

## **Chapter 5**

### **Certification of PE Samples**

PE samples are used to judge the performance of laboratories and data quality; therefore, PE samples must be certified on the basis of the following:

- Determination of the reference values. The reference values of PE samples are concentration values assigned to target analytes deemed to be within statistical limits. They must be based on scientifically valid and legally defensible procedures. Reference concentrations should be close to the true or prepared concentrations and are usually determined as the mean measured concentrations by a group of laboratories under control conditions.
- Determination of acceptance ranges of the reference concentrations based on symmetrical statistical prediction intervals around the mean measured concentrations.

PE samples sent to each laboratory must be equivalent to the PE samples upon which the acceptance limits were determined. Prior to determination of acceptance limits, the homogeneity, stability, and reproducibility of PE samples must be determined and proven within limits to ensure equivalent samples.

Steps to ensure certified, equivalent PE samples are discussed in this chapter. Sections include the following:

- Initial sample verification
- Steps to ensure homogeneity, stability, and reproducibility
- Tests for homogeneity, stability, and reproducibility
- Determination of reference values and acceptance limits
- Use of hybrid approach
- Statistical analysis
- Other considerations
- Documentation
- Standard operating procedures
- Confidentiality and ethical considerations

#### **5.1. Initial Verification of PE Sample Composition.**

Before certification of PE samples, the PE sample composition must be verified. Initial verifications ensure that there are no gross errors in the PE sample production process and serve as a baseline for evaluation of the certification process. Use these guidelines to complete verification.

- Use several reliable laboratories to verify the composition of the PE samples with multiple definitive methods of different measurement principles in addition to the analytical methods being used for proficiency testing. Although the composition of fortified PE samples is well known, conduct initial verification to ensure that the mean measured concentrations of prepared values are within acceptance ranges of analytical errors (including preparation and measurement errors).
- Be sure methods used for verification analysis have a standard deviation of lower than  $0.3F$ , where  $F$  is the target standard deviation for the proficiency test of concern.
- Determine the composition of real-world PE samples with appropriate qualitative and quantitative analyses besides the analytical methods being used for laboratory evaluation. The composition of real-world PE samples is therefore based on the mean value of measured concentrations.

## **5.2. Ensuring Homogeneity, Stability, and Reproducibility.**

PE samples sent to individual laboratories must be equivalent and have to remain equivalent prior to the expiration of sample holding times.

**5.2.1. General Guidelines.** General principles to guarantee homogeneity, stability, and reproducibility include:

- Test for homogeneity, stability, and reproducibility both within and between production batches.
- Use any generally accepted test procedures to ensure the consistency of analytes in each PE sample across the production run and through the life span of use at a 95% confidence level. Do not use PE samples that failed to pass the testing criteria in the USACE PE Program. See Section 5.3 for tests of homogeneity, stability, and reproducibility that can be performed by one or more reliable laboratories.
- Maintain proper documentation as evidence that PE samples are sufficiently homogeneous, stable, and reproducible.

The remainder of this section gives guidelines for ensuring equivalent samples for fortified aqueous, fortified soil, and real-world PE samples.

**5.2.2. Fortified Aqueous PE Samples.** Due to the nature of aqueous solutions, homogeneity is not a concern. However, the following steps are necessary to ensure stability and reproducibility of fortified aqueous PE samples. Additionally, stability and homogeneity of spiking reagents and solutions must be monitored.

#### **5.2.2.1. General Guidelines.**

- Spike the chemical standard solutions directly into the sample containers where loss of sample components to the walls of the glassware may be a problem.
- Designate experienced personnel to use dedicated syringes, pipetters, and glassware to minimize variability and maintain reproducibility between individually prepared PE samples.

#### **5.2.2.2. Stability.**

- Prepare and preserve PE samples properly to maintain stability within method-specified sample holding times.
- Check, at a minimum, stability of mean analyte concentration at the end of sample holding times. Inorganic analytes should be within  $\pm 10\%$  of the initial mean concentrations; organic analytes should be  $\pm 15\%$ .
- Select clean, inert containers, and consider chemical compatibility for selection of containers, starting materials, and stock solutions.
- Use ASTM Standard D4515 to determine the expiration date of PE samples under specific storage conditions recommended by the USEPA.

