Quality Assurance/Quality Control in the GC Pesticides Laboratory

1. SCOPE AND APPLICATION

1.1. This SOP details the Quality Assurance (QA) and Quality Control (QC) procedures for the GC-Pesticides Work Group.

1.2. Quality Assurance consists of all of the practices undertaken in a laboratory to insure the data generated are as accurate and precise as possible. It includes not only quality control measures, but can be as specific as the cleaning of glassware and preparation of standards. This SOP will concentrate on Quality Control measurements that are used to measure and track the Quality Assurance in the GC Pesticides lab. It will touch briefly on some general guidelines for QA. Refer to the individual preparation or analysis SOPs for more specific details on QA.

1.3. Most of the QA/QC practices described here are common throughout the Chemistry Section.

2. DEFINITIONS

2.1. The quality control measurements used in the GC lab are: Accuracy, Precision, Blank Evaluation and Detection Limits (method detection and practical quantitation limits-MDL/PQL). These are briefly defined as follows:

2.2. Accuracy is the term which describes the degree of deviation (bias) between a known amount of analyte added to a sample and the actual recovery amount of the analyte. It is expressed as the percent recovery.

2.3. Precision is the term which describes the degree of replication between duplicate samples. It is calculated and expressed as the Relative Percent Difference (RPD) between duplicate sample results.

2.4. Blank Evaluation is used to assess the degree of contamination resulting from the sample preparation and analysis steps.

2.5. Detection limits (MDL/PQL) are established during the validation of a method. These limits define the sensitivity of a method. Because "zero" has no meaning when an analyte is not detected, a method analyte must have a limit set which defines the lowest concentration that can be reliably seen when it is detected.

2.5.1. Method Detection Limit (MDL/LOD): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is also referred to as the Limit of Detection (LOD).

2.5.2. Practical Quantitation Limit (PQL/LOQ): Usually set at 4 times the MDL, it is a more reliable measurement limit. Although the MDL can be detected at a 99% confidence, the PQL is usually the point where the analyte can be quantitated more accurately. The PQL is also referred to as the Limit of Quantitation (LOQ).

3. IN-LAB QUALITY CONTROL SAMPLES

3.1. For every batch of 20 samples, the following quality control samples are prepared and analyzed:

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3.2. One Laboratory Reagent Blank (used to evaluate contamination in the laboratory)

3.2.1. This is a reagent blank that is treated exactly as a sample, including exposure to all glassware, equipment, solvents and reagents used with other samples. The lab blank is used to determine if the method analytes or other interferences are present in the laboratory environment, reagents or equipment.

3.2.2 If contaminants are present that interfere with the determination of any analyte, detection limits MUST be elevated accordingly! Raising the detection limit should be used with caution to ensure that action levels are not exceeded. If a lab blank is found to be contaminated, the source of contamination must be found and eliminated. If samples passed the holding time, the results will be reported with a "V" qualifier (ref 8.6) up to ten times the amount found in the blank.

3.3. Two Laboratory Control Samples (LCS and LCSD)

3.3.1. An LCS is a reagent blank that is fortified at sample extraction with a known amount of the analyte(s) of interest and with any surrogates used.

3.3.2. LCSs are usually prepared in duplicate. It is used to assess the method accuracy (i.e., analyte percent recovery) without the effects that a true sample matrix may contribute. If prepared in duplicate, it is also used to assess method precision (as Relative Percent Difference).

3.4. Matrix Spike Samples (for assessing method accuracy and, if performed in duplicate, for assessing precision on "real" samples, in the presence of matrix effects.)

3.4.1. Sample matrix spikes are samples that are fortified at sample extraction with a known amount of an analyte(s) of interest.

3.4.2. Every attempt is made to prepare sample spikes in duplicate, in order to assess the true method precision in the presence of matrix effects. Spike recoveries (accuracy) are indicators of sample matrix interference, loss of analyte and contamination. Historical percent recoveries are used to calculate method bias and the confidence range of the bias. If insufficient sample is available to prepare matrix spikes in duplicate, LFB's precision has to be used to assess method precision.

3.5. Spiking Policy

3.5.1. For methods that include 1-10 single component targets, spike all components.

3.5.2. For methods that include 11-20 single component targets, spike at least 10 or 80%, whichever is greater.

3.5.3. For methods that include more than 20 single component targets, spike at least 16 components.

3.5.4. For methods containing single and multiple component targets, follow the criteria for determining the number of single component analytes, spike all target analytes (single component and multiple component targets) over a 2-year period.

