GRAVIMETRIC (PRECIPITATION) METHODS

Note: Make enough copies of **Pages 1-9** to **assess each test method** in use at the laboratory, one method at a time

CHEMISTRY TEST METHOD EVALUATED: _____

____ **5.5.4.1.2(a)** Does the laboratory have an **in-house methods manual** for each accredited **analyte** or **method**
Note: This manual may consist of copies of published or referenced test methods

____ **5.5.4.1.2(b)** Does the laboratory **clearly indicate** in its methods manual **any modifications** made to the referenced test method and **describe any changes or clarifications** where the referenced test method is ambiguous or provides insufficient detail

Does each test method in the in-house methods manual include or reference, where applicable:

____ **5.5.4.1.2(b)(1)** **Identification** of the test method
____ **5.5.4.1.2(b)(2)** Applicable **matrix or matrices**
____ **5.5.4.1.2(b)(3)** **Method Detection Limit**
____ **5.5.4.1.2(b)(4)** **Scope & application**, including components to be analyzed
____ **5.5.4.1.2(b)(5)** **Summary** of the test method
____ **5.5.4.1.2(b)(6)** **Definitions**
____ **5.5.4.1.2(b)(7)** **Interferences**
____ **5.5.4.1.2(b)(8)** **Safety**
____ **5.5.4.1.2(b)(9)** **Equipment & supplies**
____ **5.5.4.1.2(b)(10)** **Reagents & standards**
____ **5.5.4.1.2(b)(11)** Sample **collection, preservation, shipment, & storage**
____ **5.5.4.1.2(b)(12)** **Quality control**
____ **5.5.4.1.2(b)(13)** **Calibration & standardization**
____ **5.5.4.1.2(b)(14)** **Procedure**
____ **5.5.4.1.2(b)(15)** **Calculations**
____ **5.5.4.1.2(b)(16)** Method **performance**
____ **5.5.4.1.2(b)(17)** Pollution **prevention**
____ **5.5.4.1.2(b)(18)** **Data assessment & acceptance criteria** for quality control measures
____ **5.5.4.1.2(b)(19)** **Corrective actions** for out-of-control data
____ **5.5.4.1.2(b)(20)** Contingencies for **handling out-of-control or unacceptable data**
____ **5.5.4.1.2(b)(21)** **Waste management**
____ **5.5.4.1.2(b)(22)** **References**
____ **5.5.4.1.2(b)(23)** **Tables, diagrams, flowcharts, validation data**

____ **D** Does the laboratory ensure that the **essential standards** outlined in Appendix D are incorporated into the method manuals and/or Quality Manual

COMMENTS:

CHEMISTRY TEST METHOD EVALUATED: _____

____ **5.5.4.2.2(a) C.1** Has the laboratory performed a **satisfactory demonstration of method capability** prior to the acceptance & institution of this test method

Note: Demonstrations of capability are done in an applicable & available **clean quality system matrix sample** in a quality system matrix where **no target analytes or interferences present** at concentrations that impact the results of a specific test method

Note: These following steps are **may not be applicable** for tests with which **spiking is not an option** and for which Quality Control samples are **not readily available**

Note: Actual sample spike results, such as **4 consecutive matrix spikes** (or quality control samples of analytes that do not lend themselves to spiking), within the **last 12 months** may be used to meet this Standard

Note: A demonstration of capability is **not required** in cases where samples are analyzed with this test method in use by the laboratory **before July 1999** & where there have **been no significant changes** in instrument type, personnel, or test method, in which case the analyst's documentation of continued proficiency is acceptable (the laboratory must have records on file to show that a demonstration of capability is not required)

Note: Continuing demonstration of method performance, per the QC requirements in App. D (e.g., laboratory control samples), is required thereafter

____ **C.1** Does the laboratory **document** in its Quality Manual **other adequate approaches** to **Demonstration of Capability** if the procedure below is **not required** by the mandated test method or regulation and if the laboratory **elects not to perform** this procedure

____ **C.1(a)** Is the **quality control sample** used for this Demonstration of Capability obtained from an **outside source**

Note: If an outside source is not available, the laboratory may prepare this sample with stock standards that are **prepared independently** from those used in instrument calibration

