for each parameter/analyte are based on the 95% and 99% prediction intervals which are set as the warning and control limits, respectively.

6.1.6.3. Evaluation Criteria. Described in this section are the general evaluation rules and acceptance criteria for all, single-analyte, and multiple-analyte analyses; metal analysis by AA; and metal analysis by ICP. The number of target analytes is based on the target analytes in the PE samples instead of the number of analytes cited by the analytical methods.

6.1.6.3.1. All Chemical Analyses.

- All method-specific QC data are within project- or method-specified acceptance criteria.
- False positives or negatives are treated as outside control limits.

6.1.6.3.2. Single-Analyte Analyses.

- Each individual analyte is within control limits.

6.1.6.3.3. Multiple-Analyte Analyses. The number of target analytes that are allowed outside warning and control limits is based on the probability of pass/fail status of target analytes under a binomial distribution.

- For analyses with two to five target analytes: All target analytes are within warning limits with the exception of no more than two target analytes between warning and control limits.
- For analyses with six to fifteen target analytes: All target analytes are within warning limits with the exceptions of no more than two target analytes outside warning limits and no more than one of the two target analytes outside control limits.
- For analyses with sixteen to forty-five target analytes: All target analytes are within warning limits with the exceptions of no more than four target analytes outside warning limits and no more than two of the four target analytes outside control limits.
- For analyses with forty-six to eighty-five target analytes: All target analytes are within warning limits with the exceptions of no more than six target analytes outside warning limits and no more than three of the six target analytes outside control limits.

6.1.6.3.4. Metal Analysis by AA.

- All target analytes are within control limits.

6.1.6.3.5. Metal Analysis by ICP. The number of target analytes that are allowed outside warning and control limits are based on the probability of pass/fail status of target analytes under a binomial distribution.

- For analyses with two to five target analytes (e.g., Categories I and IV metals): All target analytes are within warning limits with the exception of no more than two target analytes between warning and control limits.
- For analyses with six to fifteen target analytes (e.g., Category II metals): All target analytes are within warning limits with the exceptions of no more than two target analytes outside warning limits and no more than one of the two target analytes outside control limits.
- For analyses with sixteen to thirty target analytes (e.g., Category III metals): All target analytes are within warning limits with the exceptions of no more than three target analytes outside warning limits and no more than one of the three target analytes outside control limits.

6.1.7. Tentatively Identified Compounds (TIC). Some non-target analytes may exist in the water or soil/sediment PE samples for volatile and semivolatile organic analyses. A laboratory

shall use NIST/USEPA/Mass Spectral Data Center (MSDC), or any other USEPA-approved mass spectral libraries to tentatively identify and quantify up to ten non-target volatile organic compounds and twenty non-target semivolatile organic compounds that exhibit the strongest ion current signals. These compounds must not be system monitoring compounds. Identification of these compounds, based on spectral interpretation procedures, will be evaluated and integrated into the evaluation process for volatile and semivolatile organic PE sample results.

6.1.8. Requested Corrections. The Program Manager will send a copy of the line-item summary report to the laboratory for information and/or any needed corrective actions. Due to confidentiality, the reference values and the warning and control limits of any batch of PE samples shall not be disclosed to laboratories until the batch is discontinued. A laboratory will be allowed to provide revised data for failed parameters if problems such as calculation or transcription errors can be identified. If a laboratory is requested by the Program Manager to check its proficiency testing results, the laboratory shall return revised results for failed parameters within five calendar days.

6.1.9. Unavailable PE Samples. For parameters without available PE samples (e.g., radioactivity, air toxics, petroleum hydrocarbons, etc.) from the USACE, the laboratory validation for these parameters will be based solely on the qualification documents of the laboratory. The documents shall include:

- Copies of laboratory QA manual, method SOPs, and in-house method performance data for MDL, precision, and bias. See EM 200-1-3 for SOP requirements. If an SOP is deemed unacceptable, the laboratory will have 20 calendar days to submit a revised SOP to the Program Manager for a second review.
- Laboratory certificates or licenses.
- The most recent two rounds of PE sample results from other government and/or private agencies.