3.5.5. For more details see 2009 TNI Standard, V1M4, Sec. 1.7.3.3 (Ref. 8.1)

3.6. Other Quality Control measures that may be used are:

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3.6.1. Instrument Blank (a solvent injection on the GC, to assess presence of possible instrument contaminants)

3.6.2. Internal Standard - a pure analyte(s) of known amount that is added to the final sample extract prior to GC analysis. It is used to measure the relative response of other analytes and surrogates and is useful in correcting for injection variations. It is also used as a retention time reference peak, to correct for retention time drift during an analysis sequence. The internal standard must be an analyte that is not expected to be found in the sample.

3.6.3. Surrogate- a pure analyte(s) that is added to all samples, blanks and spikes before extraction. Surrogates should be similar in behavior to the method analytes, but SHOULD NOT be expected to appear in the sample. Surrogate recoveries give an indication of method accuracy and are a good check for gross inaccuracy (i.e., lost sample, incorrect volumes, concentration problems, etc.) in all of the samples.

4. EXTERNAL QC SAMPLES

4.1. There are field QC samples that are assessed along with the samples. These are:

4.1.1. Field Duplicate Samples- two separate samples collected at the same time and from the same site under identical circumstances and treated exactly the same through all field and lab procedures. Duplicate analyses give a measure of the precision associated with the sample collection, preservation and storage, as well as with the laboratory procedures.

4.1.2. Field Blank - reagent water added to a sample bottle at the time of sample collection. It is treated exactly as a sample, including exposure to the sampling site conditions, storage, preservation and all laboratory procedures. It is used to determine if method analytes and/or other interferences are present in the field environment.

4.1.3. Equipment Blank - After sampling, the equipment (baler, etc.) is rinsed with reagent water and collected as a sample. This blank is evaluated to insure that the field equipment did not contaminate the samples.

4.1.4. Trip Blank - This is generally used only when sampling for volatile organic compounds. A trip blank is prepared in the lab by filling up the sample bottle with reagent water and sending the filled, capped bottle out to the collection site with the other associated sample bottles. The trip blanks goes on the entire sampling "trip", so it is exposed to all aspects of the sampling collection, storage and transportation. The trip blank sample bottle remains closed at all times and is used to determine if any method analytes or interferences have diffused into the sample bottle through its bottle cap.

4.1.5. Field Spikes - These can be matrix or reagent water fortified samples that are used to assess the stability and method performance of an analyte(s). These may be "blind" spikes, which are unlabelled as spikes and are therefore unknown to the laboratory personnel. This is an excellent way to determine true method performance.

5. QC CALCULATIONS/REPORTING CONVENTIONS

5.1. Accuracy (expressed as % Recovery) of LFBs and matrix spikes is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Measured conc.of Spike} - \text{Measured conc. in unspiked sample}}{\text{True Value}} \times 100$$

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5.2. Precision (as Relative Percent Difference-RPD of the measured recovered concentration of duplicate LFBs and matrix spikes, or RPD of duplicate sample results) is calculated as follows:

$$RPD = \frac{|A - B|}{(A + B)} \times 200\%$$

where:

A = measured concentration of spike 1 (or sample concentration from sample 1)

B = measurd concentration of spike 2 (or sample concentration from sample 2)

Note that this value is the Difference between the measured recovered concentrations from samples A and B, divided by the Average of the 2 values.

5.3. Acceptance Limits are established for accuracy and precision by evaluating Matrix Spike / LCS recoveries. These limits are used in assessing the acceptability of subsequent accuracy/precision of a spike and in determining if the value is a true and accurate reflection of the method performance. Limits are established for each matrix (i.e., sediment, water, tissue). Statistical recovery limits for LFB/MS and surrogate recoveries are typically based on the QC Manager statsitics for the last five calendar years (if available). The limits are recalculated, at least annually. The results of statu=istical calculations are saved at FLDEP1\DEAR\LABS\LAB5\CHEMISTRY\ORGANIC\QC LIMITS STATS. The statistical recovery limits are then entered into QC Manager limits tables. The initial QC limits are replaced with statistical ones whenever enough data points are accumulated. At least 20 points are required, but it is preferable to wait for about 50 points or more. If enough data points is available for LFBs but not for matrix spikes then LFB statistical limits may be applicable for both categories on temporary basis.