#### **5.2.2.3. Spiking Standards.**

- Check the homogeneity and stability of the spiking reagents and solutions on a routine basis. For liquid spiking solutions, warm the solutions to ambient temperature and vigorously shake to ensure a homogeneous mixture without precipitation.
- Prepare, verify, and use a new spiking reagent or solution if necessary.

**5.2.3. Fortified Soil PE Samples.** Homogeneity, stability, and reproducibility are all major concerns for fortified soil PE samples. Soil PE samples for explosives and volatile organic compounds are prepared by fortifying pre-weighed clean soils in vials and ampules, respectively. The entire amount of soil PE sample in a vial or ampule is used for each proficiency testing so that homogeneity in a vial or ampule is not a concern, but reproducibility of individual PE samples is a major concern. Use the following steps to ensure reproducibility of fortified soil PE samples. Additionally, stability and homogeneity of spiking reagents and solutions must be monitored.

**5.2.3.1. General Guidelines.** Follow these steps to ensure reproducibility:

- Grind solid spiking reagents into fine particles of similar size to that of sample matrices if individual soil PE samples are subsampled from a large quantity of fortified soil PE bulk materials.
- Use dedicated equipment and experienced personnel to ensure the reproducibility within and between batches.

### **5.2.3.2. Spiking Standards.**

- Check the stability of the fortified soil PE samples and the spiking reagents on a routine basis and prior to use to ensure that no substantial changes in analyte concentrations have occurred. The frequency of stability checks depends on the characteristics of PE samples and reagents and the storage conditions.
- Refer to control charts and trend tests of historical data to determine significant degradation of analyte concentrations.

**5.2.4. Real-World PE Samples.** USACE routinely uses real-world soils and sediments to prepare real-world PE samples. Homogeneity and stability are major concerns for real-world PE samples. Sample reproducibility depends on homogeneity and stability of the bulk sample materials. Use these guidelines to ensure homogeneity:

#### **5.2.4.1. PE Sample Homogeneity.**

- Use PE sample materials of sufficient quantity and homogeneity to ensure representative subsamples with low sampling errors. (See Appendix D for more information on sampling error.)
- Check the homogeneity of PE materials by analysis of replicate PE samples from different sections of the bulk PE sample materials. The results should show no significant differences in concentrations for the replicates analyzed. A soil PE sample must be homogeneous to such a degree that residual difference between the compositions of PE samples will contribute virtually nothing to the variability of the results of participant laboratories.

**5.2.4.2. PE Sample Stability.** Most real-world soil or sediment PE samples are very stable under proper storage conditions. Because real-world PE samples are usually used for an extended time period, the stability of the bulk PE sample materials should be monitored using these guidelines:

- Carry out stability studies at elevated temperatures to accelerate the rate of sample degradations and reduce time to obtain sufficient data.
- Establish an expiration date for real-world PE samples.
- Analyze bulk PE sample materials periodically against set criteria for acceptable stability.
- Control chart results to document the validity of accepted values and their control limits and to detect any temporal trend in measured concentrations as an early warning. See Section E.6.5 of Appendix E for an example trend test.

### **5.3. Testing for Homogeneity, Stability, and Reproducibility.**

Experimental and statistical considerations for each of these areas are described below.

#### **5.3.1. Homogeneity.** Follow these guidelines for tests of homogeneity:

##### **5.3.1.1. Experiment Design.**

- Test homogeneity for each analyte in every type of PE sample material or test analytes known to be most sensitive to problems.
- Use judgmental sampling to collect samples where heterogeneity is expected. Use random sampling only when there is no expected or suspected heterogeneity.
- Select multiple (e.g., five or more) PE samples from each of the beginning, middle, and end of a production run or from each of the top, middle, and bottom sections of a bulk real-world PE sample material.
- Test samples in replicate (e.g., duplicate or triplicate) to yield a minimum of 30 tests. The number of samples taken and replicate determinations depends on the level of uncertainty and the budget. If a highly precise method is used for homogeneity determination, perform duplicate tests on each of eight to ten randomly selected samples. A highly precise method means that the repeatability standard deviation is less than 30% of the total standard deviation for the proficiency testing of concern. For a less precise method, perform triplicate tests on each of five samples in random order to avoid systematic time variations.

