UNITED STATES DEPARTMENT OF DEFENSE

Data Validation Guidelines Module 5:

Data Validation Procedure for Metals by ICP-MS

Environmental Data Quality Workgroup

11/09/2022

Data Validation Guidelines Module 5

NEBELSICK.JOHN.D.1231361207 Digitally signed by NEBELSICK.JOHN.D.1231361207
Date: 2022.11.09 09:28:40 -06'00'

John Nebelsick Date
Army Principal

GILLETTE.JOHN.S.1123328350 Digitally signed by GILLETTE.JOHN.S.1123328350
Date: 2022.11.09 10:38:34 -06'00'

John S. Gillette, Ph.D. Date
Air Force Principal

ADELSON.JORDAN.M.1268693137 Digitally signed by ADELSON.JORDAN.M.1268693137
Date: 2022.11.09 10:02:34 -05'00'

Jordan Adelson, Ph.D. Date
Navy Principal, EDQW Chair

Table of Contents

1.0 Purpose 1
2.0 Procedure 1
2.1 Introduction 1
2.2 Deliverables 1
2.3 Validation Stages 2
3.0 Stage 1 Validation 2
3.1 Sample Results 3
3.2 Chain of Custody (CoC) 4
3.2.1 Sample Preservation 5
3.2.2 Holding Times 6
3.3 Field QC 6
3.3.1 Field Blanks 6
3.3.2 Field Duplicates (can also be called replicates) 9
4.0 Stage 2A Validation 10
4.1 Method Blanks 11
4.2 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) 12
4.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Laboratory Duplicate (LD) 13
4.4 Dilution Test (DT) and Post Digestion Spike (PDS) 15
4.4.1 Method of Standard Addition (MSA) 16
4.5 Sample Dilutions and Reanalysis 16
5.0 Stage 2B Validation 17
5.1 Sequence and Preparation Logs 17
5.2 Tuning (Mass Calibration) 18
5.3 Initial Calibration 18
5.4 Initial (Secondary Source) and Continuing Calibration Verification 20
5.5 Initial Calibration and Continuing Calibration Blank (ICB/CCB) 21
5.6 Low Level Calibration Check Verification (LLCCV) 22

5.7 Interference Check Solutions (ICS) or Spectral Interference Checks (SIC) 23
5.8 Internal Standards (IS) 25
6.0 Stage 3 Validation 26
6.1 Samples and Field QC Recalculations 27
6.2 Method QC Recalculations 28
6.2.1 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) 28
6.2.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD) or Laboratory Duplicate (LD) 28
6.2.3 Method Blank (MB) 28
6.2.4 Dilution Test (DT) or Post Digestion Spike (PDS) and Serial Dilution (SD) 29
6.3 Instrument QC Recalculations 29
6.3.2 Initial Calibration, Initial/Continuing Calibration Verification (ICV/CCV), and Low-Level Calibration Check Verification (LLCCV) 29
6.3.3 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) 30
6.3.4 Interference Check Solutions (ICS) or Spectral Interference Checks (SIC) 30
6.3.5 Internal Standards (IS) 30
6.4 Standards Traceability 31
6.5 Detection/Quantitation Limit Studies (Optional) 32
7.0 Stage 4 Validation 33
7.1 Raw Sample Results 33
7.2 Spectral, Chemical, and Physical Interferences 33
7.3 Instrument Detection Limits (IDLs) and Linear Ranges (LR) 34
Figure 1: Graphical Workflow for Qualification of Results Based on MS/MSD or LD and DT or PDS Results 35
Appendix A: Method QC Tables 36
Appendix B: Formulas used in Stages 3 and 4 Data Validation 41

Module 5: Data Validation Procedure for Metals by ICP-MS (SW-846 6020)

1.0 Purpose

This document provides guidance on the validation of metals analyzed via Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) by SW-846 Method 6020. The objective of this procedure is to provide the end user with a clear understanding of the quality and limitations of the data through documented validation procedures and to encourage consistency in the validation and reporting of metals data generated for Department of Defense (DoD) projects. The users of this document should apply these data validation procedures to definitive data only.

Project Specific requirements as identified in the Quality Assurance Project Plan (QAPP) should always supersede the requirements of this document.

This document assumes the user is familiar with data validation conventions and qualifiers used in the *DoD General Data Validation Guidelines* (Rev. 1 2019). This document is not intended to obviate the need for professional judgment during the validation process. If a validator feels that the data cannot be reported as required by the QAPP in a scientifically defensible manner, they should use the QAPP point of contact to discuss their concerns.

This document references the *Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) Optimized Worksheets (March 2012)*. Other QAPP formats are equally acceptable, as determined by the project team.

2.0 Procedure

2.1 Introduction

This document was written with primary consideration to SW-846 method 6020B with Quality Control (QC) criteria identified in the DoD Quality Systems Manual (QSM) Version 5.4. However, some projects require other revisions such as method 6020A. Validation should proceed using the acceptance criteria for the method version specified in the QAPP. Appendix A summarizes the QC checks and the required frequency and acceptance criteria for method 6020B and the QSM Version 5.3 requirements.

It is recognized that the more common wording for metals analysis would use “elements”; however, for consistency in the way these data validation guidance documents are written, the word “analyte” will be used throughout.

2.2 Deliverables

Laboratory data deliverables consist of a combination of forms and raw data. The manner in which laboratories label their forms is not dictated nor specified. **The labeling convention below is used for simplicity and does not include all possible forms available.**

- Cover Sheet
- Case Narrative
- Sample Receipt and Conditions Summary
- Sample Results Summary

- Linear Range Check Summary
- Laboratory Control Sample Recovery Summary
- Matrix Spike/Matrix Spike Duplicate/Laboratory Duplicate Summary
- Method/Calibration Blank Summary
- Interference Checks Summary
- Tuning (Mass Calibration) Summary
- Initial Calibration Summary
- Initial/Continuing Calibration Verification Summary
- Low Level Calibration Check Standard Summary
- Internal Standard Summary
- Serial Dilutions Summary
- Post Digestion Spike Recovery Summary
- Sequence and Digestion Logs

2.3 Validation Stages

The types of laboratory data deliverables, staged data validation, and the relationship between the two are outlined in the *DoD General Data Validation Guidelines*.

Stage 1 data validation consists of a review of sample results forms, associated sample receipt summaries (chain of custody), and field QC data.

Stages 2A and **2B** data validation consist of review of summary forms only.

Stages 3 and **4** data validation require review of both summary forms and all associated raw data.

Both the laboratory deliverable requirements and the level of validation should be specified in the QAPP or other planning documents. Data review guidelines and how they apply to the different validation stages are indicated in the following sections.

Note: Any required stage of validation that reveals significant deviations from project requirements may require a higher stage of validation to uncover the source. Data validators are encouraged to communicate with their points of contact identified in the QAPP (such as the UFP-QAPP Worksheet #6) to resolve discrepancies.

3.0 Stage 1 Validation

To ensure that the analytical method protocols outlined in the QAPP were performed (*representativeness*); to verify sampling and reporting *completeness*; to evaluate the performance of field blanks; and to verify compliance with project *sensitivity* needs, the following documents should be reviewed:

- Cover Sheet
- Table of Contents
- Case Narrative
- Sample results form or equivalent Laboratory Report
- Chain of Custody (CoC) forms, Laboratory Receipt Checklists, and other supporting records
- Field QC forms and supporting records

Stage 1 is the validation of investigative and field QC samples.

3.1 Sample Results

Examine the Laboratory Report sample results (can also be called Form I) and verify the following information, ensuring that:

- Holding times have been met, as applicable.
- All sample identification labels are unique and match the chain of custody.
- All project analytes identified in the QAPP and listed on the chain of custody have been analyzed and are reported.
- All laboratory reported Limits of Detection (LODs) and Limits of Quantitation (LOQs) are equal to or less than QAPP required LODs/LOQs (before adjustment for sample-specific conditions, such as dilution or moisture content).
- All project required LODs have been met and are lower than the LOQs.
- All project required Detection Limits (DLs) have been met and are lower than the LODs.
- All project required LOQs have been met and those LOQs are less than the project required action levels for both detects and non-detects.
- All reported units (e.g., mg/kg) are accurate and reflect the requirements of the project and that units are consistent with the type of sample matrix.
- All required field QC samples (such as equipment blanks, and field duplicates) have been included in the Laboratory Report at the frequency specified in the QAPP.
- Soil samples have been reported on a dry weight basis, unless specified by the QAPP to report on a wet weight basis.
- Each laboratory report has a case narrative that explains all non-conformities with the data.

Evaluation of the Laboratory Report

Any samples received for analysis that were not analyzed should be noted in the data validation report, along with the reason(s) for failure to analyze the samples, if the reason(s) can be determined; conversely, samples that were analyzed but were not requested should also be noted.

Analytes that have project action levels less than the laboratory's LOQ may reveal a severe deficiency in the data and a failure to meet project goals and should be noted in the data validation report. Analytes that have LODs or LOQs (before adjusting for sample-specific factors) that differ substantially from those presented in the QAPP may also have an impact on the ability to meet the project goals and should be noted in the data validation report. Errors in reported units and case narrative non-conformities that call into question the quality of the data should also be discussed in the data validation report.

Errors in quantitation limits or missing and misidentified samples may require higher than Stage 1 validation. Data validators are encouraged to reach out to their point of contact identified in the QAPP (such as the UFP-QAPP Worksheet #6) when preparing the data validation report.

For sample results (assuming no other qualifications due to data quality issues):

Qualification of data is based upon the reporting requirements of the QAPP.

The QSM requires reporting non-detects as **U**-qualified at the LOD and requires reporting detects between the DL and LOQ with a **J** qualification. There are several ways that a project team may change these reporting requirements for project-specific reasons which are outlined in the QAPP. These changes are not recommended for typical projects and must be technically justified in the QAPP. They could include reporting non-detects as **U**-qualified at the DL; reporting non-detects and detects below the LOD as non-detects with **U** qualification at the LOD; or reporting non-detects and detects below the LOQ as non-detects with **U** qualification at the LOQ. These varying reporting conventions are summarized in the following table:

Table I: Reporting Requirements

Reporting Requirements (listed below)	**Non-detects or results < DL**	**Results < LOD**	**Results < LOQ**
Standard QSM Reporting	LOD value **U**	Reported Result **J**	Reported Result **J**
*Reporting results to DL	DL value **U**	Reported Result **J**	Reported Result **J**
Reporting results to LOD	LOD value **U**	LOD value **U**	Reported Result **J**
Reporting results to LOQ	LOQ value **U**	LOQ value **U**	LOQ value **U**

***Note:** non-detects reported at the DL have a 50% false negative rate. For further discussion please see *Fact Sheet: Detection and Quantitation – What Project Managers and Data Users Need to Know*, DoD Environmental Data Quality Workgroup, October 2017.

3.2 Chain of Custody (CoC)

Examine the CoC form (some information may be included on Laboratory Receipt Checklists) for legibility, and check that all ICP-MS analyses requested on the CoC have been performed by the laboratory. Ensure all required analytes have been reported. Ensure that the Sample Identification on the laboratory sample results form (Form I [or equivalent]) matches the Sample Identification on the CoC. Ensure the CoC was signed and dated during transfers of custody. Read the laboratory case narrative for additional information.

Evaluation of the CoC

Any discrepancies in sample naming between the CoC and sample results form should be noted in the data validation report with the correct sample name being identified in the report and on the annotated Form I (if applicable), if the correct sample name can be determined. These corrections should also be verified in any associated electronic data deliverables (EDDs).

