

## II. Quality Control

### A. Introduction

ENCO adheres to strict quality control practices in order to assure our clients that the data provided are accurate and reliable. We are required by the EPA to analyze one duplicate, one sample spike, and one blank with every 5-10% of samples analyzed, depending on the method used. This means every 10-20th sample is dosed (in duplicate) with the analyte(s) in question and analyzed. In addition to matrix spikes, ENCO also analyzes Laboratory Control Samples (LCS) with each analytical batch. The LCS is prepared like the matrix spikes, except contaminant-free lab matrix is used in place of the sample. This allows us to place more control on procedural errors that may adversely affect the accurate analyses of the associated samples.

The quality control data contained in our reports are the method precision and accuracy. The method accuracy is represented by the percent recovery of a known spike concentration from a sample matrix. The method precision is represented by the relative percent difference between the duplicate samples or duplicate spiked samples.

Our in-house quality control program assures you that the information you receive is accurate. Should you desire additional quality control measures applied to your program, please call us to discuss additional options.

This section explains many of the terms and concepts behind laboratory quality assurance and quality control.

## B. Basic Definitions:

**QUALITY:** The totality of features and characteristics of a product or service that bear on its ability to satisfy stated or implied needs; Conformance to standards.

**GRADE:** An indicator of category or rank related to features or characteristics that cover different sets of needs for products or services intended for the same functional use; Level of technological development, intensity of standards; reflection of differences in content or design.

What's the difference between grade and quality?

**EXAMPLE:** A Rolls Royce is a high-grade automobile, whereas a Yugo is a lower grade automobile. However, if the Rolls Royce is not manufactured to its own specifications, the Rolls is not a quality product. If the Yugo is manufactured to its own specifications, it is considered to be a quality product or at least a quality Yugo! So, grade refers to the actual standard or expectation behind a product or service, and quality refers to the ability to meet a standard or expectation.

What are your:                      Standards?  
   Needs?  
   Expectations?

In considering the above, what are the project objectives? What is the regulatory driver (what rules are you trying to comply with)? What is the end use of the data, and who are the end users? What stated standards or data quality objectives must you comply with? How quickly do you need the deliverables, and to what level of detail? What subjective expectations do you have of the laboratory?

Effective communication of the above parameters to the laboratory helps ensure quality deliverables.

**Quality Control:** A system of operational means for the fulfillment of quality requirements (standards). QC is performed by the analyst as a routine and inclusive part of the analytical protocol. Results are reported with data as deliverables.

**Quality Assurance:** A system for monitoring the fulfillment of quality requirements, and communicating the fulfillment both internally and externally. QA functions are performed by a neutral entity; results are reported to management. QA is a check on the appropriateness (function and frequency) of QC measures taken in the laboratory. QC is a subset of QA.

**Method Detection Limit (MDL)** - The minimum level of analyte that can be detected with 99% confidence that the analytical response is greater than zero. The MDL is assessed by analyzing at least seven replicates of reagent water which have been fortified at low levels with the analyte(s) of interest, then processed through the entire analytical method. The actual MDL value is three times the standard deviation of the seven replicates.

**Limit of Detection (LOD)** – The smallest amount of concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). This definition is based on DOD requirements. The results for an MDL study can be reported as an LOD.

**Limit of Quantitation (LOQ)** – The lowest concentration that produces a quantitative result within specified limits of precision and accuracy. For DOD projects, the LOQ must be set at or above the concentration of the lowest initial calibration standard.

**Practical Quantitation Limit (PQL)** -- The level of analyte that can be routinely detected and quantified in a real matrix. EPA defines the PQL as 12 times the standard deviation obtained from the MDL study (as above).

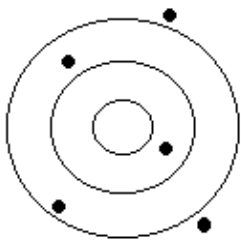
**Reporting Limit (RL, or RDL)** -- A level at which a laboratory routinely reports analytical results. The RL is determined by the laboratory based upon factors such as the analyte's MDL, PQL, lowest calibration standard, and any applicable regulatory limits.

**C. Data Quality Objectives:**

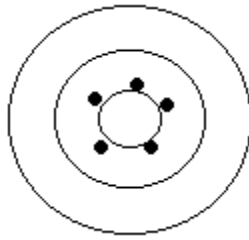
**PRECISION** -- The measure of mutual agreement between individual analytical results. Precision is assessed using replicate analyses.

**ACCURACY** -- The degree of agreement of an analytical measurement with an accepted reference value. Accuracy is assessed using fortified samples and external samples of known concentration.