##### **5.3.1.2. Statistical Analysis.** Guidelines for statistical analysis include:

- Use a traditional analysis of variance (ANOVA) F test to test the significance of the between-sample component of variances. If the F test is not significant at  $\alpha = 0.05$  level, the PE samples may be considered homogeneous. (See Section E.5 of Appendix E for an example calculation of a homogeneity test.)
- If the F test is significant, perform an additional test to assure that the significance represents a difference that could truly affect the evaluation of proficiency testing. The test compares the total standard deviation (include both between- and within-sample standard deviations) with the acceptance limits (i.e.,  $3\sigma$ ) of the PE sample. If the total standard deviation is less than 10% of the acceptance limit of target analyte, the PE sample can still be considered sufficiently homogeneous and used in the USACE PE Program.
- Where the results show the material to be not sufficiently homogeneous, reprocess the material (i.e., additional grinding and mixing), recheck the homogeneity, or select an alternative material. Another option is to relax the target standard deviation for that particular material to account for the variance the material will contribute to individual results. Except in minor excursions from sufficient

homogeneity, use such a practice with great care because it would destroy the utility of the proficiency test and the confidence of participant laboratories.

**5.3.2. Stability.** Stability is discussed for fortified and real-world PE samples along with guidelines for sample handling and spiking standards.

**5.3.2.1. Fortified PE Samples.** For fortified PE samples, follow these guidelines for stability testing:

- Use multiple samples (e.g., at least five) randomly selected from the production run.
- Conduct tests in duplicate at the end of the sample holding times as specified by the analytical methods used for laboratory evaluation.
- Compare results with the results of the initial verification tests. The means of the analytical results should not be statistically different at  $\alpha = 0.05$  level using a conventional  $t$  test. See Section E.6 of Appendix E for an example calculation of a stability test. If the means are significantly different, compare the difference with the size of the corresponding acceptance limits. If the difference between the means is less than 10% of the acceptance limits (i.e.,  $3F$ ) of PE samples, the PE samples are considered sufficiently stable for the specific analytes.
- Retain and test one PE sample for each batch of PE samples prepared for samples with established shelf-lives.
- Control chart the results of these tests to document the continual validity of the sample stability.

**5.3.2.2. Real-World PE Samples.** For real-world PE samples, follow these guidelines:

- Conduct stability testing over an extended time period to cover the anticipated shelf-life.
- Conduct the initial test at the end of the method-specified sample holding time to ensure that there is no significant change in the composition of the PE sample. Thereafter, conduct tests at fixed intervals to assure long-term stability until the supply of the PE samples is exhausted.
- Use an experiment design similar to that of fortified PE samples.
- Use control charts to detect any trend in measured concentrations over time.

**5.3.2.3. Sample Handling.** The instability of PE samples may be caused by packing and shipping processes. Therefore, pack and mail PE samples for stability testing to the PE Sample Provider in the same way as to participant laboratories.

**5.3.2.4. Spiking Standards.** Test stability for spiking standards using these steps:

- Verify purity of prepared or purchased spiking reagents or solutions prior to the first use.
- Check the concentration of spiking reagents or solutions before each use and on a quarterly basis with appropriate methods.

- Use only spiking reagents or solutions with mean measured concentrations within  $\pm 10\%$  (for inorganic) and  $\pm 15\%$  (for organic) of the prepared values or the initial mean measured concentrations with a conventional two-sample  $t$  test at  $\alpha = 0.05$  level. Otherwise, discard the spiking reagents or solutions.
- Use control charts to monitor the stability and trend of degradation of spiking reagents or solutions over an extended time period.

**5.3.3. Reproducibility.** Although dedicated syringes, pipets, glassware, and personnel will be used to minimize the variations of PE samples produced within and between batches, check reproducibility of PE samples on a routine basis to ensure that equivalent PE samples are continually produced. Because certain PE samples of short holding times are prepared on an as needed basis, evaluate both within- and between-batch reproducibilities.

**5.3.3.1. Within-Batch Testing.** Follow these steps for within-batch reproducibility testing:

- Perform tests of multiple PE samples (e.g., at least five or more) randomly selected from a production batch.
- Test each sample in duplicate or triplicate, yielding a minimum of 15 tests.
- Use a traditional ANOVA  $F$  test to test the significance of the within-batch component of variances as for homogeneity tests. If the  $F$  test is not significant at the  $\alpha = 0.05$  level, the PE samples may be considered equivalent and the production process reproducible.
- If the  $F$  test is significant, conduct an additional test to assure that the significance represents a difference that truly could affect the evaluation of the results. To do this, compare the size of total within-batch variances with the acceptance limits of PE samples. If the total within-batch standard deviation is less than 10% of the acceptance limits (i.e.,  $3\sigma$ ) of the PE samples, the within-batch PE samples are considered sufficiently reproducible.