If the receiving laboratory transferred the samples to another laboratory for analysis, both the original CoCs and transfer CoCs should be present. If the transfer CoCs are not present or if there is missing information (such as location of the laboratory), it should be documented in the data validation report. Make note in the data validation report when signatures of relinquish and receipt of custody were not present.

3.2.1 Sample Preservation

Evaluate sample handling, transport, and laboratory receipt from the CoC and laboratory receipt checklists to ensure that the samples have been properly preserved and handled. The QAPP (such as UFP-QAPP Worksheet #19) should provide specific preservation requirements. The following are general guidance if project specifications were not stipulated.

Metals by ICP-MS

- Metals samples should have been submitted in polytetrafluoroethylene (PTFE), linear polyethylene, polypropylene, or glass bottles (aqueous) or jars (soil). Glass bottles (preserved with acid) may not be appropriate if analyzing for Silica.

- Aqueous samples for <u>total</u> metals analysis should have been preserved with nitric acid to a pH ≤ 2.

- Aqueous samples for <u>dissolved</u> metals analysis should have been both filtered and preserved with nitric acid to pH ≤ 2 on site prior to shipment to the laboratory. If this was not possible, the laboratory should have received an unpreserved aliquot to filter as soon as possible, prior to acid preservation and storage until digestion and analysis.

- Aqueous samples do not require thermal preservation.

- Soil samples do not require thermal preservation, although it is recommended to minimize loss of volatile compounds in the solid matrix containing metals of interest.

Evaluation of Preservation

If the pH of aqueous samples is > 2 upon receipt, the laboratory may add nitric acid to the samples upon receipt. If the samples are preserved in the laboratory, no data qualifiers should be applied, but the actions should be noted in the data validation report.

If the pH of aqueous samples is > 2 upon receipt, and the laboratory did not preserve the samples, detects should be qualified as estimated with a negative bias **J-** and non-detects as **X**, exclusion of data recommended.

If <u>dissolved</u> metals were required by the QAPP and the samples were not filtered, then qualify all detects as **X**, exclusion of data recommended. Excessive particulates (> 2000 mg/L) may cause interferences in the nebulizer; use professional judgement in qualifying non-detects. Samples not affected by excessive particulates may not need qualification. The lack of sample filtration should be noted in the data validation report whether samples are qualified or not.

3.2.2 Holding Times

Holding times for metals are measured from the time of collection (as shown on the CoC) to the start time of acid digestion or sample analysis (as applicable). Holding times for metals in aqueous and soil samples is 6 months.

Based on requirements from QSM version 5.4, holding time exceedances are calculated as follows:

For a test with a recommended maximum holding time measured in hours, the holding time shall be tracked by the hour. For a test with a recommended holding time measured in days, the holding time shall be tracked by the day. For a test with a recommended maximum holding time measured in months, the holding time shall be tracked by the month. One month is defined as 30 days.

For example, an exceedance of holding time for a sample with a 48-hour holding time will occur when the 49th hour is reached (e.g., a sample with a 48-hour holding time collected at 830 AM on April 4th must be analyzed or extracted by 9 AM on April 6th, or an exceedance will be considered to have occurred). An exceedance of holding time for a sample with a 14-day holding time will occur when the 15th day is reached (e.g., a sample with a 14-day holding time collected at 840 AM on April 4th must be analyzed or extracted by 12AM on April 19th, or an exceedance will be considered to have occurred). An exceedance of holding time for a sample with a 6- month holding time will occur when 6 months have passed (e.g., a sample with a 6-month holding time collected at 830 AM on April 5th must be analyzed or extracted by 12AM on October 2nd, or an exceedance will be considered to have occurred).

Evaluation of Holding Times

If the holding time is exceeded, qualify all associated detects as estimated **J-** and all associated non-detects as estimated **UJ** and document that holding times were exceeded.

If holding times for metals are grossly exceeded (defined as 2x the holding time, or 360 days), detects should be qualified as estimated **J-** and non-detects as **X**, exclusion of data recommended.

3.3 Field QC

Field QC can consist of various blanks, field duplicates, and field replicates.

3.3.1 Field Blanks

The purpose of blanks is to identify potential cross-contamination at different stages of sampling and cleaning of equipment for reuse. Not every field blank type may be utilized during any given sampling event and there may be more blank types than described in this document. Field blanks may be varied throughout the sampling events of a project. The types of blanks and their collection frequency should be stipulated in the QAPP. Generally, the blanks are collected once a day or one per twenty field investigative samples, by each sampling team, and may be matrix dependent.

Below are the common types of field blanks for metals analysis.

An **equipment blank** (also called a **rinse or rinsate blank**) is an aliquot of reagent water subjected to all aspects of sample collection (usually poured over or through the sample collection device). Analytes detected in equipment blanks indicate the possibility of cross-contamination between samples due to improper equipment decontamination. Equipment blanks are usually collected at a frequency of one per twenty investigative samples (per matrix per sampling technique), or as specified in the QAPP.

A **source blank** may be collected from each source of water used during each sampling event. This type of field blank may be analyzed to assess whether the chemical nature of the water used in decontamination may have affected the analytical results of site samples. A source blank is usually collected once per source prior to sample collection.

Evaluation of Field Blanks

Determine which field blanks apply to samples in the sample delivery group (SDG) from the CoC or any QC sample associative listing. If the applicability of multiple field blanks cannot be determined, communicate with the point of contact identified in the QAPP to inquire if applicability can be determined.

Note: SDGs can be called by different names such as SEDD Lab Reporting Batch, depending on the project.

Ensure that units are correct when applying field blank qualifications.

Note: it may not be appropriate to make a direct quantitative comparison for aqueous field blanks (such as equipment blanks reported as µg/mL) to a solid parent sample (such as a soil sample reported as mg/kg). At best, only a qualitative comparison can be made during a Stage 1 assessment, as raw data and/or digestion logs would be needed for unit conversion.

Professional judgment should be applied to any equipment blank result that was associated with a contaminated source water blank. Generally, when multiple blank type contaminations are present, the evaluation should not involve a ‘hierarchy’ of one blank type over another. Each blank is evaluated separately and independently. The final validated result should be assessed on the blank with the highest value (i.e., greatest effect on sample analyte concentration). For example, if both a source water blank and an equipment blank were collected in the same batch and the source water blank was also used as the equipment blank water (and both were found contaminated), the sample results would be qualified based on the blank with the higher contaminant concentration.

The source blank water should be analyte free (undetected or as defined by the QAPP) and provided with the sample bottle kit by the contracted laboratory performing the analysis. To ensure the origin of the water used, consult with the field sampling team leader (as some sampling teams may obtain their source water separately from the laboratory) via appropriate channels identified in the QAPP (such as UFP-QAPP Worksheet #6).

If analytes (as appropriate) are detected in the field blanks, the procedure for the qualification of associated sample results is summarized below.

Compare the results of each type of field blank with the associated sample results. The reviewer should note that the blank analyses may not involve the same units or volumes as

the associated samples. These factors should be taken into consideration when applying the 5x criteria discussed below, such that a comparison of the total amount of contamination is actually made. Care should be taken to account for any dilution factors when doing comparisons between detects in the sample and the blank.

If an analyte is detected in the field blank (at any concentration), but not in the associated samples, no action is taken.

If field blanks were not collected at the proper frequency required by the QAPP, then use professional judgment to qualify the data, and make note of this in the data validation report.

If an analyte is detected in the field blank (at any concentration) and in the associated samples, the action taken depends on the relative concentrations between the same and the blank (Table II).

If a field blank has a negative blank result with an absolute value greater than the Detection Limit (DL) or Limit if Detection (LOD) as defined in the QAPP, then it should be evaluated against sample results (Table III).

Table II: Sample Qualification in the Presence of Blank Contamination

	Sample		
Row Number	**Result**	**Validated Result**	**Validation Qualifier**
1	**non-detect or detect ≤ LOD**	**Report at LOD**	**U**
2	**> LOD but ≤ 5x blank**	**Report at Sample Result**	**J+**
3	**> LOD and > 5x blank**	**Report at Sample Result**	**None**

LOD = Limit of Detection **LOQ** = Limit of Quantitation **DL** = Detection Limit
Note 1: The laboratory blank contamination qualifier (typically, **B**) is a part of the laboratory report. The validation qualifier is identified in the validation report with reason codes for the qualifiers traceable to the blank contamination. See the General Data Validation Guidelines appendices 5 and 7 for examples. During the data usability assessment, the DUA team has both sets of information available.

Note 2: The Data Validation Subgroup acknowledges the differences in the QSM requirements for qualification of the method blank by the laboratory and qualification of all blanks by the validator. The method blank, having gone through only the laboratory processing steps and not the field sample handling, should be the most controlled of the blanks. Additionally, the laboratory may reprocess the method blank and samples in order

to address the contamination. The laboratory does not evaluate the results of or qualify data based upon field, equipment, trip, or other blanks.

The Data Validation Subgroup encourages project development teams to set acceptance requirements for blanks based upon project DQOs. In the absence of those project-specific requirements, these guidelines are written to allow for a higher blank contamination tolerance resulting in a more conservative approach to qualification based upon potential contamination. In other words, the assumption that detects in samples are attributed to contamination rather than true sample concentration is minimized, thus minimizing the assumption of false positives.

It is expected that during data usability analysis, the DUA team will review qualifications from the laboratory and from the validator as well as comments contained in the laboratory case narrative and the validation report. The DUA team can then take into consideration whether they believe it more appropriate to consider a result biased high non-detect based upon decision criteria and other quality measures within the data set.

Table III: Sample Qualification in the Presence of Negative Blank Concentrations

Row Number	Negative Blank Result	Sample Result	Validated Result	Validation Qualifier(s)
1	**DL < |[blank]| ≤ LOQ**	**Non-detect**	**Report at LOD**	**UJ**
2	**DL < |[blank]| ≤ LOQ**	**≥ DL but ≤ 5x |[blank]|**	**Report at Sample Result**	**J-**
3	**DL < |[blank]| ≤ LOQ**	**≥ 5x |[blank]|**	**Report at Sample Result**	**None**
4	**|[blank]| > LOQ**	**Detects and non-detects**	**Report at Sample Result**	**X**

LOD = Limit of Detection **LOQ** = Limit of Quantitation **DL** = Detection Limit

3.3.2 Field Duplicates (can also be called replicates)

Field duplicates consist of either colocated or subsampled (split) samples. Field duplicates for groundwater and surface water samples are generally considered to be colocated samples. Soil duplicate samples may be split samples or colocated, as specified in the QAPP. Field duplicate results are an indication of both field and laboratory precision; the results may be used to evaluate the consistency of sampling practices.

Evaluation of Field Duplicates

Check to ensure that field duplicates were collected and analyzed as specified in the QAPP. If the sampling frequency is less than the frequency stated in the QAPP, no qualification of the associated sample results is necessary, but the incident should be discussed in the data validation report.

The QAPP should describe the manner in which field duplicates will be evaluated. This should include the acceptance criteria for Relative Percent Difference (RPD) or absolute difference and when it is appropriate to use RPD or absolute difference. For example, the QAPP may specify that RPD be calculated when detected results are reported for the duplicates(s) and both results are greater than or equal to the LOQ or specify that absolute difference should be calculated when results for one or more of the duplicates are below the LOQ. The QAPP should also specify how to evaluate duplicates when one or more results are not detected. For example, the QAPP may specify the use of the LOD as the value for determining absolute difference when one or more results are not detected.