5.3.1. Accuracy Acceptance Limits consist of both Warning Limits and Control Limits:

5.3.1.1. Warning Limits are based on 95% confidence level. This calculation will give an upper and a lower warning limit for the accuracy values. Warning Limits are used in evaluating data trends.

$$\text{Upper Warning Limit (UWL)} = \text{Mean} + t_{(0.95)}\,\text{Sd}$$
$$\text{Lower Warning Limit (LWL)} = \text{Mean} - t_{(0.95)}\,\text{Sd}$$

5.3.1.2. Control Limits are based on 99% confidece interval level. This calculation will give an upper and a lower control limit for the accuracy values. Limits are used in accepting or rejecting recovery data and in determining whether a system is out of control. EPA defines an out-of control system as one in which there are seven successive data points on the same side of the mean value.

$$\text{Upper Control Limit (UCL)} = \text{Mean} + t_{(0.99)}\,\text{Sd}$$
$$\text{Lower Control Limit (LCL)} = \text{Mean} - t_{(0.99)}\,\text{Sd}$$

Where:

- Sd is the standard deviation of the population
- Mean is the average of all points
- $t_{(0.99)}$, $t_{(0.95)}$ are the Student's coeficients for 99% and 95% confidence intervals respectively.

5.3.2. Precision Acceptance Limit

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5.3.2.1. Warning and Control Limits are based on a 95% and 99% confidence levels, respectively. For precision, only the upper limits are relevant.

$$UWL = D_3 P$$
$$UCL = D_4 P$$

Where D_3 and D_4 are Shewhard factors representing 95% and 99% confidence limits for pairs of duplicates.

For most analysis in GC group statutory control limits for precision of <30% are used.

5.3.3. The accuracy and precision limits are calculated from a minimum of the latest 20 data points. If any data point is outside of the acceptance control limits, the batch of samples must be re-extracted provided that samples are not expired. If samples are expired for re-extraction, then for failing analytes, the results must be qualified according to Lab SOP **LB-027**. In addition, a comment is added to the LIMS report detailing the outlier data.

5.3.4. Quality Control Limits for LFBs, MATRIX SPIKES, PRECISION, and SURROGATES, initially should be established based on either the criteria stated in the methods or initial validation data. When sufficient QC data (20 data points or more) become available, the quality control limits should be re-evaluated statistically and re-set when deemed scientifically appropriate.

5.3.5. If consistent deviations from QC limits, deemed to be caused by systematic errors of the procedure, are observed in LCS recoveries/precision, the analyst must proceed with 5.3.5.1.1 and 5.3.5.1.2.

5.3.5.1.1. Locate and correct the source of problem

5.3.5.1.2. Repeat the test for all parameters that failed to meet criteria

5.3.6. Repeated failure, however, will indicate a general problem with the measurement system. If this occurs, repeat 5.3.5.1.1. and 5.3.5.1.2. until the problem is solved.

5.3.7. In case the failures cannot be corrected, a new Initial Demonstration of Capability must be completed and new QC limits must be established within the acceptance criteria provided by the method.

5.3.8. For qualifying data in case of LCS failure due to a Systematic Error, see Laboratory SOP **LB-027** Footnote 4 (See Ref. 8.3).

5.4. Rounding of Numbers

5.4.1. For rounding of numbers follow the Laboratory SOP **LB-024** (See Ref. 8.2). For all reported data, round results to 2 significant figures.

5.5. LIMS Reporting Codes/Conventions (ref 8.6)

5.5.1. Samples that are analyzed after expiration must be reported with a qualifier (Q).

5.5.2. For sample results that are below the MDL report the MDL followed by the letter U.

5.5.3. For sample results that are below the PQL but above the MDL, report the sample result followed by the letter I.

5.5.4. For samples that are analyzed in duplicate (in-lab duplicates, NOT field duplicates) report the average of the results followed by the letter A.

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5.5.5. For data that are reported as positives but are below MDL the reported value must be followed by the letter T.

5.5.6. For some other conditions that require using qualifiers follow the rules in Laboratory SOP **LB-027** (see Ref. 8.3).

5.5.7. Report all water and TCLP results in ug/L, all sediment, tissue and waste samples in ug/kg. Sediment samples are reported on dry weight basis, while tissue and waste samples on wet weight basis.

6. MDL/PQL DETERMINATION/METHOD VALIDATION

6.1. MDL and PQL values are initially determined during validation of a new method and must be verified at least once per year or everytime singnificant changes were made in the procedure.

6.2. MDL calculation use EPA's recommended method (40 CFR pt. 136 Appendix B, see Ref. 9.3)

6.2.1. Estimate the MDL by analyzing a set of standards on the appropriate instrument and examining the chromatographic peak. The peak should at least have signal to noise ratio (S/N) of 5.