**5.3.3.2. Between-Batch Testing.**

- Select by random multiple (e.g., at least five or more) PE samples from different production batches.
- Use similar procedures to the within-batch reproducibility testing.

**5.4. Determination of Reference Values and Acceptance Limits.**

**5.4.1. Determination of Reference Values.** A reference value is usually derived from:

- A theoretical or established value based on scientific principles.
- An assigned or certified value based on experimental work of a certain national or international organization.

- A consensus or certified value based on collaborative experimental work under the auspices of a scientific or engineering group.
- The mean of a specified population of measurements if the above items are unavailable.

Reference values of PE samples are generally determined from the mean measured values, which should be close to the true or prepared values. When reference values are determined from the mean measured values, they reflect the recovery of target analytes or the bias of a specific analytical method. Therefore, reference values of PE samples might not be the same as true or prepared values.

**5.4.2. Determination of Acceptance Limits.** The acceptance limits of PE samples are determined by prediction intervals. These intervals are based on the statistical uncertainties from the means measured or reported values from round-robin testings. Test the reference values and the acceptance limits of PE samples meticulously both internally and externally prior to and during proficiency testing. See Section E.9 of Appendix E for an example determination of reference value and acceptance limits based on data from a round-robin testing.

**5.4.3. Common Approaches.** Several other approaches may also be used to determine the reference values and acceptance limits of PE samples. Based on technical and economical considerations, the common approaches of the USACE PE Program are listed below in the order of declining preference.

- Method performance data analysis
- Referee laboratory analysis
- Round-robin testing
- Error propagation analysis

These approaches are often used concurrently or sequentially, depending on PE sample requirements and available resources and technical information. The rest of this section explains each approach.

**5.4.3.1. Method Performance Data Analysis.** If reliable, published method performance data are available, the reference values and the acceptance limits of PE samples can be determined from method performance data published in literature or PE studies such as USEPA Water Supply (WS)/Water Pollution (WP) Programs. Method performance data are typically presented as linear regression equations that relate true or prepared concentrations to mean measured concentrations and standard deviations. Determine values and limits by following these steps:

- Set acceptance limits using the predicted means and standard deviations. Linear regression equations may only be used for prepared values that fall within the linear range of the method or the results might be biased.

- Base the warning and acceptance limits on 95% and 99% prediction intervals, respectively. (See Sections 5.4.2 and 6.1.6 for details on determination and use of warning and acceptance limits, respectively.)
- Make sure the method and matrix to be used in proficiency testing match those used to develop the method performance data to ensure reliability.
- Be sure concentrations of target analytes in the PE samples fall within the same concentration ranges as method performance data.

**5.4.3.2. Referee Laboratory Analysis.** This section describes qualifications of referee laboratories, how to use them, adjusting acceptance limits, analytical requirements, and establishing acceptance limits.

**5.4.3.2.1. Qualification of Referee Laboratories.** If reliable, published method performance data are not available, referee laboratory analysis shall be used to establish the reference values and acceptance limits. These laboratories use the mean measured concentration and the 95% and 99% prediction intervals to establish the reference values and the warning and acceptance limits of PE samples. Qualifications of referee laboratories include:

- Reliable with high performance standards.
- Validated and approved by the Program Manager according to the procedures described in USACE EM 200-1-1.
- Follow stipulated methods to prepare and analyze PE samples.

**5.4.3.2.2. Using Reference Laboratories.** Follow these steps to use referee laboratories:

- Send PE samples to referee laboratories for characterization before shipping to participating laboratories. However, send PE samples with short holding times to participating laboratories and a minimum of four referee laboratories at the same time.
- Investigate excessive high or low recoveries. Measured concentrations should be within 10% of the prepared concentration for the majority of target analytes. Analytes of poor recoveries and low concentrations may exceed 10%, but this may be acceptable on a case specific basis.
- Resubmit one or two PE samples periodically to check any potential degradation or temporal trends in analyte concentrations.

**5.4.3.2.3. Adjusting Acceptance Limits.** Because of the high performance of referee laboratories, their acceptance limits could be too tight. Adjust for this by:

- Ask referee laboratories to use multiple chemists, each using his/her own instruments, standards, reagents, etc., to prepare and analyze PE samples to simulate typical laboratory performance. If

use of a common instrument cannot be avoided, each chemist should establish new calibration curves to simulate independent analyses.

