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# WHITEPAPER

Analytical and Measuring Instruments

## Quality Assurance / Quality Control at the Environmental Laboratory

## ■ Introduction

This is an introduction to quality assurance of chemical measurements as performed in an environmental laboratory. Every environmental laboratory, particularly "certified" or accredited labs, will operate under a formalized QA/QC program. The QA accreditation may be by organizations such as The NELAC Institute (TNI), the American Association for Laboratory Accreditation (A2LA), a state accreditation, a USEPA Region's Drinking Water Certification, or perhaps even an ISO 17025 accreditation. All of the mentioned accreditation bodies (AB) use ISO 17025 as a basis for accreditation. All laboratory accreditations require a Quality Management System (ISO 9000) is in place. The 17025 accreditation contains laboratory and instrument-specific quality control and quality assurance procedures that must be followed.

Quality assurance is defined as the records kept on the results of the routine analysis of quality control samples. Many laboratories mistakenly assume that merely running quality control samples constitutes an adequate quality assurance program. This is incorrect. In fact, without proper and ongoing documentation of quality control sample results, quality assurance does not even exist.

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## ■ Definitions

**Quality Control** consists of either the analysis of samples of known quantities for the purpose of verifying a method's accuracy or the repeat analysis of a sample to determine the method's precision. Quality control samples may be relatively clean interference-free matrices, or complex matrices that duplicate the sample. Results may either be recorded as absolute or relative percent recovery.

**Blanks** consist of all reagents used in a test and may contain everything in the sample except the analyte of interest. The purpose of the blank is to assess laboratory contamination. High or variable blank values indicate a contamination that needs to be located and eliminated.

**Blank Spikes** are blanks to which a known amount of analyte has been added. Blank spikes largely determine whether significant analyte is lost during sample processing. Since the blank matrix is interference-free, a high blank spike result is further indication of contamination, or an inadequate calibration. A Blank Spike is similar to a Laboratory Control Sample (LCS).

**Blank Spike Duplicates** measure the ability of a method to duplicate analytical results in an interference-free matrix. Bad precision indicates either loss of analyte (lower than expected recovery) or contamination.

**Matrix Spikes** are real samples to which a known amount of analyte has been added. Subtracting the amount of analyte determined in an un-spiked portion enables calculation of the percent analyte recovered from samples of that matrix. The volume of analyte added should be no more than 5% of the total volume of the solution spiked. The amount spiked should be about 10 times the detection limit, or 2 – 10 times the estimated un-spiked sample concentration. A spike level less than the un-spiked sample concentration will not work. Matrix spikes that fail QC acceptance criteria only apply to the particular sample spiked. If the Blank spike or LCS passes, the results of that analytical batch are still valid.

**Matrix Duplicates** are repeat analyses of a sample matrix used to evaluate precision. If the amount of analyte is expected to be near or below the Method Detection Limit (MDL), **Matrix Spike Duplicates** are often run, allowing precision to be evaluated.

**Method Detection Limit (MDL)** is a statistically determined number that represents the lowest concentration of analyte that can be detected with the confidence of not being a false reading. The EPA-approved method for calculation of MDL multiplies the standard deviation of seven replicate tests by 3.14. The replicate tests should be blank spikes with an analyte concentration 3-5 times the calculated MDL. This method for determining the MDL can be found at 40 CFR part 136 Appendix B. All environmental laboratories are required to measure MDL using this method.

It is important for all users of this statistically derived MDL to realize the great inaccuracies associated with this number. The MDL that is determined by analysis of replicates made on purified water only applies to the purified water. This number generated also only applies to the analyst that made the determination and the instrument that was used. Also, statistically speaking there is no real accuracy or precision associated with this number, as variability can be as high as 100%.