____ **C.1(b)** Are the analytes diluted in a volume of **clean quality system matrix** sufficient to prepare **4 aliquots** at the **specified concentration** or to a concentration approximately **1-4 times** the **limit of quantitation**

____ **C.1(c)** Are **at least 4 such aliquots prepared & analyzed** according to the test method

Note: These analyses may occur either concurrently or over a period of days

____ **C.1(d)** Does the laboratory **calculate the mean recovery** in the appropriate reporting units & the **standard deviation** of the population sample (n-1) in the same units for **each parameter of interest** using **all of the analysis results obtained**

Note: When it is not possible to assess mean & standard deviation, such as **for presence-absence & logarithmic values,** the laboratory must assess performance against established & documented criteria

____ **C.1(e)** Are the mean and standard deviation for each parameter **compared** to the corresponding **acceptance criteria for precision & accuracy** in the test method (if applicable) or in laboratory-generated acceptance criteria (if the method or analyte is non-standard)

____ **C.1(e)** Does the laboratory consider the performance unacceptable & **not analyze actual samples** for parameters that **fail the acceptance criteria**

____ **C.1(f)** When one or more parameters **fail** at least one of the **acceptance criteria**, does the analyst:

- **Locate & correct** the source of the problem, then **repeat the test** for all parameters of interest, OR
- **Repeat the test** for all parameters that failed to meet criteria

Note: Repeated failure from employing the second option above indicates a general problem with the entire measurement system, and the analyst must then perform the first option above

CHEMISTRY TEST METHOD ASSESSED: _____

____ **C.1** Is an **initial evaluation** performed for **all analytes to be added** to an existing accredited test method (for analytes not currently found on the laboratory's list of accredited analytes)

____ **5.5.2.6(c)(3)** Does each Analyst have **documentation** of **continued proficiency** by at least **one of the following once per year:**

- Acceptable performance of a **blind sample** (single blind to the analyst)
- An initial measurement system evaluation or another demonstration of capability
- Successful performance of a blind performance sample on a **similar test method** using the **same technology** (acceptable limits must be determined prior to analysis)
- At least **4 consecutive** laboratory **control samples** with **acceptable levels** of precision & accuracy (the acceptable limits must be determined prior to analysis)
- Analysis of **authentic samples** that have been analyzed by **another trained analyst** with **statistically indistinguishable results**

____ **5.5.4.2.2(d)** **C.2** Does the laboratory use the **NELAC-specified certification statement** to document the **completion of each Demonstration of Capability** (initial & continuing)

____ **C.2** Are copies of these certification statements retained in the **personnel records** of each **employee performing the test method**

____ **5.5.4.2.2(d)** **C.1** Does the laboratory **retain & make available all associated supporting data** necessary to **reproduce the analytical results** summarized in the appropriate certification statement

____ **5.5.4.2.2(e)** **C.1** Does the laboratory **complete a demonstration of capability each time** there is a **change** in **instrument type, personnel, or test method**

____ **5.5.4.2.2(f)** Does the laboratory **fully document** the achievement of **demonstration of capability requirements** for each **specialized work cell**

Note: A work cell is defined as a group of analysts with specifically defined tasks that together perform the test method

____ **5.5.4.2.2(g)** Does the laboratory demonstrate & document acceptable performance through **acceptable continuing performance checks** (e.g, laboratory control samples) **each time** that **membership** in a work cell **changes**

____ **5.5.4.2.2(g)** Do the **new members** of the work cell **work with experienced analysts** in the specialty area

____ **5.5.4.2.2(g)** Does the laboratory **repeat a Demonstration of Capability** with the new work cell if the **first 4 continuing performance checks** following the change in personnel **produce a failure** in any sample batch acceptance criteria

____ **5.5.4.2.2(g)** Does the laboratory **repeat a Demonstration of Capability** if the entire **work cell is changed or replaced**

____ **5.5.4.2.2(h)** Is the **performance of the work cell** as a group **linked to the training records** of the **individual members** of the work cell