6.2.2. After obtaining the estimated MDL, at least 7 replicate lab fortified blanks are prepared (on laboratory pure water, Ottowa sand or other pure matrix) at up to 2-5 times of that level. These LFBs are then analyzed. The standard deviation and relative stndard deviation for the mesurements are calculated. The relative standard deviation should be acceptable, based on EPA method or other references results (usually less than 30%). If this was achieved, the MDL is calculated using the formula:

$$MDL = t \times S$$

where: t is the Student coeficient (t=3.143 for 7 replicates; t=2.998 for 8 replicates) and S is the standard deviation calculated for at least 7 replicates

6.2.3. The repoted MDL is usually set higher than calculated one to address real matrices

6.2.4. The MDLs are determined in both primary and confirmatory columns and the highest one is used to determine the reported MDL

6.2.5. The PQL is set usually at 4 times the MDL .

6.3. These MDLs and PQLs are used when reporting data. However, these MDL/PQL values may be adjusted when analyzing real samples, to account for differences in matrix interferences, sample wet/dry weight and amount of sample analyzed.

7. QUALITY ASSURANCE

7.1. The following are general guidelines to use in assuring good and complete data are reported. This is not a complete list of guidelines!

7.2. All data and quality control data are reviewed by a supervisor before being accepted as final.

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7.3. All maintenance or analytical problems are reported to a supervisor.

7.4. Field sampling problems such as contamination, labeling, and holding times are reported to a supervisor and noted with the results.

7.5. Document quality control from all analysis sets in an established LIMS.

7.6. Document QC deviations in the final LIMS report by adding appropriate comments and by flagging any affected results with the proper code.

7.7. Method interferences may be caused by contaminants in reagents, glassware, instrumentation, and highly contaminated samples. All of these contaminants must be routinely monitored by analysis of sample preparation blanks. To avoid method interferences, take the following general precautions:

7.7.1. Solvents

7.7.1.1. Use only the specified grade of solvents at all times. If interferences from solvents are suspected, analyze a concentrated aliquot of the solvent to check this. Remove any contaminated solvent from production IMMEDIATELY. Label solvents as contaminated and dispose.

7.7.1.2. Never use solvents from unlabelled bottles.

7.7.1.3. Never pipet solvents directly from bulk solvent. Always transfer the required volume of solvent to a labelled beaker and pipet from this. Dispose of the unused portion.

7.7.2. Reagents

7.7.2.1. Use the purity of reagents recommended by the appropriate SOP.

7.7.2.2. Store all the reagents appropriately in a clean environment, and with a proper label, which includes the date and initials of the person who prepared the reagent.

7.7.3. Use scrupulously cleaned and checked glassware. See Lab SOP **CM-031** for details

7.8. BE SENSITIVE TO CONTAMINATION AT ALL TIMES! If a highly contaminated sample has been analyzed with other non-contaminated samples, be sure that any positives reported in the other samples are True! Positive results seen in other samples may be carry-over from this highly contaminated sample.

8. REFERENCES

8.1. 2009 TNI Standard, Volume 1, Module 4, Section 1.7.3.3.

8.2. DEP SOP LB-024, *Significant Figures: Policy of the DEP Chemistry Section.*

8.3. DEP SOP LB-027, *Standard Operation Procedure for Reporting Qualified Data.*

8.4. DEP SOP CM-031, *Glassware Cleaning and Muffle Furnace Protocols in the Organic Preparations Laboratory*.

8.5. C.F.R. Appendix B to Part 136. Definition and Procedure for the Determination of the Method Detection Limit .

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8.6. Chapter 62-160, Florida Administrative Code.

9. APPENDIX OF SIGNIFICANT CHANGES

4/12/2016	Section 3.2.2; raising the detection limit discussed, application of the "V" qualifier added with referemce to chapter 62-160, FAC (FDEP response to CERP audit, section 6a)
	Section 5.3; calculation and application of recovery limits for LFBs and Matrix spikes clarified. (FDEP response to CERP audit, section 6b)
	Reference 8.6 to Chapter 62-160 FAC added (FDEP response to CERP audit, section 6c)
	Section 5.5.7 expanded to indicate that sediment samples are reported on dry weight basis, while tissue nd waste sample on wet weight basis. (FDEP response to CERP audit, section 6d)
4/6/2017	QC calculations for recovery limits explained in details.

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