Additionally, the QAPP should define what is considered a major or minor exceedance of the RPD or absolute difference criteria. For example, RPD greater than 50% in aqueous matrices and 100% in soil matrices or absolute difference greater than 2x LOQ in aqueous matrices and 4x LOQ in soil matrices may be considered a major exceedance.

For field duplicate results, if the RPDs or absolute differences are greater than the criteria stated in the QAPP, qualify the associated sample results for detects as estimated **J** and for non-detects as **UJ.** If the RPDs or absolute differences are greater than the QAPP-defined value for a major exceedance, qualify the associated results as **X, recommended for exclusion.** Any non-conformities should be noted in the data validation summary.

The associated sample results may include samples in the SDG which are similar to the parent sample or be limited to the parent and field duplicate samples if no other samples in the SDG are sufficiently similar to warrant qualification. The validator should note their reasoning for applying qualifications (e.g., the samples are contained “in the same SDG, collected on the same day, prepared together [and] contained in the same analytical sequence” (NFG 2017)).

Some sampling schemes (such as Incremental Sampling Methodology (ISM) if used to collect metals soil samples) require specific replicate calculations (e.g., relative standard deviation), which should be specified in the QAPP.

It should be noted that RPDs or absolute differences for field duplicates are generally not calculated or reported by the laboratory and should be calculated by the validator.

The equation for RPD calculations is given in Appendix B.

4.0 Stage 2A Validation

Note: Stage 2A includes all of Stage 1

Stage 2A requires the review and qualification of the following summary documents.

- Method Blank Summary
- Laboratory Control Sample/Laboratory Control Sample Duplicate
- Matrix Spike/Matrix Spike Duplicate or Laboratory Duplicate

- Dilution Test or Post Digestion Spike Summary
- Serial Dilution Summary

Stage 2A is the validation of preparation batch specific QC data in addition to any sample specific parameters included in Stage 1.

Generally, a “preparation batch” of samples consists of up to twenty field samples (maximum) along with a method blank, laboratory duplicate or matrix spike/matrix spike duplicate, and laboratory control sample. They are meant to be analyzed together on a single instrument. While these samples would ideally be analyzed together on a single instrument, laboratories may choose to split up a batch over multiple instruments to maximize efficiency. In such cases, the data validation report should clearly differentiate between preparation or digestion batches and analytical batches or sequences when discussing the QC associated with the samples. The use of multiple instrumentation should be noted in the data validation report. The validator should engage their QAPP point of contact to determine whether a stage 2B review of sequence logs is needed.

4.1 Method Blanks

A method blank is used to identify contamination originating in the laboratory that may have a detrimental effect on project sample results. The validator should identify samples associated with each method blank using a method blank summary form (or equivalent). Verify that the method blank has been reported per batch.

Compare the results of each method blank with the associated sample results. The reviewer should note that the blank analyses may not involve the same weights, volumes, percent moistures, or dilution factors as the associated samples.

These factors should be taken into consideration when applying the 5x criteria (discussed in section 3.3.1), such that a comparison of the total amount of contamination is actually made. Care should be taken to factor in the percent moisture or dilution factor when doing comparisons between detects in the sample and the method blank.

Evaluation of Method Blanks

If no method blank was analyzed, qualify detects in samples with no associated method blank as **X**, exclusion of data recommended. Non-detects do not require qualification.

If gross contamination exists (defined as greater than a Project Action Limit) in the method blank(s), all analytes affected in all associated samples in the preparation batch should be qualified **X** due to interference. This should be noted in the data validation comments.

If an analyte is detected in the method blank, but not in the associated samples, no action is taken.

If an analyte is detected in the method blank and in the associated samples, the action taken depends on both the blank and sample concentrations. Tables II and III (Blank and Negative Blank Qualifications) and section 3.3.1 on evaluation of results are also applicable to the method blank.

Additionally, there may be instances where little or no contamination was present in the associated method blanks, but qualification of the sample was deemed necessary.

Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result but are absent in the undiluted sample result. It may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, the data should be qualified. In this case, the 5x rule does not apply. The sample value should be reported as a non-detect and the reason should be documented in the data validation report.

Multiple blank contaminations (such as a batch with field blanks and a method blank) does not establish a 'hierarchy' of one blank over another. Each blank must be evaluated individually. Blanks should not be qualified due to the results of other blanks.

4.2 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)

An LCS is an analyte free sample matrix spiked with known amounts of the analytes of interest and taken through all sample preparation, cleanup, and analytical steps. LCSs establish the method precision and bias for a specific batch of samples. Analysis of LCSDs may be required by the QAPP or may be used as an indication of batch precision in instances where matrix spike duplicate analysis is not possible (e.g., a limited volume of sample).

LCS and, if analyzed, LCSD recoveries should be within the QC limits specified in the QAPP or as listed in the QSM. If an LCSD was analyzed, the RPDs should be within the QC limits specified in the QAPP or as listed in the QSM.

An LCS is analyzed in every preparation batch of 20 environmental samples.

Evaluation of LCS/LCSD

Verify that an LCS was analyzed with each batch of samples.

Verify that results (from appropriate summary form), percent recoveries, RPDs (if applicable) and acceptance limits were reported for all target analytes.

If the spike percent recovery control criteria displayed in the deliverable are not the same range (i.e., outside or wider than) as those stipulated in the QAPP or the DoD QSM, reference the required control ranges for evaluation instead of the summarized ranges in the deliverable. The project team should be informed to implement changes to the current deliverables or those to be created in the future.

In-house control limits are acceptable for any analytes not specified in the QAPP or DoD QSM. No qualification is necessary for any reported in-house control limit that is within its control range.

If the LCS percent recoveries were greater than the upper control limit, qualify detects for the analyte in associated samples as estimated with a positive bias **J+**. Non-detects should not be qualified.

If the LCS percent recovery is less than the lower control limit but ≥ 60%, qualify associated detects as estimated with a negative bias **J-** and associated non-detects as **UJ**.

If the LCS percent recovery is < 60%, qualify associated detects as estimated with a negative bias **J-** and associated non-detects as **X**, exclusion of data recommended.

If the LCS/LCSD was not spiked with all target analytes, notify the project team by following the notification protocols outlined in the QAPP (such as UFP-QAPP Worksheet #6) and qualify all detects and non-detects for those analytes not spiked as **X**, exclusion of data recommended.

If the LCS/LCSD RPDs were greater than the acceptance limits, qualify detects for the analyte in the associated sample(s) as estimated **J** and associated non-detects as UJ.

If the QAPP requires the use of a Standard Reference Material (SRM), the control limits specified by the SRM should be the basis for decisions regarding qualification of data. If the SRM falls outside of the specified control limits, the LCS evaluations as listed above should be used for the SRM, as applicable.

Professional judgment should be utilized in qualifying data for circumstances other than those listed above.

4.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Laboratory Duplicate (LD)

Note: Please refer to flow chart (Figure 1) for graphical workflow for qualification of results based on MS/MSD or LD and DT or PDS results.

MS/MSD and LD (sometimes referred to as a Sample Duplicate or Matrix Duplicate that is not spiked) data are used to determine the effect of the matrix on a method's recovery efficiency and precision for a specific sample matrix. LD analyses are also performed to demonstrate acceptable method precision by the laboratory at the time of analysis. If the QAPP does not specify a statistical sampling design, each preparatory batch should have one site specific MS and either a LD or MSD. For sample designs that rely on Incremental Sampling Methodology (ISM), three or more replicates may be specified by the QAPP.

Field blanks should not be used as the parent sample for the MS/MSD or LD analyses.

Note: If a field blank was used for the MS/MSD or LD, the information must be included in the data validation report, but the data should not be qualified. Sample matrix effects should not be observed with field blanks; therefore, no site-specific matrix effects can be determined from a field blank.

The MS and MSD should be spiked per QSM requirements with all target analytes. If the parent sample for the MS/MSD was from another site or project (for example, not enough sample collected, or multiple site samples analyzed within a single batch), the reason should be documented in the data validation report, and sample results should not be qualified due to any non-conformities noted in non-site-specific matrices.

Evaluation of MS/MSD and LD

Verify that MS/MSD analyses were performed at the specified frequency.

Verify that the MS/MSD were spiked with all target analytes, and that percent recoveries and RPDs were reported for all target analytes. If the MS/MSD was not spiked with all target analytes, notify the project team by following the notification protocols and qualify all

detects and non-detects in the parent sample for those analytes not spiked as **X**, exclusion of data recommended.

Recovery criteria for MS and MSD are applicable where the spike concentration is at least 2 to 4 times greater than the native analyte concentration, or as defined in the QAPP. If this is not the case, the MS and MSD percent recovery criteria do not apply. This should be noted in the data validation report.

If the MS/MSD or LD results do not meet the technical criteria, apply the action to all samples in the same preparation batch of the same matrix, if the samples are considered sufficiently similar. Exercise professional judgment in determining sample similarity when making use of all available data, including: samples of the same matrix from the same project site with similar analyte concentrations; site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data; and laboratory data for other parameters. If no samples in the SDG are sufficiently similar to the parent sample, only the parent sample should be qualified. This should be noted in the data validation report.

Compare the percent recovery for each analyte with LCS control limits established by the QAPP or DoD QSM. If the spike percent recovery control criteria displayed in the deliverable are not the same range (i.e., outside or wider than) as those or stipulated in the QAPP or the DoD QSM, reference the required control ranges for evaluation instead of the summarized ranges in the deliverable. The project team should be informed to implement changes to the current deliverables or those to be created in the future. Follow the notification protocols outlined in the QAPP (such as UFP-QAPP Worksheet #6).

For ISM laboratory sub-samples, the RSDs of the replicates should be evaluated against the criteria established in the QAPP. If the RSDs are greater than the acceptance limits, qualify detects for the analyte in the associated sample(s) as estimated **J**. Non-detects should be qualified as estimated **UJ**.

If the MS or MSD percent recoveries were greater than the upper control limit, qualify detects for the analyte in the associated samples as estimated **J+**. Non-detects should not be qualified.

If the MS or MSD percent recoveries were less than the lower acceptance limit but ≥ 30%, qualify detects for the analyte in the associated samples as estimated **J-** and non-detects as estimated **UJ**.

If the percent recoveries were < 30%, qualify detects for the analyte in the associated samples as estimated **J-** and non-detects as **X**, exclusion data recommended.

If the MS/MSD or parent sample result/LD pair RPDs were greater than the acceptance limits (≤ 20% per QSM), qualify detects for the analyte in the associated sample(s) as estimated **J**. Non-detects should be qualified as estimated **UJ**. Evaluation of LD RPD when one or more results are below LOQ may require evaluation of absolute differences or qualitative evaluation in a manner similar to field duplicate evaluations, see method requirements or refer to section 3.3.2.

MS/MSD exceedances due to the presence of a target analyte in the parent sample at > 4x the spike concentration should not necessarily result in any qualifications. If a Post

Digestion Spike (PDS) or Dilution Test (DT) was performed and can be evaluated for the analyte in question, use the PDS or DT results and apply professional judgment to determine if the associated data should be qualified. Document which target analytes were affected and the application of professional judgment in the data validation report.

Note: The above qualifiers assume no PDS or DT was performed for failed MS/MSD control limits. If a PDS or DT was performed, see section 4.4 for possible qualifiers. If matrix interference effects are confirmed, then an alternative test method should be considered or the current test method modified, so that the analysis is not affected by the same interference. The use of a standard-addition analysis procedure may also be used to compensate for this effect (Section 4.4.1 below).

4.4 Dilution Test (DT) and Post Digestion Spike (PDS)

If a MS or MSD failed the percent recovery acceptance limits for a target metal, a PDS or DT, also known as a serial dilution (SD), should be performed, preferably using the same sample used for MS/MSD analysis. This is the case even when the MS/MSD failed due to the parent sample being ≥ 4x the spiking concentration.