____ **5.1.1** Does the laboratory's **procedure for demonstrating its capability** to perform the method, the **analyst's capability** to perform the method, or the **acceptance criteria** for precision & accuracy **comply with the requirements specified** in the **mandated test method**

Note: See page 10 for such Demonstration of Capability procedural requirements & acceptance criteria

CHEMISTRY TEST METHOD ASSESSED: _____

____	**D**	Does the laboratory have **procedures** for developing **acceptance/rejection criteria** for each Chemistry test method (where no regulatory or method criteria exist)
____	**D**	Does the laboratory **assess & evaluate** all **quality control measures** on an **on-going basis**
____	**D**	Does the laboratory **use** quality control **acceptance criteria** to determine the **validity of the data**
____	**5.5.9.2(d)** **App. D**	Does the laboratory's **Chemistry data** indicate that the **quality control protocols** in the test methods manual **are being followed** (by all analysts)
____	**5.1.1**	Does the laboratory's **acceptance criteria** for blanks, laboratory control samples, duplicates, & matrix spikes **fulfill the requirements** in **mandated test methods** **Note:** See page 10 for acceptance criteria
____	**5.1.1**	Does the laboratory fulfill **additional requirements** specified in the **mandated test method** or **regulation** **Note:** See page 10 for the additional requirements stated in test methods
____	**D.1.1.1(a)**	Does the laboratory process the method blank along with & under the **same conditions** as the associated samples to **include all steps** in the analytical procedure
____	**D.1.1.1(a)**	Does the laboratory have procedures in place to determine if a **method blank is contaminated**
____	**D.1.1.1(b)**	Does the laboratory analyze **method blanks** at a frequency of at least **one per preparation batch or one per 20 environmental samples** analyzed together with the same method & personnel using the same lots of reagents
____	**D.1.1.1(c)**	Does the method blank consist of a quality system matrix **similar to associated samples** & known to be **free of the analytes of interest**
____	**D.1.1.1(d)**	Does the laboratory **critically evaluate** each method blank as to the nature of any **interferences & the effect** on the analyses of each **sample within the batch**
____	**D.1.1.1(d)**	Is the source of the contamination **investigated** & measures taken to **minimize or eliminate the problem**
____	**D.1.1.1(d)**	Are **all samples** associated with a **contaminated blank reprocessed** for analysis or **reported** with appropriate **data qualifying codes** **Note:** Such sample results can be reported with data qualifiers: - If the analyte concentration in the blank is **at or above the reporting limit** AND **is greater than 1/10 of the amount measured** in any sample OR - If the method blank contamination **affects the sample results** as per test method requirements or individual project data quality objectives
____	**D.1.1.1(d)**	Does the laboratory **document all corrective actions** taken with respect to a contaminated blank

CHEMISTRY TEST METHOD ASSESSED: _____

____ **D.1.1.2(b)** Does the laboratory analyze at least **one laboratory control sample** (LCS or QC Check Sample) **per preparation batch or one per 20 environmental samples** analyzed together with the same method & personnel using the same lots of reagents

Note: This Standard does not apply to analytes for which spiking solutions are not available (e.g. Total Suspended Solids, Total Dissolved Solids, Total Volatile Solids, Total Solids, pH, Color, Odor, Temperature, Dissolved Oxygen, or Turbidity)

Note: The matrix spike may be used in place of this control sample as long as the acceptance criteria are as stringent as for the laboratory control sample

Note: The LCS may consist of media containing known & verified concentrations of analytes or as a Certified Reference Material

____ **D.1.1.2(c)** Does the laboratory **include all target analytes** in the LCS spike mixture over **a 2-year period**

____ **D.1.1.2(c)** Are all analyte concentrations in the LCS **within the calibration range** of the test method

____ **D.1.1.2(c)** Are the components spiked into the LCS **as specified by the mandated test method** or other regulatory requirement or as requested by the client

Note: In the absence of such requirements, the minimum number of analytes to spike are:

- For methods with 1-10 target analytes, spike all analytes
- For methods with 11-20 analytes, spike at least 10 analytes or 80%, whichever is greater
- For methods with more than 20 target analytes, spike at least 16 analytes