- Consider double blind PE samples to further reduce experimental bias, especially for the standard deviation.

**5.4.3.2.4. Analysis Requirements.** Guidelines for referee laboratories include the following:

- Ten replicate samples must be available from referee laboratory analysis for establishing acceptance limits.
- Sample extractions or digestions must be performed singly on separate days by one of several chemists or technicians.
- Each sample set must consist of one PE sample and accompanying QC samples, which include a method blank, a blank spike, a blank spike duplicate, and an independent reference sample.
- Samples must be analyzed by multiple operators on multiple instruments utilizing individually prepared calibration curves.
- QC acceptance criteria are method-specific and must be used to evaluate the recovery of analytes, not to reject data.
- All data meeting the minimal method-specific calibration criteria shall be used to calculate initial acceptance limits.
- Outliers that are not sustained by scientific reasoning or technical evidence shall not be removed from the data set before the standard deviations are calculated.

**5.4.3.2.5. Establishing Acceptance Limits.** To establish acceptance limits, follow these guidelines:

- For initial acceptance limits based on a few referee laboratory analyses, adopt the 99% and 99.9% confidence intervals around the mean measured concentration as the initial warning and control limits, respectively.
- When more data from participating laboratories are available, update the initial acceptance limits based on the mean measured concentration and the 95% and 99% prediction intervals of the pooled data.

**5.4.3.3. Round-Robin Testing.** Similar to referee laboratory analysis, in round-robin testing PE samples are analyzed by peer laboratories under control conditions. Data are combined to form a consensus. The number of participating laboratories is usually much larger than that of referee laboratory analysis, and the performances of the participating laboratories are unknown. The reference values and acceptance limits are determined based on the mean reported values and the associated prediction intervals. For example, the true values of target analytes in real-world PE samples are usually unknown so that the mean reported values from a round-robin testing are usually considered as the true values and are used as the reference values. Use normal 95% and 99% prediction intervals around the mean reported values as the warning and control limits, respectively. Due to complicated

sample matrices, the mean measured value and the acceptance limits for each target analyte in real-world PE samples are often matrix- and method-specific. Follow these guidelines for round-robin testing:

- Use it to verify the appropriateness of existing reference values and acceptance limits that are established with other approaches.
- Use other approaches of expectantly higher reliability, such as referee laboratory analysis, to verify the results of round-robin testing.
- Use round-robin testing or referee laboratory analysis to determine reference values and acceptance limits of fortified soil PE samples. It is difficult to determine these values using other methods because analytes' leachable levels must be known, and analytes in the spiking solution react with a solid matrix.

**5.4.3.4. Error Propagation Analysis.** Acceptance limits may also be calculated from error propagation analysis. Sometimes calculation is the only way to determine the true values and acceptance limits; it is very accurate and straightforward for fortified PE samples. The acceptance limits of fortified aqueous PE samples can be determined through error analyses of the sample preparation and analysis steps. Error propagation rules are used as guidelines to estimate determinate and indeterminate errors that would be experienced by the laboratory being evaluated. Indeterminate errors are always judgment calls and would be based on experience. The Factor-2 criterion (i.e., indeterminate errors are approximately equal to two times determinate errors) may be used as a good approximation for inclusion of indeterminate errors. The result is a relative error that can be multiplied by the expected target concentration of each analyte to obtain acceptance limits. Follow these guidelines for error propagation analysis:

- Use several referee laboratories and consensus values to characterize PE samples if biases are known to exist but cannot be accounted for.
- Ask PE Sample Providers to analyze four replicate samples from each batch of PE samples to confirm accuracy and precision if initial control limits are based on error propagation analysis or fixed percentages of true values.
- Ensure that the correct number of significant figures is retained during error propagation analysis.