A DT is performed when a MS or MSD fails the percent recovery acceptance limits and a target analyte concentration is within the calibration range of the instrument and is considered sufficiently high (minimally, a factor of 25x greater than the Lower Limit of Quantitation (LLOQ) for Method 6020B or 50x greater than the LOQ for the QSM). The DT is an analysis of a 5x dilution that should agree to within ± 20% of the original target analyte concentration (± 10% for the QSM). If not, then a chemical or physical interference effect should be suspected. The MS is often a good choice of sample for the DT, since reasonable concentrations of the target analytes are present.

A PDS test is used when a MS fails control acceptance limits established by the QAPP or QSM. The test only needs to be performed for the specific target analytes that failed the original MS limits, and only if the spike concentration added was greater than the concentration determined in the unspiked sample (Method 6020B). The spike addition should be based on the original concentration of each target analyte of interest in the sample. Criteria apply for samples with concentrations < 50 X LOQ prior to dilution. The recovery of the post-digestion MS should fall within a ± 25 % (75-125%) acceptance range (or 80-120% if QSM requirements are applied), relative to the known true value.
Evaluation of DT and PDS

If the target analyte(s) had a sufficiently high concentration that a DT was run, then no qualification is required if the DT passes acceptance criteria. Make note of the DT in the data validation report.

If the DT exceeds ± 20% (± 10% for QSM) then qualify the affected target analyte(s) in the associated samples as estimated **J**. Non-detects should not be qualified.

If a PDS was performed on a MS that failed acceptable limits:

If the MS percent recoveries failed low (<30%) but the PDS was acceptable within ± 25% (within ± 20% if QSM requirements are applied) then qualify detects in the associated samples as estimated **J** and non-detects as estimated **UJ**. If the PDS also fails, then qualify detects as estimated **J-** and non-detects as **X**, exclusion of data recommended.

If the MS percent recoveries fail low but still are ≥ 30%, and the PDS was acceptable (within ± 25% as per 6010B or ± 20% as per QSM) then qualify detects in the associated samples as estimated **J** and non-detects as estimated **UJ**. If the PDS also fails, then qualify detects as estimated **J-** and the non-detects as estimated **UJ**.

If the MS percent recoveries fail high, and the PDS was acceptable (within ± 25% as per 6010B or ± 20% as per QSM), then qualify detects in the associated samples as estimated **J** and non-detects do not require qualification. If the PDS also fails, then qualify detects as estimated **J+** and the non-detects do not require qualification.

4.4.1 Method of Standard Addition (MSA)

A technique that is sometimes employed with known complex matrices is called the Method of Standard Addition (MSA). It is applied when a sample matrix cannot adequately match the standards matrix used in the initial calibration. The MSA helps resolve a sample matrix that may be enhancing or depressing an analyte signal, and thus providing information that can properly characterize a sample result (see EPA 6020B, section 9.13).

The MSA is a technique that is not routinely used by a laboratory. The use of MSA should be specifically outlined in the QAPP it is typically employed when the DT or PDS have failed criteria.

Evaluation of MSA

If a MSA was required by a QAPP and was not performed by the laboratory, notify the project team by following the notification protocols outlined in the QAPP (such as UFP-QAPP Worksheet #6) and qualify all detects and non-detects for those MSA metal analyte(s) as **X**, exclusion of data recommended.

The MSA technique helps compensate for any analyte enhancement/suppression due to matrix affects. As such, when properly utilized MSA data should not require any qualification. In those cases where MSA has been applied incorrectly, qualify all detects and non-detects for those MSA metal analyte(s) as **X**. In all cases, the use of MSA should have been noted in the laboratory case narrative and should be discussed in the data validation report.

4.5 Sample Dilutions and Reanalysis

Laboratories may dilute samples due to high analyte concentrations or reanalyze samples due to quality control non-conformities, and document both sets of results. Generally, the laboratory will only report one value for a given analyte in the official laboratory report (or equivalent form). In these instances, if the results of multiple analyses are reported for the same analyte for a sample, the validator should evaluate all available results to determine which is the appropriate final result. The validator should consider the application of appropriate qualifiers to the reported results within the scope of the project due to elevated LODs/LOQs or other quality control non-conformities. Qualifiers apply only to the reported results in the official laboratory report.

Evaluation of Sample Dilutions and Reanalysis

Results reported from dilutions leads to elevated LODs for non-detects. The data validation report should indicate the reason for all reported dilutions (including cases where the laboratory did not perform an undiluted analysis) resulting in elevated sensitivity limits for non-detected results.

When reanalysis has occurred due to quality control non-conformities, the validator should ensure that the non-conformity was corrected during the reanalysis. If that is not the case, then the appropriate qualifier should be placed on the reported results.

In some cases, using professional judgment, the validator may determine that an alternate result was more appropriate than the one reported. In those cases, explain the rationale for accepting the alternate result in the data validation report.

In some cases, reanalysis may lead to exceedances of holding time. Use professional judgment to evaluate the results and apply the appropriate qualifiers (if required, see section 3.2.2).

5.0 Stage 2B Validation

Note: Stage 2B includes all of Stage 1, and Stage 2A

Stage 2B requires the review and qualification of the following summary documents.

- Sequence and preparation logs (including any Instrument Blanks)
- Initial Calibration Summary (any equivalent to include Initial Calibration, Linear Regression or RSE)
- Initial/Continuing Calibration Verification Summary (any equivalent to include Initial and Continuing Calibration Verifications)
- Initial/Continuing Calibration Blank Summary
- Low Level Calibration Verification Summary
- Interference Check Summary (any equivalent to include ICS or SIC)
- Internal Standard Summary

Stage 2B is the validation of instrument specific QC data.

5.1 Sequence and Preparation Logs

Sequence logs are reviewed by the data validator to ensure all QC samples (both batch and instrument specific) had been analyzed within a specific batch, in the correct order. Preparation logs are reviewed by the data validator to ensure that samples had the proper extraction performed, within specified holding times. The logs themselves do not require validation. However, non-conformities uncovered in the review of the logs may point the validator to specific samples that require further review. Non-conformities uncovered in preparation or sequence logs should be noted in the data validation report.

Sequence logs are helpful in identifying when multiple instrumentation is used to analyze a batch of samples. For example, it is not uncommon to analyze a single batch of twenty samples at the same time on two or more different instruments. At a minimum, each instrument must be calibrated independently. Batch QC should be reviewed on each instrument, as appropriate. Non-conformities involving the use of multiple instruments should be noted in the data validation report.

Sequence logs are also helpful in identifying excess use of instrument blanks. A common problem is the use of multiple instrument or rinse blanks to 'clean' or flush deposition on the sampler, skimmer cones, spray chamber, or nebulizer in order to achieve acceptable QC results but allowing sample throughput without benefit of blank runs. Such non-conformities should be noted in the data validation report and associated data should be qualified as **X**.

5.2 Tuning (Mass Calibration)

Daily and prior to initial calibration of the instrument, mass calibration and resolution verification checks are analyzed in the mass regions of interest using the mass spectrometer tuning solution that contains analytes that represent all of the mass regions of interest (i.e., 10 µg/L Li, Co, In, and Tl) in order to verify that the resolution and mass calibration of the instrument are within the designated specifications. The mass calibration and resolution verification acceptance criteria must be met prior to the analysis of samples. If the mass calibration differs by more than 0.1 atomic mass unit (u) from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 u full width at 10% peak height.

Evaluation of Tuning

If ICP-MS instrument mass calibration verification was outside the acceptance criteria, qualify associated detects and non-detects as **X**, exclusion of data recommended. Samples should not have been run without a valid mass calibration verification in accordance with the DoD QSM or as specified in the QAPP. Note: If the ICP-MS instrument is run in multiple gas modes, qualification may only apply to those analytes which are quantitated from the mode in which the calibration verification was outside acceptance criteria.

5.3 Initial Calibration

The objective of initial calibration is to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing an acceptable calibration curve.

ICP-MS instruments should be calibrated for all target analytes plus any required for interference correction. The average of at least three readings (of a single injection) is used for both calibration standard and sample analyses. Single standard and multi-point calibration curves are both acceptable.

ICP-MS instruments must be calibrated daily, each time the instrument is set up, and after calibration verification failure.

Method 6020B: A calibration blank and at least one standard must be used in establishing the analytical (calibration) curve. If a multi-point curve is used at least three standards must be employed, and one of the standards must be at or below the Lower Limit of Quantitation (LLOQ).

The QSM requires a minimum of one high standard and a calibration blank. If a multi-point curve is used, at least three standards must be employed. The LOQ must lie at (lowest calibration point) or within a multi-point calibration curve.

Linearity for a multi-point curve is determined using linear regression analysis, inversely weighted linear regression analysis, or Relative Standard Error (RSE).

The multi-point curve correlation coefficient (r) must be ≥ 0.995, the coefficient of determination (r^2) must be ≥ 0.99, or the RSE must be ≤ 20%.

Note: Method 6020B establishes the Lower Limit of Quantitation (LLOQ) as spiked replicates at the lowest point of a multi-point calibration curve. The DoD QSM establishes the Limit of Quantitation (LOQ) as the lowest calibration point or within the calibration curve. If employing calibration with a calibration blank and a single high standard, the LOQ or LLOQ is determined by analyzing a series of low standards that establish precision and bias at the stated LOQ/LLOQ. The QAPP or other planning documents should verify which reporting convention is acceptable for the project.

Evaluation of Initial Calibration

If target analytes were not calibrated, qualify associated detects and non-detects as **X**, exclusion of data recommended. Samples should not have been run without a valid calibration in accordance with the DoD QSM.

Any manipulation of calibration points (such as 'dropping' calibration levels at the ends of a multi-point calibration curve) to achieve acceptance criteria should have a technical justification documented in the laboratory report. Use professional judgment to evaluate the data. If no technical justification is provided, then make note of this in the data validation report and qualify the associated data as **X**, exclusion of data recommended.

If Method 6020B is applied, the lowest calibration standard can establish the LLOQ. Detects below the LLOQ are qualified as estimated **J**.

If the LOQ (QSM criteria applied) is not the lowest calibration standard within the calibration curve (but is still within the calibration curve), then any detects that fall between the LOQ and the lowest calibration standard should be qualified as estimated **J**. Detects below the lowest calibration standard are also qualified as estimated **J**.

If the concentration of the lowest standard in the initial calibration was greater than the LOQ, qualify all detects between the DL and the lowest standard as **X**, exclusion of data recommended. Detects above the low standard do not require qualification. Non-detects do not require qualification.

For multi-point curves:

If an insufficient number of calibration standards was used, qualify all associated detects estimated **J** and all associated non-detects estimated **UJ**.

If the r value is < 0.995; the r^2 value is < 0.99; or the RSE is > 20%, qualify all associated detects as estimated **J** and all non-detects as estimated **UJ**.

If the acceptance criteria are grossly exceeded (defined as r value < 0.95; r^2 value < 0.90; or RSE > 30%) qualify associated detects as estimated **J** and non-detects as **X**, exclusion of data recommended.

All target analyte results that are within the linear range but above the calibration range should first be diluted to within the calibration range before they are reported. As an alternative, a high-level check standard to verify the linear range (within ± 10%) can be used. If sample results are reported above the calibration range without dilution or analysis of a linear range check standard, qualify all detects as **X**, and make note of the lack of dilution(s) or linear range check standard(s) in the data validation report. Non-detects do not require qualification.