**Minimum Level** or reporting limit is the lowest calibration standard, or a concentration of 3.18 times the MDL. The minimum level is approximately 10 times the standard deviation of the noise and represents the point where data has an accuracy and precision of within about 30 % of its true value. A more accurate determination of the minimum level is to plot RSD and Recovery of collected multiple laboratory data and set the Minimum Reportable Level at the lowest point where both accuracy and precision are within 30%.

**Calibration** is a representation of a response that is in proportion to an amount. In modern instrumentation, the calibration is an electronic signal relative to an amount of analyte. A graphical plot of concentration versus signal is represented by a calibration curve, which is hoped to be linear, but may be second or third order depending on the measurement method and concentration range. Calibration could, however, also represent mass measured on a balance or volume measured with a burette.

Calibration curve accuracy is often assessed using the correlation coefficient; however, a good correlation does not guarantee an accurate calibration. The slope and y intercept data should be monitored, and should not significantly change. Keep track of calibrant, or CCV, response over time.

**Calibration Verification** is the first step in guaranteeing the accuracy of a calibration curve. The **Initial Calibration Verification (ICV)** standard is a mid-point standard solution derived from a source other than the stock material used to prepare the calibration standards. The ICV is analyzed as an unknown and expected to be within 5% of its known value. Often, the ICV standard is purchased and certified; the ICV guarantees that the calibration standards were prepared accurately. The **Continuing Calibration Verification (CCV)** is a midpoint calibration standard from the same stock used for the calibration standards. This solution is analyzed at regular intervals throughout the run to demonstrate that results are still "in control". If a CCV fails, the reason for failure should be determined and corrected. With some instruments, recalibration may be necessary. Only results bracketed by acceptable CCV results should be reported.

**Initial Demonstration of Capability (IDC)** is a procedure used to qualify the analyst to run samples. Each analyst should perform an IDC and the documentation kept on file to demonstrate that the analyst is capable of collecting data with known accuracy and precision. At minimum, four quality control samples of a matrix similar to the sample matrix are analyzed using all steps of the procedure and compared to known acceptance criteria of accuracy and precision. Often, these Quality Control samples can be purchased.

**Laboratory Control Sample (LCS)** is a standard of known concentration in a matrix similar to the samples. The LCS can be purchased, prepared internally, or be a previously analyzed sample. It is preferable to have an LCS in large quantity so that the concentration is always the same. The LCS is carried through the entire sample preparation and analysis process. If an LCS fails its quality control acceptance criteria, the entire analysis batch is suspect.

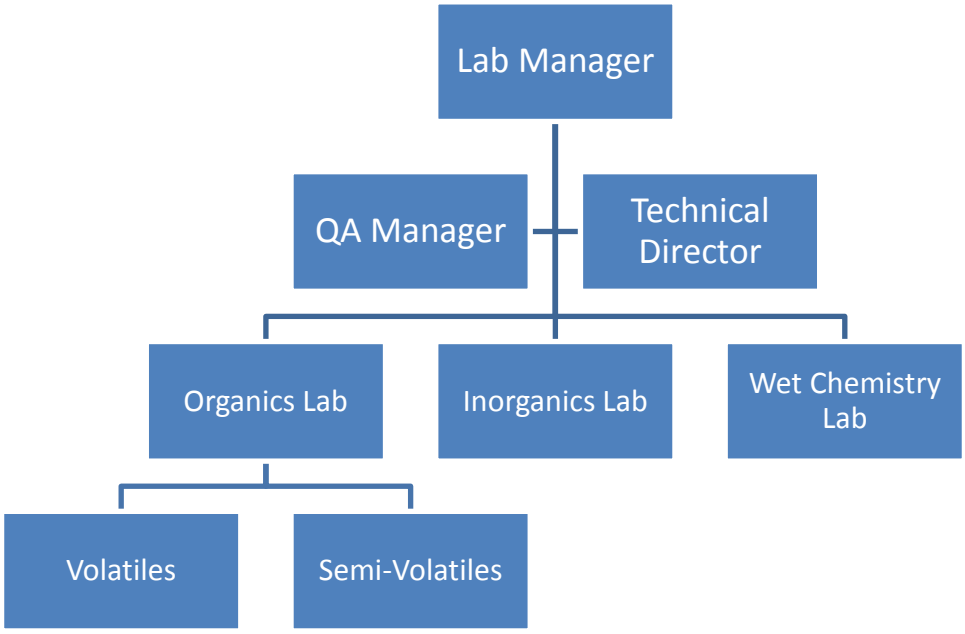
**Methods** are written sets of procedures that the laboratory must use to analyze contaminants in environmental samples. The analyte, a maximum allowed concentration in a certain matrix, such as drinking water, wastewater, or solid waste, and the method are all prescribed in Part 40 of the US Code of Federal Regulations (40 CFR). Drinking water methods must be followed exactly; wastewater methods allow some flexibility, and solid waste methods are issued as guidance. Many states, however, prescribe the solid waste methods, forcing laboratories to follow them word for word.