## **5.5. Hybrid Approach.**

USACE procedures for determining acceptance limits vary depending on the type of PE samples and the method performance information available. The preferred choice is published method performance data based on round-robin testings. If method performance data are unavailable, the USACE adopts a hybrid approach of referee laboratory analysis and round-robin testing. Steps involved in this approach include the following:

- Use the mean measured value of the results of referee laboratories to establish reference values.
- Use the 99% and 99.9% confidence intervals around the mean measured value to establish initial acceptance limits.
- Send the new PE sample along with a developed PE sample to participating laboratories and collect results for statistical analysis.
- Pool all data when a minimum twenty data points have been returned including those of referee laboratories.
- Reanalyze statistically to establish revised reference values and acceptance limits. Base the revised acceptance limits on 95% and 99% prediction intervals of the pooled data. They should be similar to the initial ones.
- Investigate possible sources of errors if the revised reference values and acceptance limits are substantially different from the initial ones.
- Statistically analyze PE results from peer laboratories on a regular basis to check for significant variations in bias and precision of PE sample analysis.
- Readjust the reference values and acceptance limits of PE samples one more time based on additional (e.g., a minimum of forty data points) new or pooled data.
- Monitor acceptance limits on a routine basis and adjust on an annual basis if needed.

## **5.6. Statistical Analysis.**

General considerations for statistical analysis as well guidelines for distribution and outlier tests are given in this section.

**5.6.1. General Considerations.** Before applying any statistical techniques to analytical data, a preliminary data review is conducted to determine whether the data support underlying assumptions or if data modifications are necessary before further statistical analysis. The preliminary data review typically includes:

- Calculations of some basic statistical quantities including number of observations, measures of central tendency, dispersion, and distribution symmetry. These are useful for making inferences concerning the population used as a basis for the data.
- Graphical representations which are used to identify patterns and relationships within the data, confirm or disprove a hypothesis, and identify potential problems. This review reveals the structure of the data and identifies appropriate approaches and limitations of data use.

**5.6.2. Distribution Tests.** Chemical data can usually be analyzed using normal or Gaussian statistics. Acceptance limits for PE samples are determined from data sets that show normal distributions. Data can be tested for normal distribution using graphical representations such as normal probability plots, frequency plots, or histograms.

- Use a normal probability plot to determine whether data have a normal distribution, especially if a non-normal distribution is suspected.
- Use log-transformed data to test for normal distribution if the analytical method is highly variable and shows negative control limits for analyte recoveries.
- Test for the presence of outliers in a data set (see Section 5.6.3). Acceptance limits should not be determined from data sets that are strongly influenced by outliers.
- Use a larger population of samples or other statistical techniques such as outlier removal, non-parametric statistics, etc. to determine acceptance limits.

**5.6.3. Outlier Tests.** Outliers are measurements that are extremely large or small relative to the rest of the data and, therefore, are suspected of misrepresenting the population. Statistical outlier tests give evidence that an extreme value does not fit the distribution of the remainder of the data. Follow these steps for outlier testing:

- Use graphical representations such as frequency plots, histograms, normal probability plots, etc., to identify possible outliers.
- Evaluate suspected outliers with statistical tests such as Dixon's test, Grubbs' test, Cochran's test, Rosner's test, Walsh's test, or Youden Ranking test. (Refer to a statistical reference book or statistician to determine the proper test to use based on the data acquired.)
- Correct, retain, or discard outliers. The final judgment of whether an outlier is discarded or retained depends on the scientific judgment of the analyst and not just the outcome of the outlier test. Extreme values may be justifiably retained in a data set if other evidence outweighs the outlier test result.
- Discard an outlier value if there is a defensible explanation.
- Retain outlier if no good scientific judgment for its exclusion is found.
- Perform statistical analysis of the data set (e.g., mean and standard deviation) on both the full (outlier included) and the truncated (outlier excluded) data sets to measure the effect of the removed outlier.
- Discard scientifically indefensible outliers if the outlier exerts a large influence on the data set (e.g., it creates a large standard deviation or produces a large change in the calculated mean such that prediction intervals are useless).
- Document all statistical tests as well as the scientific judgments for discarding or retaining questionable data points.
- Use a minimum of 15 data points after rejection of outliers to calculate acceptance limits.

### **5.7. Other Considerations.**

Other guidelines for ensuring the quality of PE samples given in this section include data accuracy, data comparability, program-wide statistical results, and PE Sample Provider requirements.

**5.7.1. Data Accuracy.** Accuracy of analyte concentrations in real-world PE samples depends on the amount of data available or affordable. To determine the composition of real-world PE samples, send split PE samples to a minimum of four referee laboratories. The consensus value from several referee laboratories should be a better estimate of true value than any single measurement.

**5.7.2. Data Comparability.** All PE samples must be analyzed with the same methodology by participating laboratories as well as the referee laboratories. Any deviations from the standard methods may make data not comparable.