If dilution(s) were performed that were within the calibration range of the initial calibration, then qualification of the data is not necessary. Make note in the data validation report that dilution(s) were performed.

If linear range check standard(s) were within criteria, then qualification of the data is not necessary. Make note in the data validation report that linear range check standards were used.

When sample results are reported at more than one dilution due to analyte concentrations exceeding the calibration curve, the lowest LODs are generally used for the non-detects unless a QC criterion has been exceeded.

5.4 Initial (Secondary Source) and Continuing Calibration Verification

The initial calibration curve should be verified with a standard that has been purchased or prepared from an independent source each time initial calibration is performed. This standard is called the secondary source or Initial Calibration Verification (ICV). The ICV should contain all of the metals that are reported. Note that multiple ICVs may be analyzed to encompass all of the target metals.

The ICV is associated with all sample results in the analytical batch. The percent recovery for each target analyte in the ICV must recover within ± 10% (90-110%).

Continuing calibration verification (CCVs) checks may be standards from the same source as the calibration standards. CCVs must be analyzed after every 10 field samples and at the end of the analytical run and must contain all target analytes. Field sample results are associated with bracketing CCVs, the CCV that ran before and the CCV that ran after each 10 field samples. The percent recovery for each target analyte in the CCV must recover within ± 10% (90-110%). In the case that a CCV does not meet acceptance criteria, the QSM gives the laboratory the option to immediately run two additional consecutive CCVs, both of which must meet acceptance criteria.

Evaluating the ICV and CCV

Verify that the ICV was analyzed immediately following the initial calibration and contained all target analytes. Verify the CCVs were analyzed at the proper frequency (after every 10 field samples and at the end of the analytical run). Verify that the percent recoveries for all target analytes in both the ICV and bracketing CCVs were within 90-110% of the true values.

If the ICV (second source) has not been performed after an initial calibration or if samples have been analyzed prior to a valid ICV, qualify all associated data as **X**, exclusion of data recommended. No samples should have been analyzed in accordance with QSM requirements.

If the CCV has not been analyzed (either continuing or end-of-run), qualify all associated data as **X**, exclusion of data recommended. No samples should have been analyzed without a valid CCV.

If any ICV percent recovery was > 110% or < 90% qualify all associated detects and non-detects as **X**, exclusion of data recommended.

If the CCV percent recovery was > 110% or < 90% qualify all associated detects and non-detects since the last acceptable CCV as **X**, exclusion of data recommended. This includes the end-of-run CCV.

5.5 Initial Calibration and Continuing Calibration Blank (ICB/CCB)

Initial and Continuing Calibration Blanks (ICB and CCBs) are assessed to determine the existence and magnitude of contamination problems associated with sample extraction and analysis. If problems with any blank exist, all associated data must be carefully evaluated to determine whether there is any bias associated with the data, or if the problem is an isolated occurrence not affecting other data.

An ICB should be analyzed immediately after the ICV. If a single point calibration is used, the calibration is forced through the ICB, but a second ICB is analyzed as a check and must not contain target analytes above half the LOQ. ICBs apply to all samples in the associated analytical run. A CCB must be analyzed immediately after each CCV. The CCV/CCB analysis is considered a set. CCB non-conformances apply only to samples bracketed by the CCB. Each sample must have an associated ICB and bracketing CCBs.

If the ICB consistently has target analyte concentrations greater than half the LOQ, the LOQ should be re-evaluated. ICB or CCB results indicate instrument-level contamination and should be compared to the raw values of the samples, if available. Since the raw data is usually not available in Stage 2B, the ICB and CCB detects should be converted to the reporting units for comparison, including percent moisture and dilutions in the conversion as applicable.

The laboratory acceptance criteria in the DoD QSM varies depending on the amount of contamination in the blank (and the associated sample result) and the type of corrective action required. For validation, all detects and negative results in the blanks are evaluated against the sample results.

Evaluation of ICB and CCB

Verify that ICB and CCBs were analyzed at the required frequencies.

The criteria outlined in Section 3.3.1 (Field Blanks) and summarized in Table II (Blank Qualifications) and Table III (Negative Blank Qualifications) are also applicable to ICB and CCB evaluations.

If the ICB was not analyzed, then all associated data (detects and non-detects) should be qualified as **X**, exclusion of data recommended. The QSM does not allow data to be reported without a valid ICB.

For ICBs that are qualified based on Table II or Table III, apply the action to all associated samples reported from the analytical sequence.

For CCBs that were not analyzed at the required frequencies, then all associated data that was not bracketed by valid CCBs should be qualified as **X**, exclusion of data recommended. The QSM does not allow data to be reported without valid CCBs that bracket all the samples.

For CCBs that are qualified based on Table II or Table III, apply the action to all associated samples analyzed between a previous acceptable analysis of the CCB and a subsequent acceptable analysis of the CCB in the analytical sequence.

Negative blank results with absolute values greater than the LOD should also be evaluated against sample results.

If an analyte is detected in a blank but the associated sample results are non-detects, the results should not be qualified.

If an analyte is detected in a blank and the associated sample results are > 5x the absolute value of the associated blank result(s) or non-detect, no data qualification is required.

5.6 Low Level Calibration Check Verification (LLCCV)

The accuracy at the low end of the initial calibration curve must be verified with a standard or readback verification (containing all target analytes) at the LLOQ for Method 6020B (less than or equal to the LOQ for QSM). If a multiple-point calibration was performed, the lowest concentration standard may be re-quantitated against the calibration curve.

Alternately, if a single-point calibration was performed, a separate standard containing all target analytes must be analyzed prior to sample analysis. The LLCCV is analyzed daily, after calibration, and the percent recovery for each analyte in the LLCCV should be within ± 20% (80-120%) of the true value.

For Method 6020B requirements, in addition to a daily low-level readback or verification, a mid-point readback verification or standard is also run at the mid-point of the Linear Range or middle calibration point for a multipoint calibration, after the initial calibration is complete. All reported analytes should be within ± 10% of true value. The ICV/CCV (and qualification criteria listed in section 5.2) can be used as the mid-point verification.

Evaluation of the LLCCV

Verify that the lowest concentration standard was re-quantified against the appropriate calibration curve or that a separate standard containing all analytes at the LLOQ (less than or equal to the LOQ for QSM) was analyzed prior to sample analysis.

Verify that the percent recovery for each target analyte was 80-120%.

If a LLCCV was not analyzed, qualify associated detects as estimated **J** and non-detects as **X**, exclusion of the data recommended.

If the LLCCV percent recovery was > 120%, qualify associated detects less than the ICV or CCV concentration (whichever is lower) as estimated **J+**. Detects greater than the ICV or CCV concentration and non-detects should not be qualified if the ICV or CCV was acceptable.

If the LLCCV percent recovery was < 80%, but ≥ 50%, qualify associated detects less than the ICV or CCV concentration (whichever is lower) as estimated **J-** and non-detects as estimated **UJ**. Detects greater than the ICV or CCV concentration should not be qualified if the ICV or CCV was acceptable.

If the LLCCV percent recovery was < 50%, qualify associated detects less than the ICV or CCV concentration (whichever is lower) as estimated **J-** and non-detects as **X**, exclusion of data recommended. Detects greater than the ICV or CCV concentration should not be qualified if the ICV or CCV was acceptable.

5.7 Interference Check Solutions (ICS) or Spectral Interference Checks (SIC)

The Interference Check Solutions (ICSs) or Spectral Interference Checks (SICs) verify that interference levels are corrected by the data system within appropriate limits. ICS or SIC analyses must be run after the initial calibration and prior to sample analysis.

- SIC applies to method 6020B
- ICS applies to previous versions of Method 6020 and QSM Version 5.3 requirements.

Note: The QAPP should specify which criteria (Method 6020B or QSM Version 5.3) is applicable for the data that is being validated.

ICS analyses consist of the evaluation of two solutions. One solution (ICS-A) is composed of relatively high concentrations of common interfering analytes only and is evaluated to determine the effect of interferences below the calibration range (< 1/2 LOQ). The other solution (ICS-AB) is composed of the same high concentrations of interfering analytes and spiked with known concentrations of the target analytes. It is evaluated to determine the effect of interferences on detects within the working range of the instruments.

ICS-A: Absolute value of concentration for all non-spiked project analytes < 1/2 LOQ (unless there is a noted trace impurity on the Manufacturer's certificate of analysis from one of the spiked analytes).

ICS-AB: Within ± 20% of true value (not needed if instrument can read negative responses).

For SIC in Method 6020B, mixed element SIC solution is used daily to check that the instrument is free from interference from elements typically observed in high concentrations and to check that any interference corrections applied are still valid. The SIC solution must be used regardless of whether or not interelement corrections are applied. They evaluate both potential elemental and molecular-ion isobaric interferences and the accuracy of any correction equations.

The mixed element SIC solution is analyzed at the beginning of an analytical run or once every twelve hours. The concentration measured for any unspiked target elements must be less than 2 times ± the LLOQ. If this criterion is not met then sample analysis may not proceed until the problem is corrected, or alternatively, the LLOQ may be raised to twice the concentration observed in the SIC solution.

Evaluation of Daily ICS or SIC

Verify that ICS-A, ICS-AB or SIC analyses were performed at the correct frequency for each sequence. For an interference check that does not meet criteria, apply the action to all sample results reported from the analytical sequence.

ICS and SIC analyses only apply to samples with interferent concentrations which are comparable to (within 10% of the concentration) or greater than their respective levels.

Results for the interfering analytes in the ICS-A, ICS-AB and SIC must fall within 20% of the true value. Results for the spiked target analytes in ICS-AB must fall within the control limits of ± 20% of the true value.

Results for the unspiked target analytes in ICS-A must be < 1/2 LOQ (or less than ± the LLOQ for the SIC). Some target analytes may be present as contaminants from the solution components rather than interferences. If it can be demonstrated that an analyte detect is the result of contamination via analysis by another analytical method or from the manufacturer's certificate of analysis, the result for that analyte must be the less than the LOD after the known contaminant true value is subtracted.

For samples with concentrations of interfering analytes which are comparable to (within 10% of the concentration) or greater than their respective levels in the interference check, recommended actions for ICS or SIC are summarized below.

If ICS or SIC analyses were not performed, qualify all applicable associated sample results as **X**, exclusion of data recommended.

If the result for an analyte not present in the ICS is ≥ 1/2 LOQ (greater than or equal to true value + the LLOQ for the SIC), qualify detects < 5x the unspiked analyte's concentration as estimated **J+**. Non-detects should not be qualified. Detects ≥ 5x the unspiked analyte's concentration should not be qualified.

If the result for an analyte not present in the ICS is greater than or equal to the LOQ (greater than or equal to true value + 2x the LLOQ for the SIC), this is considered a gross interelement correction failure. Qualify detects < 5x the unspiked analyte's concentration as **X**, exclusion of data recommended. Non-detects should not be qualified. Detects ≥ 5x the unspiked analyte's concentration should be qualified as estimated **J+**.

If the result for an analyte not present in the ICS is negative with an absolute value ≥ 1/2 LOQ (greater than or equal to true value + the LLOQ for the SIC), qualify detects < 5x the unspiked analyte's concentration as estimated **J-** and non-detects as estimated **UJ**. Detects ≥ 5x the unspiked analyte's concentration should not be qualified.

If the result for an analyte not present in the ICS is negative with an absolute value greater than or equal to the LOQ (greater than or equal to true value + 2x the LLOQ for the SIC), this is considered a gross interelement correction failure. Qualify detects < 5x the unspiked analyte's concentration as estimated **J-** and non-detects as **X**, exclusion of data recommended. Detects ≥ 5x the unspiked analyte's concentration should not be qualified.

