Quality Assurance/Quality Control in the Semi-Volatile Organics (BNA-GC/MS) Laboratory

1 SCOPE AND APPLICATION

1.1 This SOP details the Quality Assurance (QA) and Quality Control (QC) procedures for the BNA 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 BNA lab. It will touch briefly on some general guidelines for QA. Refer to the specific preparation or analysis SOPs for more specific details on QA.

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

2 DEFINITIONS

2.1 The quality control measurements used in the BNA laboratory are: Accuracy, Precision, Blank Evaluation and Detection Limits (method detection and practical Quantitation limits-MDL/PQL). They are briefly defined as following:

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

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

2.4 Blank Evaluation is used to assess the degree of contamination occurring 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): The minimum concentration of an analyte that can be identified measured and reported with 99 % confidence that the analyte concentration is greater than zero.

2.5.2 Practical Quantitation Limit (PQL) - Usually set at 2-5 times the MDL, it is a more reliable Quantitation 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.

3 IN-LAB QUALITY CONTROL SAMPLES

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

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

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used to determine if the method analytes or other interference are present in the lab environment, reagents or equipment.

3.2.2 If contaminants are present and they interfere with the determination of any analyte, detection limits MUST be elevated accordingly! If a lab blank is found to be contaminated, the source of contamination must be investigated and corrective actions must be taken.

3.3 One Laboratory Fortified Blank (LFB)

3.3.1 A LFB is a reagent blank that is fortified at sample extraction with a known amount of the analyte(s) of interest.

3.3.2 A LFB may be prepared singly or in duplicate. It is used to assess the method accuracy (i.e., analyte % 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 Percentage 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 are prepared in duplicate to substitute.

3.5 Other Quality Control measures that may be used are:

3.5.1 Instrument Blank (a solvent blank, to assess presence of possible instrument contaminants)

3.5.2 Internal Standard - a pure analyte(s) of known amount that is added to the final sample extract prior to analysis. The internal standard must be an analyte that is not expected to be found in the sample. The internal standard is used to measure the relative response of other analytes and surrogates; this process is known as the internal standard Quantitation technique, which corrects for injection variations. Because it is used in the Quantitation of analytes, the area response of the internal standard in a sample may not vary by more than 50 % from the continuing calibration standard. The internal standard is also used as a retention time reference peak.

3.5.3 Surrogate- a pure analyte(s) that is added to all samples, blanks and spikes at sample 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. For BNA analysis, the acceptance limits for surrogate recoveries are taken from the EPA Contract Laboratory Program (CLP) limits listed see Table. The recoveries must be within the following acceptance limits. If any of the above surrogate falls outside control limits, re-extract the effected sample with proper QC even after expiration and follow DEP SOP LB-027 for reporting.

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Compound	% Rec Water & Sediment
Base/Neutral Surrogates	
Nitrobenzene-d5	30-150
2-Fluorobiphenyl	30-150
Terphenyl-d14	30-150
Acid Surrogates	
Phenol-d5	20-150
2-Fluorophenol	20-150
2,4,6-Tribromophenol	30-150

3.5.4 Check the Matrix Spike and Lab Fortified Blank recoveries. They must be within the current acceptance range (range is updated when enough data points accumulated, see the Quality Manual, Table 5 for the acceptable ranges for each analyte and matrix). For EPA 625 method the limits are set by the method.

3.5.5 In QCManager, if any QC failures in the batch are detected during calculations, do not add any comments to the effected samples. Other comments and qualifiers may be added as required.

3.5.6 In Data Review, if any QC failures are detected for any analyte during calculations, the effected analyte in each sample is automatically qualified with a comment ("QC failure(s) observed"). This comment is coded in Data Review calculations so that it is only appended once in the case of multiple QC failures.

3.5.7 Following DEP SOP LB-027, the effected data must be qualified with a proper comment in the final report explaining any deviation from the routine limits whenever the spikes or surrogates and or CCVs are out of range. The following can be used as needed: One or more results were qualified due to non-systematic CCV failures (or matrix spike failures or LCS failures or lab QC failures).

3.5.8 Rules for J qualifying data: Failing LFBs (recoveries or RPDs): For all samples in the batch, the component with the failing QC is J'd and appended with a comment.
Failing matrix spike recoveries or sample/matrix spike precision: The component with the failing QC for the spiked/duped sample only is J'd and appended with a comment.