**Holding time** is the maximum time that a sample can be held before the analysis begins. The holding time may require certain preservatives, such as acids or refrigeration. The holding time may also be split into the maximum time to extraction and then the maximum time an extract can be stored prior to analysis. Holding times are often not experimentally determined, but must always be met.

A **Batch** is a group of up to 20 samples extracted, processed, and/or analyzed together for the same constituents. The batch must be bracketed by a passing CCV and includes a Method Blank, LCS, and MS/MSD. The QC samples included in the batch are not considered part of the 20 samples, making a standard batch size of 20 samples equal to a minimum of 24 injections or analyses.

## ■ Laboratory Organizational Structure

It is the responsibility of the environmental laboratory to carry out testing that satisfies the needs of customers and the requirements of regulatory authorities. The laboratory has an overall manager responsible for the financial aspects of the lab, a technical director responsible for selection of methods and instruments and the training of laboratory personnel to ensure they are capable of running the methods, and a QA director that reports directly to upper management. While there are numerous variations in the organizational structure, the main goal is to demonstrate that the laboratory is impartial and that personnel are not forced to make decisions, or "fudge" results under pressure. Below is a sample organizational chart.



Each of the laboratory sections mentioned in the chart analyze aliquots of the environmental samples received at the laboratory using EPA-approved methods. Each section manager is responsible to ensure that samples are analyzed within holding times and that all quality control requirements of the methods are met. Each manager is also responsible for the profitability of his/her section. Commercial laboratories compete on throughput (aka turnaround time) and detection limits. Thus, the technicians, chemists, and managers desire instrumentation that not only meets the method requirements, but also makes their own lives easier by being easy to operate and trouble-free.

## ■ Generalized Calibration and Analysis Scheme

Most inorganic methods require calibration each day immediately prior to the analysis of samples. Once the instrument is calibrated, the calibration is verified using a standard prepared from an independent source, or the ICV. Assuming the ICV passes the QA acceptance criteria the analysis begins. Since chromatographic methods can take so long to calibrate, it is acceptable to use previous calibrations assuming a continuous calibration verification (CCV) standard passes all QA acceptance criteria. Therefore, for routine analysis using chromatography methods, the daily calibration requirement listed in the generalized scheme below can be omitted.

Calibrate full scale expected*
Analyze the ICV*
Analyze the MB*
Analyze the LCS*
Analyze Sample 1
Analyze Sample 1 Matrix Spike*
Analyze Sample 1 Matrix Spike Duplicate*
Analyze Sample 2 – 10
Analyze CCV*
Analyze Sample 11 – 20
Analyze CCV*

The asterisk * represents a decision point that must be made by the analyst during sample analysis, or when reviewing the batch once the analysis is completed.

## ■ Conclusion

This is an introduction to the quality control and quality assurance practices at a modern environmental laboratory. Some statements have been generalized in an effort to condense the document for easier reading.

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