If an ICS or SIC displays recovery for an analyte > 120%, qualify positive sample results as estimated **J+**. Non- detects are not qualified.

If an ICS or SIC displays recovery for an analyte < 80%, but ≥ 50%, qualify positive sample results as estimated **J-** and non-detects as estimated **UJ**.

If an ICS or SIC displays recovery results for an analyte are < 50%, qualify positive sample results as estimated **J-** and non-detects as **X**, exclusion of data recommended.

The following Table IV summarizes the evaluation of ICS or SIC analyses.

Table IV: ICS/SIC Qualifications

Target Analyte	***Sample Result***	***Qualifier(s)***
%R > 120%	Non-detect	None
%R > 120%	Detect	**J+**
%R ≥ 50% < 80%	Non-detect	**UJ**
%R ≥ 50% < 80%	Detect	**J-**
%R < 50%	Non-detect	**X**
%R < 50%	Detect	**J-**
Positive Unspiked Analyte		
> LLOQ or ½ LOQ	Non-detect	None
> LLOQ or ½ LOQ	Detect < 5x [unspiked]	**J+**
> LLOQ or ½ LOQ	Detect ≥ 5x [unspiked]	None
Negative Unspiked Analyte		
Absolute value > LLOQ or ½ LOQ	Non-detect	**UJ**
Absolute value > LLOQ or ½ LOQ	Detect ≤ 5x |[unspiked]|	**J-**
Absolute value > LLOQ or ½ LOQ	Detect > 5x |[unspiked]|	None

Method 6020B SIC (LLOQ); DoD QSM ICS (1/2 LOQ)

5.8 Internal Standards (IS)

An appropriate internal standard is necessary for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The

lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Internal standards should be added to all calibration standards, blanks, instrument QC checks, samples, and batch QC.

The intensities of each internal standard are monitored to ensure that they do not decrease below 30% with respect to their intensity during the initial calibration. If this occurs, a significant matrix effect must be suspected. Under these conditions, the IDL has degraded, and therefore the correction capability of the internal standardization technique must then be questioned. If this happens, the analyst should have taken action to address the issues. Examine the internal standard intensities in the nearest clean matrix, i.e., the calibration blank. If the low internal standard intensities are also observed in the nearby calibration blank, the analyst should have terminated the analysis, corrected the problem, recalibrated the instrument, verified the new calibration, and reanalyzed the affected samples. If drift has not been demonstrated to occur in nearest clean matrix, the analyst should have addressed matrix effects by diluting the affected sample. Samples should have been diluted five-fold (1:5), taking into consideration the need to add the appropriate amounts of internal standards, and reanalyzed. If the first dilution does not eliminate the problem, the dilution process is repeated in an iterative fashion, using ever-increasing dilutions, until the internal standard intensities exceed the 30% acceptance limit. Results are reported as corrected using the appropriate dilution factors.

Evaluation of IS

Internal Standard percent recoveries in the samples should be within 30-120% of the IS recoveries in the Initial Calibration Blank (ICB). Verify that internal standards were added to all analytical runs.

If the percent recovery is < 30% in samples, qualify detects and non-detects **X**, exclusion of data recommended.

Detects for analytes quantitated using an IS percent recovery > 120% should be qualified estimated **J-**. Non-detects should be qualified as estimated **UJ**.

If extremely high area counts are reported (> 150% of the area for associated standards), detects and non-detects should both be qualified **X**, exclusion of data recommended.

6.0 Stage 3 Validation

Note: Stage 3 validation includes all of Stage 1, Stage 2A and Stage 2B

The following documents are used for a Stage 3 validation

- Raw Data (including any laboratory forms, instrument outputs, spreadsheets, or handwritten calculations necessary for recalculation and re-quantification)
- Standards Traceability forms and worksheets
- Optional Detection Limit studies (Instrument Detection Limits, Method Detection Limits)

Stage 3 validation includes the recalculation and re-quantification of selected samples, and method and instrument QC. The types of results that should be recalculated and re-

quantified include target analytes, analytes with detects above the LOQ, and field QC samples (blanks and duplicates). For method QC results, spiked recoveries and method blanks should be considered. For instrument QC, calibrations (including regressions), calibration verifications, and internal standards should be recalculated and re-quantified. Some calculations may include the need to review standards preparation and serial dilutions.

6.1 Samples and Field QC Recalculations

When choosing samples, field QC and analytes for recalculation and re-quantification, consideration should be given to the laboratory's batching scheme to ensure a representative subsample of recalculations is performed. Additionally, if priority contaminants or contaminants of concern are identified in the QAPP, those analytes should be selected for re-quantification and recalculation. Other circumstances that should be prioritized for recalculation and re-quantification are diluted samples, re-runs of samples due to QC failures such as internal standard anomalies, and field QC blank failures.

Recalculation and re-quantification should be performed on the designated percentage of the samples per SDG (or however defined in the QAPP, such as percentage of total project samples) per analytical suite. As a minimum, it is recommended that 10% of the data should be recalculated and re-quantified unless specific instructions are given in the QAPP.

Calculations must include appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207, and 208 *m/z* for lead (to compensate for any differences in the abundances of these isotopes between samples and standards). Sample recalculations should include the raw instrument result, re-quantified from the instrument response against the calibration function, and the final reported sample result, including associated internal standard and any dilution, preparation factor, or percent moisture (if applicable). The equations in Appendix B can be used to calculate a sample result from the corresponding reported calibration or regression function, as appropriate. The minimum of three readings for each result should have an RSD less than 5% and the reported result should be the average from these three readings.

Verify that one or more of the laboratory's reporting limits (such as limit of quantitation) are calculated correctly for the non-detects and reported accordingly. If a detection limit study was identified by the QAPP, recalculate one or more analyte detection limits.

Re-quantitate all detected target analytes in the 10% sample data chosen. For some samples, all results may be non-detects, therefore recalculation would not be necessary. Field sample results reported as non-detect should be verified as having a value where the absolute value is less than the DL. Verify that sample-specific results have been adjusted correctly to reflect percent solids, original sample mass/volume, and any applicable dilutions.

Re-quantitate all detects found in the field QC blanks (such as field blanks or equipment blanks). Field QC sample duplicate recalculations should include re-quantification of the same detected analyte sample/duplicate pair and verification of the percent difference (%D), or relative percent difference (RPD), as reported.

When recalculations require rounding of data, that rounding should be completed only once at the end of all calculations to minimize rounding errors. Calculations should be rounded to the significant figures of the underlying criteria. For example, an LCS criteria of 90-107% would still be considered acceptable if the recalculation was 107.4%

Evaluation of Sample and Field QC Recalculations

If the laboratory's quantitation or reporting limits (however defined) are calculated incorrectly, then continue to recalculate limits until it is determined that the problem is systemic (such as incorrect equations used) or isolated (such as a transcription or rounding errors).

For systemic (defined as widespread and major in nature) issues that cannot be corrected through a revised laboratory report, qualify all results as **X**, exclusion of data recommended.

For isolated cases, use professional judgment. It may be necessary to engage the point of contact as identified in the QAPP to communicate with the laboratory, so they can provide revised (corrected) results. In all cases, if calculation errors affect project target analytes, the point of contact should be notified, and all affected results noted in the data validation report, including listing the calculation errors.

6.2 Method QC Recalculations

Re-quantification of batch QC sample results should use raw instrument response in tandem with the reported calibration slope; the preparation information; and percent moisture for solid samples to recreate the reported result.

6.2.1 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)

To check that the spike percent recovery was calculated and reported correctly, using the equation in Appendix B, re-quantitate and then recalculate 10% of the target analytes as outlined in the UFP-QAPP Worksheet #12 or #15. Use a random 10% of the analytes in the LCS/LCSD if contaminants of concern have not been specifically identified. Recalculate RPDs (if applicable) from LCS/LCSD pairs that would result in the qualification of a sample.

6.2.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD) or Laboratory Duplicate (LD)

Re-quantitate 10% of the target analytes as listed in the UFP-QAPP Worksheet #12 or #15 for both the MS and the MSD (or LD). Use a random 10% of the analytes in the MS and MSD if contaminates of concern have not been identified. The RPDs of the recalculated MS/MSD pairs (or Sample Result/LD pairs) should be calculated from the MS/MSD concentrations, not from the recoveries.

6.2.3 Method Blank (MB)

Method blank analytical results are assessed to determine the existence and magnitude of contamination problems associated with sample extraction (if applicable) and analysis. If problems with any method blank exist, all associated data should be carefully evaluated to determine whether there is any bias associated with the data, or if the problem is an isolated occurrence not affecting other data. Results may not be corrected by subtracting any blank values.

Re-quantitate one or more detects found in the method blank (if applicable) from the reported regression curve. Method Blank results reported as non-detect should be verified as having a value where the absolute value is less than the DL. The summary forms provided should display the uncensored value, or the actual concentration whether negative or positive.

6.2.4 Dilution Test (DT) or Post Digestion Spike (PDS) and Serial Dilution (SD)

To check that the spike percent recovery was calculated and reported correctly, re-quantitate, and then recalculate 10% of the target analytes as outlined in the UFP-QAPP Worksheet #12 or #15 for at least one DT or PDS sample, if applicable. Use a random 10% of the analytes if contaminants of concern have not been specifically identified.

For any sample results (detects) that were in the linear range but required a serial dilution within the working calibration range to report the data, recalculate at least one target analyte from one or more samples that was diluted.

Evaluation of all LCS, MS, MB, DT/PDS and SD Recalculations

If transcription errors (or other minor issues such as rounding errors) are found in method QC results, use professional judgment to qualify the data. It may be necessary to engage the point of contact as identified in the UFP-QAPP to communicate with the laboratory, so they can provide revised (corrected) results. In all cases, if method QC calculation errors affect project target analytes, the point of contact should be notified, and all affected results noted in the data validation report, including listing the calculation errors.

For systemic (defined as widespread and major in nature) problems with LCS/LCSD calculations qualify all affected analytes in associated samples as **X**, exclusion of data recommended.

For systemic problems with method blanks, MS/MSD or LD, and DT/PDS calculations qualify all affected analyte detects in associated samples as estimated **J** and non-detects as estimated **UJ**.

6.3 Instrument QC Recalculations

6.3.1 Tune Check

Mass spectrometer tuning solution should be prepared to contain elements that represent all of the mass regions of interest (i.e., Li, Co, In, and Tl) in order to verify that the resolution and mass calibration of the instrument are within the designated specifications. Verify that the tuning was conducted in the mass regions of interest for the analytes reported.

6.3.2 Initial Calibration, Initial/Continuing Calibration Verification (ICV/CCV), and Low-Level Calibration Check Verification (LLCCV)

Initial calibration (ICAL) recalculations should use the raw instrument response for the target analytes and associated internal standards to recreate the calibration curve from the individual calibration standards. If multiple types of calibration curves are employed in an analytical suite, then one analyte per curve type should be recalculated.

Re-quantitate and recalculate the regression function (if used for multi-point calibration), slope, intercept, and (r) values reported for at least 10% of the target analytes per each

internal standard, preferably analytes of concern which were identified in the QAPP, per initial calibration curve type. Some MS instruments report r^2 (coefficient of Determination) values instead of (r).

The laboratory may employ a linear or weighted linear least squares regression. The low standard should be recalculated using the calibration curve and evaluated. If the ICAL included refitting of the data back to the model (RSE), then recalculate 10% of the target analytes for the RSE in each ICAL.