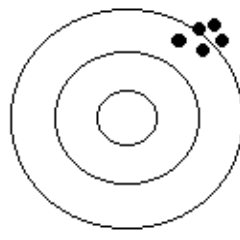
Graphical Representations:



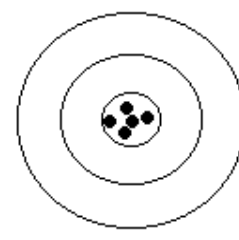
Inaccurate and Imprecise



Accurate but Imprecise



Inaccurate but Precise



Accurate and Precise

Examples of Spike Recoveries following the above descriptions:

142 %	92 %	119 %	102 %
78 %	108 %	118 %	100 %
106 %	92 %	120 %	101 %
64 %	108 %	118 %	99 %
128 %	92 %	119 %	101 %
Inaccurate and Imprecise	Accurate but Imprecise	Inaccurate but Precise	Accurate and Precise

Almost all methods have established precision and accuracy standards that must be met by the laboratory. Laboratories must first meet the method limits to establish their process (analysis) is within control, and then, on an ongoing basis, determine internal precision and accuracy limits that are within those specified in the method.

Laboratories must also demonstrate their staff is capable of generating data that meets these method (or internal, if tighter) criteria. For every procedure performed by an analyst, the laboratory must maintain an initial demonstration of capabilities (IDOC), or precision and accuracy study. This data must be generated prior to the independent analysis of any client samples, and is only required to be performed once per method per analyst.

## D. Laboratory Quality Control

- A) What you see:
- Blanks
  - Spikes (fortified samples)
  - Duplicates (lab analytical replicate)
  - Surrogates
- B) What you don't see:
- Initial Calibration
  - Continuing Calibration (calibration verification)
  - Replicate Analyses
  - Instrument Blanks
  - Degradation Checks
  - Control Limits Generation and Trend Analysis
  - Method Detection Limit Studies
  - Internal Blinds
  - External Performance Evaluations
  - Internal and Regulatory Audits
  - Internal Data Review and Validation
  - Preventative Maintenance
  - Continuing Education

**INSTRUMENT QUALITY CONTROL:** Quality Control samples used to assess initial and continuing instrument performance, including:

**Initial Calibration:** A series of reference standards used to establish a reliable (linear) analytical range. Analyzed as a prerequisite to sample analysis.

**Continuing Calibration:** Reference standards analyzed to verify instrument performance relative to an established calibration curve, or analytical range. This standard is analyzed periodically as part of each analytical batch.

**Tuning:** Part of mass spectrometer calibration protocol; a specified compound is injected and the instrument is adjusted to meet method-specific performance criteria.

**Instrument Blank:** Analysis of pure water or solvent to assess the presence or absence of target analytes or interferences at the instrumental level (as separate from method process).

**Degradation Check:** Analysis of a reference solution containing a subset of select reactive components to verify the cleanliness and inertness of the analytical system.

**METHOD QUALITY CONTROL:** Quality Control samples that are processed with an analytical batch, and are designed to provide information about actual method performance. Method QC samples include the following:

**Method Blank:** The method blank is taken through the entire preparation procedure and used to assess the presence or absence of analytical target constituents or interferences in the analytical process.

**Laboratory Control Sample (LCS):** Also called a "fortified blank" or positive control, is a laboratory clean matrix with a known amount of target analyte(s) added. Used to assess the accuracy, or bias, of the method (reagents, instrument, human error, etc.).

**LCS Duplicate:** An exact replicate of the LCS. Used in conjunction with the LCS to assess method precision.

**Sample Duplicate:** A replicate aliquot of a real sample. The sample and its duplicate are used to assess method precision. Also used in matrix-specific assessment (see below).

**Surrogate:** A compound that is similar in analytical behavior to the target analyte(s). Used mostly in organics methods to monitor the efficacy of purging, extraction, or other sample prep procedures.

**MATRIX QUALITY CONTROL:** Quality Control samples composed from real matrices (may be fortified or not), designed to provide matrix or site-specific information about method performance and applicability.

**Matrix Spike:** An environmental sample to which a known amount of target analyte is added. The matrix spike provides information about the performance of target analytes in the subject matrix, and is used to assess accuracy.

**Matrix Spike Duplicate:** An exact replicate of the matrix spike. Used to assess precision in the subject matrix relative to the matrix spike. Especially useful if no target analytes are present in the subject sample duplicates.

**Sample Duplicate:** An exact replicate of an unfortified sample aliquot, taken through the entire analytical procedure. Used to assess precision.