3.5.9 General rules: J is added to all results regardless of qualifier code (i.e. UJ, IJ, YJ etc.). The one exception is data reported as O which should not be assigned the J code. Do not want to add a J code if it already exists, i.e. no JJ's.

3.5.10 Do not load precision if matrix spike recovery is none detect and or less than PQL, load matrix spikes recoveries and make comment.

3.5.11 If analyte in sample is higher than spike level, do not load matrix spike recoveries, make comment, do not qualify result and report RPD.

3.5.12 Check the method blank for any interfering contaminants. The MDL's may have to be elevated if the blank(s) indicate contamination.

4 EXTERNAL QC SAMPLES

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

4.1 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.

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Duplicate analysis gives a measure of the precision associated with the sample collection, preservation and storage, as well as with the lab procedures

4.2 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 lab procedures. It is used to determine if method analytes and/or other interference are present in the field environment.

4.3 Equipment Blank - Before 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.

4.4 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 interference have diffused into the sample bottle through its cap.

4.5 Field Spikes- they 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 not labeled as spikes and are therefore unknown to the lab personnel. This is an excellent way to evaluate true method performance.

5 QC CALCULATIONS/REPORTING CONVENTIONS

5.1 Accuracy (expressed as % Recovery) of LFB's and matrix spikes is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Concentration detected}}{\text{True Value}} \times 100\ \%$$

5.2 Precision (as Relative Percentage Difference-RPD of the % recovery of duplicate LFB's and matrix spikes or RPD of duplicate sample results) is calculated as follows:

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

Where

A = % recovery from spike 1 (or sample concentration from sample 1)

B = % recovery from spike 2 (or sample concentration from sample 2)

Note that this value is the Difference between the % recovery from sample A and B, divided by the Average of the 2 values.

5.3 Acceptance Limits are established for accuracy and precision by evaluating LFB/spike 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) and analyte concentration level.

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

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5.3.1.1 Warning Limits are defined as the mean from a set of 20-25 data points (recovery values), +/- 2 Sigma. Sigma is the standard deviation of the n-1 population. This calculation will give an upper and a lower warning limit for the accuracy values. Warning Limits are used in evaluating data trends.

Upper Warning Limit (UWL) = Mean + 2 Sigma
Lower Warning Limit (LWL) = Mean - 2 Sigma

5.3.1.2 Control Limits are defined as the mean from a set of 20-25 data points (recovery values), +/- 3 Sigma. Sigma is the standard deviation of the n-1 population. 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 is seven successive data points on the same side of the mean value.

Upper Control Limit (UCL) = Mean + 3 sigma
Lower Control Limit (LCL) = Mean - 3 sigma

5.3.2 Precision Acceptance Limit

5.3.2.1 Warning Limits are defined as the mean from a set of 20-25 RPD values + 2 Sigma. This calculation will give an upper warning limit for the precision values. For precision, only the upper limit is relevant.

5.3.2.2 Control Limits are defined as the mean from a set of 20-25 data points (RPD values), + 3 Sigma. This calculation will give an upper warning limit for the precision values. For precision, only the upper limit is relevant. This limit is used in accepting or rejecting precision data and in determining whether a system is out of control. EPA defines an out-of control system as one in which there is seven successive data points on the same side of the mean value.

Upper Control Limit (UCL) = Mean + 3 sigma

5.3.3 Accuracy and precision limits are calculated from the latest 20-25 data points. These ranges are used in assessing the next 20 -25 data points as they in turn are generated. Once 20-25 new data points have been generated, new limits are calculated. 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, then any positive result for the unaccented analyte result is qualified with "J". In addition, a comment is added to the Laboratory Information Management System (LIMS) report detailing the reason of using the qualifier.

5.3.4 All quality control limits, including LFB, sample matrix spikes, Surrogates and CCV, 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 and 5.3.5.2.

5.3.5.1 Locate and correct the source of problem

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5.3.5.2 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 and 5.3.5.2 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-027-1 Footnote 4.