Re-quantify and recalculate the ICV, CCV, and LLCCV result and %D for at least 10% of the target analytes for every ICV, CCV, and LLCCV bracketing reported results, proportionally selecting analytes based on calibration curve types used in each initial calibration.

6.3.3 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Verify each ICB and CCB bracketing reported results by comparing the summary form results to the raw data. Re-quantify one or more detects in the ICB and each CCB (if applicable) using the reported calibration curve. Calibration Blank results reported as non-detect should be verified as having a value where the absolute value is less than the DL. The summary forms provided should display the uncensored value, or the actual concentration whether negative or positive. Verify that negative raw data values are reported appropriately.

6.3.4 Interference Check Solutions (ICS) or Spectral Interference Checks (SIC)

Verify the result and recalculate the percent recovery for at least 10% of the target analytes for every ICS or SIC bracketing reported results. Recalculate at least 10% of the reported concentrations of non-spiked metals in each ICS.

6.3.5 Internal Standards (IS)

The analyte quantitation should be evaluated for all detects by evaluating the raw data. Analyte concentrations should be calculated based on the IS associated with that analyte. Quantitation should be based on them/z in the analytical method (or laboratory SOP listed in the QAPP) for both the IS and target analytes. The analyte quantitation should be based on the regression function from the appropriate ICAL.

Recalculate IS percent recoveries reported from the raw data for at least 10% of the samples per SDG), and verify internal standard results for samples that were qualified due to out-of-control internal standard results.

If errors are discovered, request revisions of the laboratory report per the QAPP point of contact.

Evaluation of all tune, ICAL, ICV/CCV/LLCCV, ICB/CCB, ICS/SIC, and IS Recalculations

If the files provided do not match the quantitation report, the regression function reported is likely to be from another initial calibration and the laboratory report should be revised. The point of contact (UFP-QAPP Worksheet #6) should be reached to get a revised (corrected) report from the laboratory. For calculation errors for any type of regression equations that

cannot be corrected in a revised report, qualify all the data as **X**, exclusion of data recommended.

If the tuning was not conducted in the mass regions of interest for the analytes reported, qualify analytes with no associated tune as **X**, exclusion of data recommended.

The reprocessed low standard of a regression curve should be within 20% of the true value. If the recalculated concentration is not within 20% of the true value, qualify detects (at the LOQ and above) for the affected analytes as estimated **J** and non-detects as estimated **UJ** in the associated samples. If the recalculation shows gross error (> 30%), then detects should be qualified J and non-detects should be qualified as **X**, exclusion of data recommended.

Qualify all associated data as **X** if the corresponding ICV/CCV %D has been calculated incorrectly by the laboratory and cannot be corrected in a revised laboratory report.

Qualify all associated analyte detects as estimated **J** and non-detects as estimated **UJ** if the corresponding LLCCV %D has been calculated incorrectly by the laboratory and cannot be corrected in a revised laboratory report or the corresponding true value cannot be determined.

Qualify all affected analyte detects in associated samples as estimated **J** and non-detects as estimated **UJ** if the corresponding ICB/CCB detects have been calculated incorrectly and cannot be corrected in a revised laboratory report.

Qualify all associated analyte detects as estimated **J** and non-detects as estimated **UJ** if the corresponding ICS/SIC interference checks have been calculated incorrectly and cannot be corrected in a revised laboratory report.

Qualify all data as **X** if the corresponding IS has been calculated incorrectly (or if the IS has been assigned to the wrong analyte) by the laboratory and cannot be corrected in a revised laboratory report.

In all cases where instrument QC are calculated incorrectly, the UFP-QAPP point of contact should be notified and noted in the data validation report.

6.4 Standards Traceability

Evaluate the calibration standards used for the analytes of concern. From the Certificate of Analysis (however named), verify that the “true values” of each analyte of concern were correctly applied to create the calibration curve, and that all analytes of concern were in the calibration mix.

All initial instrument calibrations should be verified with a standard obtained from a second manufacturer prior to analyzing any samples. From the standard Certificate of Analysis, verify that a second source was used for the Initial Calibration Verification (ICV). The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard.

Check that the stock standards were diluted properly into working standards by recalculating the dilutions of one or more calibration standards. Recalculate one or more

method QC sample dilutions (such as LCS or MS/MSD) from the stock to the working standard.

Note: It is not the role of the data validator to evaluate the Certificate of Analysis for compliance with the *ISO-17034 Standard*, but to verify that stock and working standards were correctly applied in the creation of calibration curves.

Evaluation of Standards

Professional judgment should be used when evaluating errors in standards preparation. The point of contact identified in the QAPP (UFP-QAPP Worksheet #6) should be reached to get a revised (corrected) report from the laboratory. Issues (that do not affect the results of any target analytes) should be noted in the data validation report.

For systemic (widespread) issues that cannot be corrected by the laboratory, or issues that affect the results of target analytes, the data should be qualified as **X**, exclusion of data recommended.

For ICV standards that were not verified to be from a second source, qualify all affected data as **X**, exclusion of data recommended. No samples should have been run without a valid second source standard (per QSM requirements).

For expired standards, per QSM requirements, a laboratory cannot use a standard beyond its expiration date. All associated data should be qualified as **X** if expired standards were used. The expiration date of any working standard is based on the expiration date of the primary or stock standard.

6.5 Detection/Quantitation Limit Studies (Optional)

In some cases, a QAPP may specify the review and validation of a detection/quantitation limit study. This could include studies such as Method Detection Limits (MDLs), quarterly LOD verifications, or LOQ verifications. The QAPP should specify the criteria for evaluating the study. As a minimum, at least 10% of the raw data in the study should be recalculated.

Evaluation of Detection Limit Studies

The criteria for evaluating a detection/quantitation limit study should be listed in the QAPP. The following guidance should be enacted if the QAPP does not specify the evaluation criteria.

If transcription errors (or other minor issues such as rounding errors) are found in detection/quantitation limit studies, use professional judgment to qualify the data. It may be necessary to engage the point of contact as identified in the QAPP to communicate with the laboratory, so they can provide revised (corrected) results. In all cases, if calculation errors affect project detection or quantitation limits, the point of contact should be notified, and all affected results noted in the data validation report, including listing the calculation errors.

When calculation errors are uncovered that cannot be corrected by the laboratory and that affect detection/quantitation results, consideration should be given to qualify the study as **X**, exclusion of data recommended.

7.0 Stage 4 Validation

Note: Stage 4 validation includes all of Stage 1, Stage 2A, Stage 2B and Stage 3

Raw Data (including any instrument outputs, raw interference/background corrections data files, Spectra)

Stage 4 is a qualitative/quantitative review of detected and non-detected analytes from the instrument outputs (raw data files). Quantitation reports, instrument background corrections, and interference corrections data files are required to perform the review of the instrument outputs.

The application of qualitative criteria for metals analysis requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory through the QAPP point of contact, if necessary.

7.1 Raw Sample Results

For ICP-MS, confirm that reported results for 10% of the QC standards (including instrument and method QC) and 10% of the positive field sample result concentrations (detects at or above the LOQ) are the average of at least three readings (of a single injection).

If, in the professional judgment of the validator, there are instances of unwarranted manipulation of data then those cases should be reported to the project team as soon as practical (UFP-QAPP Worksheet #6).

The following are some (non-inclusive) instances of data manipulation that should be reported to the project team:

- Manipulation of hold time data
- Analyzing samples known to be lacking acid preservation
- Excessive use of instrument rinse blanks to ‘pass’ QC criteria
- More than three readings of a single injection (for select samples and not the entire batch)
- Running multiple CCVs and using the last one that passes criteria
- Running ICVs known to be from the same source as the calibration standards

7.2 Spectral, Chemical, and Physical Interferences

Spectral, chemical, and physical interferences must be evaluated for each instrument. The laboratory should evaluate interferences for the particular operating conditions and sample matrix. For a discussion of interferences, see 6020B section 4.

Isobaric elemental interferences refers to different elements whose isotopes have the same nominal *m/z* ratio. The ICP-MS operating software will perform the necessary calculations automatically.

Polyatomic interference refers to the combination of two or more isotopes and Divalent interference is an element consisting of a doubly charge ion. These interelement interference-effects could affect the accuracy of the analyte measurement.

For multipoint calibration methods that employ whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the calibration algorithm. The interelement interferences listed in Method 6020B (Table I) may be employed by the data validator to evaluate corrections for known interferences.

The interelement correction equations themselves are complex and instrument specific, but the accuracy of any interelement corrections is verified through the analysis of the SIC for Method 6020B. The mixed element SIC is used daily and is reviewed in Stage 2B. However, if spectral interference is observed the data validator should review the individual (single) element SIC (analyzed by the laboratory every 6 months and used to set the interelement corrections). The absolute value of the concentration observed for any unspiked analyte in the single element SIC check must be < 2x LLOQ for Method 6020B (< 1/2 LOQ for QSM ICS-A).

When uncorrected, interelement interferences may produce false positive results. However, overcorrection can cause a negative bias. If there is any indication of spectral interference from the single element SIC raw data, the validator should note this in the data validation report and qualify all associated target analytes as estimated **J** for detects and estimated **UJ** for non-detects. If, in the professional judgment of the validator, the spectral interference calls into question the validity of the data, the QAPP point of contact should be notified via UFP-QAPP Worksheet #6.

Physical interference refers to the differences in viscosity, surface tension and dissolved solids that could affect the matrix. Matrix effect should be suspected if the intensities of each internal standard decrease below 30%, with respect to its intensity during the initial calibration.

Memory or carry-over occur when analytes from a previous sample or standard measured in the current sample. The rinse period between samples should be long enough to minimize such interferences. Excessive use of instrument rinse blanks to ‘pass’ QC criteria is data manipulation that should be reported to the project team.