- Use the results of all PE sample analyses to develop control charts displaying the true concentration, recovery ranges, and bias for each target analyte. Control charts will help detect trends and prevent problems.

**5.7.3. Program-Wide Statistical Results.** Compile program-wide statistical results using these guidelines:

- Analyze the PE sample results produced by all contract laboratories on a regular basis.
- Document the mean values and the associated uncertainties of target analytes.
- Use results to adjust the acceptance limits in order to observe the relative performance of each laboratory using a given protocol against its peers. The USACE may adjust the acceptance limits on any given PE sample to compensate for unanticipated difficulties with a particular sample or analysis.

**5.7.4. PE Sample Provider Requirements.** Each PE Sample Provider is required to have in place within its own dedicated facility the capability to design, produce, test, and distribute PE samples, and to provide data analysis and reporting functions for any series of PE samples. The technical staff, instrumentation, and computer capabilities must be able to support these tasks.

## **5.8. Documentation.**

PE Sample Providers shall establish and maintain procedures to control all documents and data that relate to the design, development, production, certification, and use of PE samples. The documentation should provide clear evidence that the PE samples are developed and used with scientific and legal defensibility. The documentation should cover, but not be limited to, the following areas.

- Protocols for production of PE samples.
- Certification of PE samples with validated definitive methods by referee laboratories and/or collaborative trials.
- Demonstration of statistical control in production processes with fully established control charts.
- Demonstration of data traceability with scientific and legal defensibility.

Follow ISO Guides 31, 34, and 35 to document the preparation and contents of PE samples. At a minimum, document the following:

- PE sample name
- Unique identification number and batch number
- Description of the PE sample
- Certified compositions and uncertainties
- Intended use of the PE sample
- Instructions for the correct use of the PE sample
- Sources of the PE materials
- Preparers of the PE samples
- Name and address of the certification organization
- Stability, transportation, and storage instructions
- Preparation method of the PE sample
- Certification method of the PE sample
- Names of participating laboratories
- Name of certification officer
- Date of certification

### **5.9. Standard Operating Procedures.**

In order to prepare reliable and reproducible PE samples, it is imperative that the PE Sample Providers use SOPs. Use USEPA document QA/G-6, "Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality-Related Documents," to prepare SOPs. Follow these guidelines for writing PE sample SOPs:

- Include actual procedures used in the laboratory to ensure that reproducible results can be achieved by following SOPs.
- Prepare SOPs as part of the planning process and complete before PE sample preparation work begins.
- Submit to the Program Manager for review and approval before production.
- Avoid ambiguous statements like "air dried at ambient temperature" or "1:10 dilution" when "18 to 22°C" or "tenfold dilution" is meant. (The "1:10" may be confused with one part concentrate diluted with ten parts of diluent, which is really an 11-fold dilution.)
- Note changes and observations during preparation for subsequent SOP revisions.

## **5.10. Confidentiality and Ethical Considerations.**

Concerns of confidentiality and ethics for PE Sample Providers and participating laboratories are given below.

### **5.10.1. PE Sample Providers.** Concerns include the following:

- Data generated from PE sample analysis is confidential.
- No portion of the production, testing, distribution, data collection, or data reporting may be subcontracted by PE Sample Providers.
- PE Sample Providers shall declare that they do not have potential conflict of interest with any laboratory seeking, or having, the USACE environmental laboratory validation. PE Sample Providers shall notify the Program Manager of any actual or potential organizational conflicts of interest including, but not limited to, financial interest, sharing of personnel, facility, or instrumentation with any laboratories.
- The reference values and acceptance limits of PE samples are proprietary information of the USACE and shall not be disclosed by PE Sample Providers without written approval of the Program Manager.
- PE Sample Providers shall not sell, distribute, or provide PE samples of similar or identical design and concentration to any laboratories who may, will, or are seeking USACE environmental laboratory validation.

### **5.10.2. Participating Laboratories.** Guidelines regarding confidentiality include the following:

- The confidentiality of laboratories participating in the USACE PE Program will be maintained. The identity of participants should be treated as confidential information with limited access, and this shall extend to any subsequent remedial advice or actions applied to a laboratory exhibiting poor performance.
- Participating laboratories shall not send any PE samples or a portion of any PE samples to another laboratory for any analysis, shall not exchange information with another laboratory concerning any PE samples, and shall not attempt to obtain the target values of any PE samples from PE Sample Providers.