5.3.9 LCS failures allowable by NELAC chapter 5, Appendix D, section D 1.1.2:

> 90 analytes in the spike – up to 5 analytes are allowed to fail
71 - 90 analytes in the spike – up to 4 analytes are allowed to fail
51 - 70 analytes in the spike – up to 3 analytes are allowed to fail
31 - 50 analytes in the spike – up to 2 analytes are allowed to fail
11 - 30 analytes in the spike – 1 analyte is allowed to fail
< 11 analytes– no analytes are allowed to fail

5.4 Rounding of Numbers

See SOP **LB-024,** "Significant Figures: Policy of the DEP Chemistry Section" for details.

5.5 LIMS Reporting Codes/Conventions

5.5.1 Sample results that are below the PQL's and/or MDL's have to be reported with a remark code (qualifier) in LIMS. Samples that are analyzed in duplicate (in-lab duplicates, NOT field duplicates) must be reported with a qualifier. Samples that are analyzed after expiration must be reported with a qualifier.

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.

5.5.5 For samples that are analyzed after expiration report the result followed by the letter Q.

5.5.6 Some conditions may require two or more qualifiers. Report only one qualifier. Use the list below to assign priorities (#1 has highest):

1. U or I
2. Q
3. A

5.5.7 Request approval by the supervisor before using any qualifiers that are not listed above.

5.5.8 Report all water results in µg/L, all sediment and waste samples in µg/kg.

6 MDL/PQL DETERMINATION/METHOD VALIDATION

6.1 MDL and PQL values are initially determined during validation of a new method.

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6.2 MDL: Estimate the MDL by analyzing a standard on the appropriate instrument and examining the chromatographic peak. The peak should at least have signal–to-noise ratio (S/N) of five (5).

6.3 After obtaining the estimated MDL, seven (7) replicates lab-fortified blanks are prepared at 2-5 times the MDL level. These LFBs are then analyzed. The relative standard deviation should be acceptable, based on EPA method or other references results (usually not > 30%). If this is achieved, the MDL of that analyte is determined following EPA 40 CFR Part 136, Appendix B and Revision 1.11. If the criterion is not achieved, 7 replicates LFB's at higher concentration are prepared and analyzed until the criterion is achieved.

6.4 PQL: The PQL is usually set at 2-5 times the MDL level.

6.5 Determined MDL and PQL are used when reporting data. However, these MDL/PQL values may need to be adjusted when analyzing real samples, to account for differences in matrix interference, sample wet/dry weight and amount of sample analyzed.

7 NELAP

7.1 To keep valid NELAP certification current for all the analytes in each test method for each matrix, the technical personal need to complete all the requirements every year Initial and ongoing demonstration of capabilities. Certification is required if any changes to the SOPs, any changes in the preparation, analysis and MDL changes. For successful certification each person need to complete 4 QC samples or one Performance Evaluation sample every year.

7.2 Once a year, run each test method for routine samples and participate if available in PT samples. If no routine and PT samples are available then do 4 QC samples. Spike each analyte for each matrix.

7.3 For multi-component analytes rotate spike and prepare spike rotation schedule. For BNA analysis all the analytes for EPA 625 are spiked all the time. For 8270, only the 625 mix spike is used all the time. Other remaining 8270 mix and pesticide mix is spiked mostly for the NELAP requirement once a year.

7.4 Check instrument detection limits by running close to MDL standards (1.0 µg/mL), each time ICAL is set.

7.5 For each Method, for every analyte, run once a year MDL Check Spike by extracting and analyzing one MDL Check Spike (3 to 5 times of MDL). The following Table lists the MDL Check Spike concentration for all the BNA methods.

Table: MDL check – Amount of spike standard

Method	Reported MDL in LIMS In PPB	On Column Conc. (µg/mL) Required for MDL	Lowest ICAL Standard (µg/mL) Used for Analysis	Routine LFB's (µg/mL)	LOD Check Conc. on Column (µg/mL))	LOD Check Spike Amount (mL)	LOD Spike Conc.
W-BNA/ W-BNA-R	1	1	1	25.0	4	0.08(625/8270)	50 ppm
S-BNA	60	1.8	1	25.0	7	0.140	50 ppm
W-PAH	0.05	0.2	0.2	5.0	0.8	0.04	5 ppm
S-PAH	6.66	0.2	0.2	5.0	0.8	0.16	5 ppm
W-FL-PRO	0.25(mg/L)	85	125	850	425	0.1	500 ppm
S-FL-PRO	10(mg/kg)	85	125	850	425	0.1	500 ppm
A-PAH	100 ug	0.1	0.1	0.5	0.25		

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8 QUALITY ASSURANCE

8.1 The following are general guidelines for reporting good and complete data. This is not a complete list of guidelines!