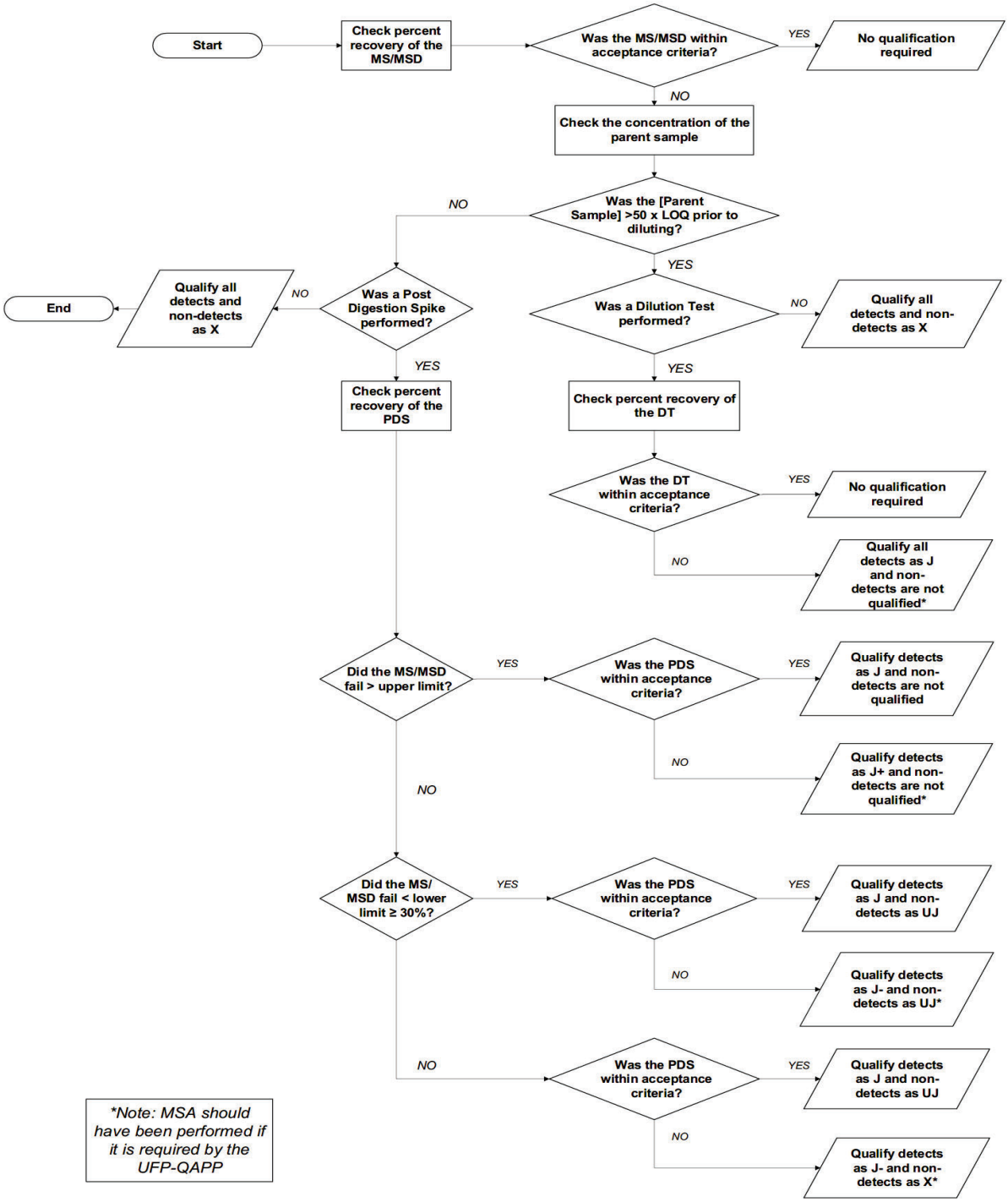
7.3 Instrument Detection Limits (IDLs) and Linear Ranges (LR)

ICP-MS instruments should have a Signal to Noise (S/N) ratio of at least 3:1. Qualitatively review instrument outputs to verify that S/N is appropriate to produce quantitative data. Instrument detection limits (IDLs) are useful means to evaluate excess instrument noise level.

Use professional judgment to review and qualify sample data that is reported with a low S/N ratio. Low ratios give evidence that background corrections were not applied or applied incorrectly. If, in the professional judgment of the validator, background interference calls into question the validity of the data, the QAPP point of contact should be notified via UFP-QAPP Worksheet #6.

The Linear Range (LR) establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the high standard in the calibration. The standard must recover within 10% of the true value, and if successful, establishes the LR. The linear range standards must be analyzed in the same instrument run as the calibration they are associated with. Qualify all detects above the LR as **X,** exclusion of data recommended.

Figure 1: Graphical Workflow for Qualification of Results Based on MS/MSD or LD and DT or PDS Results



Appendix A: Method QC Tables

Note: The following Table is based on the QSM 5.3 Standard, with Method 6020B for comparison. The Table does not include all the QC elements from the method or as listed in this guidance document.

QC Check	6020B Frequency and Acceptance Criteria	QSM Version 5.3 Frequency and Acceptance Criteria
Linear Dynamic Range (LDR) or high-level check standard	**Linear Range**: At initial set up and Daily with a high standard, if samples are reported above the Calibration Range. Must be analyzed in the same instrument run as the calibration they are associated with. The high check standard establishes the Linear Range. Within ± 10% of true value.	**Linear Dynamic Range**: At initial set up and checked every 6 months with a high standard at the upper limit of the range. Within ± 10% of true value.
Tuning (Mass Calibration)	**Mass Calibration:** Daily and prior to initial calibration to demonstrate mass calibration $\leq$ 0.1 amu from the true value and resolution < 0.9 amu full width at 10% peak height.	**Tuning:** Prior to initial calibration to demonstrate mass calibration $\leq$ 0.1 amu from the true value and resolution < 0.9 amu full width at 10% peak height.
Initial calibration (ICAL) for all analytes	At instrument set-up and Daily, prior to sample analysis. Minimum one high standard and a Calibration Blank. If a multi-point calibration is used: Minimum of 3 standards, the low standard must be ≤ LLOQ Each analyte should meet one of the linear regression options below: **Coefficient of Determination (COD)** $r^2 \geq 0.990$ **Correlation Coefficient** r) ≥ 0.995 or	Daily ICAL prior to sample analysis. Minimum one high standard and a Calibration Blank. If more than one calibration standard is used, $r^2 \geq 0.99$.

QC Check	6020B Frequency and Acceptance Criteria	QSM Version 5.3 Frequency and Acceptance Criteria
	RSE for each analyte ≤ 20%.	
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis. All reported analytes within ± 10% of true value.	Once after each ICAL, analysis of a second source standard prior to sample analysis. All reported analytes within ± 10% of true value.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence. All reported analytes within ± 10% of the true value.	After every 10 field samples and at the end of the analysis sequence. All reported analytes within ± 10% of the true value.

QC Check	6020B Frequency and Acceptance Criteria	QSM Version 5.3 Frequency and Acceptance Criteria
Low-Level Calibration Check Standard (LLCCV)	Daily; A low level check standard or readback verification at the LLOQ for single point calibrations; or at the lowest calibration standard for a multi-point calibration. All reported analytes within ± 20% of true value. Daily; A mid-level check standard (readback verification) at the mid-point of the Linear Range for single point calibrations; or at the middle calibration point for multi-point calibrations. All reported analytes within ± 10% of true value.	Daily; LLCCV should be ≤ LOQ. All reported analytes within ± 20% of true value.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV. Target analytes must be < ½ LLOQ for the ICB and < LLOQ for the CCBs.	Immediately after the ICV and immediately after every CCV. The absolute values of all analytes must be < ½ LOQ or < 1/10th the amount measured in any sample.
Internal standards (IS)	Added to every calibration standard, field sample, blank, instrument and method QC sample. IS intensity greater than 30% of intensity of the IS in the ICAL	Internal Standards are added to every field sample, standard, and QC sample. IS intensity within 30-120% of intensity of the IS in the ICAL blank

QC Check	6020B Frequency and Acceptance Criteria	QSM Version 5.3 Frequency and Acceptance Criteria
Method Blank (MB)	One per preparatory batch. No target analytes in the method blank should be ≥ ½ LLOQ unless the sample concentration is > 10x the blank contamination.	One per preparatory batch. The absolute values of all analytes must be < ½ LOQ or < 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.
Interference Check Solutions (ICS) or **Spectral Interference Check (SIC)**	**SIC:** Daily, after ICAL and prior to the beginning of every twelve hours of sample analysis. Unspiked elements should be less than 2 times the LLOQ.	After ICAL and prior to sample analysis. **ICS-A**: Absolute value of concentration for all non-spiked project analytes < 1/2 LOQ; **ICS-AB**: Within ± 20% of true value.
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD); **Matrix Spike (MS); Matrix Spike Duplicate (MSD)** **Matrix Duplicate (MD), also called Laboratory Duplicate (LD)**	One each **LCS** (or **LCS/LCSD** pair) and one **MS/MSD** pair (or **Sample result/LD** pair) per preparatory batch. For **LCS**, use ± 20% for recovery until historical limits can be generated. For **MS**, use ± 25% for recovery until historical limits can be generated. **MSD (LD)** or **LCSD**: RPD of all analytes ≤ 20% (between **MS/MSD** or **Sample result/LD, LCS/LCSD** pair).	One each **LCS** and **MS/MSD** pair per preparatory batch. **LCS**: A laboratory must use the QSM Appendix C LCS Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. **MS**: A laboratory should use the QSM Appendix C LCS limits as a basis of comparison for the **MS/MSD**. **MSD** or **MD**: RPD of all analytes ≤ 20% (between **MS/MSD** or **Sample result/MD**).

QC Check	6020B Frequency and Acceptance Criteria	QSM Version 5.3 Frequency and Acceptance Criteria
Dilution Test (DT)	Once per batch when matrix spikes display less than acceptable bias and precision. If a target analyte(s) concentration is within the Linear Range of the instrument and sufficiently high (minimally, 25x greater than the LLOQ). This sample can be the MS. 1:5 dilution should agree to within ± 20% of the original determination.	One per preparatory batch if MS or MSD fails. Only applicable for samples with concentrations > 50x LOQ (prior to dilution). Five-fold dilution must agree within ± 10% of the original measurement.
Post Digestion Spike (PDS)	Once per batch when matrix spikes display less than acceptable bias and precision. If a high concentration sample is not available for performing the DT, then a PDS on the MS should be performed. The test only needs to be performed for the specific elements that failed original MS limits, and only if the spike concentration added was greater than the concentration determined in the unspiked sample. The recovery of the post-digestion MS should fall within a ± 25 % acceptance range, relative to the known true value, or otherwise within the laboratory derived acceptance limits.	Perform if MS/MSD fails. One per preparatory batch (using the same sample as used for the MS/MSD if possible). Applies for samples with concentrations < 50x LOQ (prior to dilution). Recovery within 80-120%.
Method of Standard Additions (MSA)	If matrix interference effects are confirmed, then an alternative test method should be considered or the current test method modified, so that the analysis is not affected by the same interference. The use of a standard-addition analysis procedure may also be used to compensate for this effect.	MSA: when dilution test or post digestion spike fails

Appendix B: Formulas used in Stages 3 and 4 Data Validation

Multi-point Calibration

Linear Regression: y = mx + b

$$C_s = \frac{\left(\frac{A_s}{A_{IS}} - b\right) * \ C_{IS}}{m}$$

Where:

C_s =Concentration, Sample

A_s =Area (isotope intensity), Sample

A_{IS} = Area (isotope intensity), Internal standard

C_{IS} = Concentration, Internal Standard

b = Intercept

m = Slope

LCS Percent Recovery:

$$Percent\ Recovery = \frac{C_s}{C_K}\ x\ 100$$

Where:

C_s = Concentration, Reported

C_K = Concentration, Known

MS or MSD Percent Recovery:

$$Percent\ Recovery = \frac{C_M - C_s}{C_K}\ x\ 100$$

Where:

C_M = Concentration, MS or MSD

C_s = Concentration, Sample

C_K = Concentration, Known

Field Duplicate, MS/MSD or LCS/LCSD Duplicate Relative Percent Difference (RPD):

$$RPD = \frac{|C_s - C_d|}{(C_s + C_d)/2}\ x\ 100$$

Where:

C_s = Concentration, Sample

C_d = Concentration, Duplicate

Calculation of sample amounts:

Solids:

$$\%\ Dry\ Weight\ = \frac{g\ of\ dry\ sample}{g\ of\ sample}\ x\ 100$$

$$Concentration_{\ DW} = \frac{C\ x\ V_f x D_f}{WxS}$$

where:

Concentration on a dry weight basis:

Concentration $_{DW}$ = Concentration of a dry weight basis (mg/kg)

C = Digest concentration (mg/L)

V_f = Final volume after sample preparation (L)

D_f = Dilution Factor

W = Wet sample mass (kg)

S = % Solids/100 = % dry weight/100

Aqueous:

$$Concentration = \frac{C_r \, x \, V_f x \, D_f}{V_i}$$

where:

Concentration = (mg/L)

C_r = Raw concentration (mg/L)

V_f = Final volume after sample preparation (L)

D_f = Dilution Factor

V_i = Initial volume before sample preparation (L)