6.1.10. Remedial PE Samples. After data and SOP revisions, a laboratory must pass, at a minimum, more than 50 percent of all project-required parameters within 50 calendar days from receipt of the first set of PE samples (or from request of SOPs if PE samples are not available). If it does not, the validation process will be terminated. The Program Manager will notify all affected customers for remedial actions immediately. After a laboratory passes more than 50 percent of all parameters, the Program Manager will contact the laboratory to schedule an on-site inspection within ten calendar days. Depending on the results of an on-site inspection, the Program Manager may send an additional set of PE samples for failed parameters or any parameters with major deficiencies noted during the on-site laboratory inspection.

6.1.11. Multimedia Validation. The majority of PE samples available from the USACE are in water and/or soil/sediment matrices. See the following table for validation type awarded based on PE sample type passed.

Table 6-1. Validation Parameters

Sample Type	Validation Type
Water PE samples only.	Multimedia.
Both water and soil/sediment PE samples.	Multimedia if both matrices are passed.
Both water and soil/sediment PE samples.	Water samples only if water PE samples pass and soil/sediment PE samples fail.
Both water and soil/sediment PE samples.	No validation in any matrix type if water PE samples fail.

6.2. Post-Contract Performance Monitoring.

The following section describes procedures for post-contract performance monitoring, possible follow-up actions, and special requests for proficiency testing.

6.2.1. Continual Performance Monitoring. In order to measure laboratory performance after the validation process, the Program Manager may send additional PE samples on a quarterly or as needed basis. This depends on the laboratory’s past performance as well as the importance of the laboratory’s USACE project. These quarterly PE samples may be either single or double blind and are shipped from the field or through a fictitious contract. The results will be evaluated based on the accuracy of analyte identification and quantitation, batch-associated QC data, turnaround time, content of reports, etc. Results from the analysis will be used by the Program Manager to monitor the laboratory’s ongoing ability to produce acceptable analytical data.

6.2.2. Follow-Up Actions. The results of quarterly PE samples will be used to determine one of these follow-up actions:

- Acceptable and No Response Required: Data meets all of the evaluation criteria as previously described. No response is required.
- Acceptable but Response Explaining Deficiencies Required: Deficiencies exist in the laboratory performance. Within ten calendar days of receipt of notification from the Program Manager, the laboratory shall submit written response to describe the problems, corrective actions taken or to be taken, and supporting documentation including implementation

schedules. Based on the deficiencies and responses, the Program Manager may send additional PE samples or perform additional inspections to verify and evaluate corrective actions. If no response is received, the validation status of the laboratory may be suspended or revoked.

6.2.3. Special Requests for Proficiency Testing. Upon request from a customer(s), the Program Manager will send PE samples to evaluate laboratory performance during field sample analysis. The PE samples may be provided as single or double blind and can be specially designed to detect any suspected problems. If double blind PE samples are shipped, take following precautions to ensure the PE samples indistinguishable from regular field samples:

- Using the same bottles, labels, chain-of-custody forms, sample coolers, shipping location, etc., as those of actual environmental samples.
- Setting up a fictitious contract with the laboratory to be evaluated to hide the identity of double blind PE samples.

Customers and the Program Manager must coordinate closely to ensure the success of double blind PE samples.

6.3. Complaints and Corrective Actions.

The responsibilities of the PE Sample Providers and Program Manager for handling complaints are outlined below:

6.3.1. PE Sample Providers. PE Sample Providers shall establish, document, and maintain procedures for handling complaints from participating laboratories. Their specific responsibilities are to:

- Analyze the complaints to detect and eliminate potential causes of nonconforming PE samples.
- Notify the Program Manager of any complaints.
- Obtain approval for corrective actions
- Implement and document changes in procedures resulting from corrective actions.

6.3.2. Program Manager. The Program Manager shall investigate and resolve all complaints regarding the proficiency testing program within 20 calendar days from receipt of complaints. Other responsibilities include:

- Discontinuing use of questionable or problematic PE samples immediately until all problems are resolved and PE samples are recertified.
- Providing a yearly summary of all complaints received and resolutions taken to the HQUSACE.