8.2 Whole data is reviewed by a supervisor before being accepted as final.

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

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

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

8.6 Method interference may be caused by contaminants from reagents, glassware, instrumentation, and highly contaminated samples. All of these contaminants must be routinely monitored by daily analysis of laboratory reagent blanks. To avoid method interference, take the following general precautions:

8.6.1 Solvents

8.6.1.1 Use only solvents with specified grade at all time. If interference form solvents are suspected, analyze a concentrated aliquot of the solvent to verify. Remove any contaminated solvent from production IMMEDIATELY, and dispose.

8.6.1.2 Never use solvents from unlabeled bottles.

8.6.1.3 Never pipette solvents directly from bulk solvent. Always take the required volume of solvent into a labeled beaker and pipette from of the unused portion.

8.6.2 Reagents

8.6.2.1 Use only reagents with purity recommended by the appropriate SOP.

8.6.2.2 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.

8.6.3 Use scrupulously cleaned glassware. See appropriate SOP for further details.

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

9 REPORTING AND DOCUMENTATION

9.1 When analysis is complete, the QC Manager is used to download the final sample results into the Laboratory Information Management System (LIMS). If a sample has been diluted then make sure that the information was entered properly into the QC Manager.

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9.2 Add the appropriate qualifiers and comments to the sample data in the QC Manager after performing a complete review of the sample data and QC data. Follow DEP SOP SV-011, BNA Group Data Review/Authorization Checklist for details of data review and reporting, and Section 11 (QUALITY CONTROL). See DEP SOP LB-027, "Standard Operating Procedure for Reporting Qualified Data" for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

9.3 Definitions of the available qualifying codes are listed in DEP SOP LB-027, "Standard Operating Procedure for Reporting Qualified Data".

9.4 All quantitation reports for samples and QC should be placed in a results folder labeled with the job number, the sample numbers, and the type of analysis.

9.5 Retrieve the field folders (containing the field sheets) and check the data against the field sheets to see if it makes sense (i.e., does the equipment blank contain several hits while an effluent sample does not?) If anything looks suspicious, further research is necessary before posting results.

9.6 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of dilutions page if any. Also include a print out of sample positives from the data review and file it in the data folder.

9.7 Submit the result folder to the BNA section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the BNA GC/MS lab.

10 DATA ARCHIVAL

10.1 For the Enviroquant GC-MS system:

10.1.1 Move the valid data files (tune, ICALS, CCC, QC and sample data files) soon after collection from the hard disk of the instrument computers to the network drive \\TLHLAB3\BNA\BULK_ARCHIVE. Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or they are no longer in need.

10.1.2 Copy the processed data files for each method (625, 8270 and pest) Quantitation reports into \\TLHLAB3\BNA\BNA1 or BNA2 or BNA3 to convert in QC Manager for reporting in LIMS. These files may be deleted after all results are authorized.

10.1.3 The archived data may be retrieved by making a request to the data group or the BNA supervisor. Make sure when setting up an injection sequence to write down the name of the data files with the associated sample information in the injection log. Include mass spectrometer number in the data file name. (Example: 07502100.d indicates - year 2007; month 1 to 9 and o, n, d; day 01 to 31; instrument number 1 to 3; and file number 00 to 99) This is the only way that data files may be cross referenced to their sample ID.

11 REFERENCES

11.1 Meier, P.C. & R. Zund, "Statistical Methods in Analytical Chemistry", Vol. 123 of Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications, John Wily & Sons, Inc., New York, 1993.

11.2 "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", Environmental Protection Agency, EPA-600/4-79-019, March 1979.

11.3 Code of Federal Regulations, Title 40, Part 136, Vol. 49, No. 209, Method 625: Base/Neutrals and Acids, 10/26/84.

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11.4 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8270D, Semi-volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS).

11.5 DEP SOP LB-027. Standard Operating Procedure for Reporting Qualified Data.

11.6 DEP SOP LB-024. Significant Figures: Policy of the DEP Chemistry Section

11.7 DEP SOP SV-011. BNA Group Data Review/Authorization Checklist.

Appendix of Changes

08/24/2011 Minor changes in the SOP

07/29/2015 Minor changes in the SOP

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