**ADDITIONAL QUALITY CONTROL:** Many method-related "quality control" measures are simply method steps, or "good laboratory practices" designed to ensure consistent results. These types of procedures include:

**Second Column Confirmation:** A chromatographic technique that provides definitive information about the identity of a compound. Typically required in GC/non-MS methods unless the samples are from a well-defined matrix.

**Replicate Injections:** Used in most metals analyses; results are averaged to give final reportable number. Replicate analyses are also used in gas chromatographic methods to increase confidence level when reporting low-level results or results obtained from high-interference matrices.

**Sample Dilutions:** Some samples or sample derivatives (extracts, digestates, etc.) must be re-analyzed at one or various dilution levels to bring target analytes into the analytical range of the instrument. In general, complex or highly contaminated matrices may require multiple dilutions in order to arrive at reproducible analytical results.

## E. Quality Assurance Targets

QA Targets are the actual controlling factor in the QC protocols described above. Without criteria for rejection of results, all QC measures would be useless.

**Calibration Acceptance Limits:** Each analytical method specifies an acceptance range for the linearity of a calibration curve. Generally, a curve is considered linear when its correlation coefficient ( $r^2$ ) is at least 0.995 (1.00 is linear). Mathematical procedures for calculation of linearity are also method-specified.

**Control Limits:** Control limits are used to define acceptable performance windows for fortified samples (spikes) and replicates. The actual limits are generated by taking the average value (mean) of a population of at least 25 data points, then setting windows at two and three standard deviations from the mean. The limits at plus and minus two standard deviations are called the Upper and Lower Warning Limits, respectively, and the limits at plus and minus three standard deviations from the mean are called the Upper and Lower Control Limits. The analytical system is said to be "out of control" if precision or accuracy values, as defined below, fall outside of these control limits.

**Calibration Verification Acceptance Limits:** Limits for continuing calibration results are also method-specified. Some, calibration verification results are acceptable in the range of 85-115% of the "true" value.

**Precision:** Precision is measured as relative percent difference (RPD) between duplicates, and percent relative standard deviation (%RSD) between higher-numbered replicates. Depending on the matrix, a typical laboratory precision might be 20% or less, or as specified in the referenced procedure. NOTE: There are no established precision targets for field replicates.

**Accuracy:** Accuracy is measured as percent recovery (%R) against the known theoretical value. Spike recoveries can be quite variable, depending upon the method, sample matrix, and the target analytes. Organic compounds with low purging or extraction efficiencies generally do not recover well. Default recovery limits are usually specified in the methods.

**Method Blanks:** Control limits for method blanks are usually specified by the analytical method. In most cases, the limit for blank results is either the method detection limit (MDL), the PQL, or the reporting limit. In other cases, the limit is specified as three standard deviations from the mean blank value. Exceptions are sometimes made for common laboratory contaminants such as methylene chloride, acetone, MIBK, freon, chloroform, and phthalates.

## F. Sample Integrity

Probably the most critical and least-mentioned aspect of laboratory data generation is the importance of sample handling and tracking. Samples are carefully inspected upon arrival at the laboratory. Sample containers are checked for preservation as appropriate, logged into the tracking system, and then stored in the proper location until needed for analysis. Compromised chain-of-custody, mislabeled sample containers, or other unusual or unacceptable conditions are noted. Improper sample containers, preservation, or sample condition can all affect sample results. In such cases, the laboratory Project Manager contacts the client for further instruction. Many state regulatory bodies also require labs to report these types of anomalies to the state on receipt of samples.

Proper sample handling procedures continue at the analytical level. Method-specified procedures and/or "good laboratory practices" are followed for all sample aliquotting, splitting for multiple analyses, and storage of sample and sample derivatives (extracts, leachates, digestates, etc.).

Sample integrity procedures continue as raw data are produced. Data are processed from raw numbers into reduced results (dilutions are factored in, chromatograms are processed, results are reviewed by the analyst for consistency, etc.). The analytical results are then reviewed at the supervisory level along with accompanying quality control data. The package is either accepted or rejected based upon acceptance criteria and control limits. If reprocessing is necessary, the samples are completed and the results reviewed by the analyst and supervisor. Before data are released to the user (client), the Project Manager or Laboratory Manager reviews the entire package.

## G. Summary

All of the Laboratory Quality Assurance measures described above are utilized on a routine basis as part of the overall analytical system. The system is designed to produce the most reliable, reproducible analytical results possible within the operational parameters of the laboratory. These results can be said to be representative of the sample as delivered to the laboratory by the sampling team.

Since samples are analyzed and reported as received, obtaining results that are representative of actual site conditions is completely dependent upon the use of appropriate field techniques and field quality control protocols. The use of and adherence to proper field techniques is the responsibility of the individual submitting samples for analysis, and is completely outside the control of the laboratory.