Note: The analytes selected for spiking must be representative of all analytes reported & must represent the chemistries and elution patterns of the components to be reported, when some components interfere with accurate assessment (e.g., simultaneously spiking technical Chlordane, Toxaphene, & PCB's)

____ **D.1.1.2(d)** Does the laboratory **document the calculations for percent recovery** of the individual batch LCS

____ **D.1.1.2(d)** Are the individual analyte percent recoveries **compared to the acceptance criteria** published in the mandated test method or, where such criteria are not established, to client-specified acceptance criteria or to internal criteria determined at the laboratory

Note: The laboratory must **document the method used** to establish internal LCS recovery limits

____ **D.1.1.2(d)** Are **all samples** associated with an **out-of-control LCS reprocessed** for analysis or **reported** with appropriate **data qualifying codes**

____ **D.1.1.2(e)** For **large number of analytes** in the LCS, does the laboratory take corrective actions if **acceptance criteria** (3 standard deviations) **are not achieved**:

- for 2 analytes when the LCS contains 11-30 analytes
- for 3 analytes when the LCS contains 31-50 analytes
- for 4 analytes when the LCS contains 51-70 analytes
- for 5 analytes when the LCS contains 71-90 analytes
- for 6 analytes when the LCS contains over 90 analytes

____ **D.1.1.2(e)** Does the laboratory locate the source of error & take corrective action **if the same analyte** exceeds LCS control limits **repeatedly**

____ **D.1.1.2(e)** Does the laboratory have a written procedure to **monitor the application of marginal exceedance allowances** to LCS control limits to **ensure random behavior**

CHEMISTRY TEST METHOD ASSESSED: _____

____ **D.1.1.3** Does the laboratory document **procedures for determining the effect of the sample matrix** on test method performance

Note: These procedures relate to the analysis of quality system matrix specific QC samples & could be data quality indicators for a specific sample using a designated test method; these controls alone are not used to judge laboratory performance

____ **D.1.1.3** Does the laboratory have procedures in place for **tracking, managing, & handling matrix-specific QC criteria**

Note: These procedures must include spiking appropriate components at appropriate concentrations, calculating recoveries & relative percent difference, and evaluating & reporting results based on performance of the QC samples

____ **D.1.1.3.1(b)** Does the laboratory perform **matrix spikes** (MS) at a frequency **specified by the test method**

Note: This matrix spike analysis frequency is specified in pages xx-xx

Note: If the test method is not mandated, the laboratory must determine the frequency of matrix spike analysis as part of a **systematic planning process** (e.g., data quality objectives)

____ **D.1.1.3.1(c)** Are the components spiked into the MS **as specified by the mandated test method** or other regulatory requirement or as requested by the client

Note: In the absence of such requirements, the minimum number of analytes to spike are:

- For methods with 1-10 target analytes, spike all analytes
- For methods with 11-20 analytes, spike at least 10 analytes or 80%, whichever is greater
- For methods with more than 20 target analytes, spike at least 16 analytes

Note: The analytes selected for spiking should represent the chemistries & elution patterns of components to be reported (e.g., simultaneously spiking Chlordane, Toxaphene, & PCB's)

____ **D.1.1.3.1(c)** Does the laboratory **include all target analytes** in the MS spike mixture over **a 2-year period**

____ **D.1.1.3.1(d)** Does the laboratory **document the calculations for percent recovery & relative percent difference** in matrix spikes & matrix spike duplicates

____ **D.1.1.3.1(d)** Are the individual analyte percent recoveries **compared to the acceptance criteria** published in the mandated test method

____ **D.1.1.3.1(d)** If there is no established criteria, has the laboratory **determined internal criteria & documented the method** used to establish the limits

____ **D.1.1.3.1(d)** Are **all samples** associated with matrix spike results **outside established criteria** documented with corrective actions or **reported** with appropriate **data qualifying codes**

COMMENTS:

CHEMISTRY TEST METHOD EVALUATED: _____

____ **D.1.1.3.2(b)** Does the laboratory perform **matrix duplicates** at a frequency specified by the **required mandated test method**
Note: This matrix duplicate analysis frequency is specified in pages xx-xx

____ **D.1.1.3.2(c)** Are matrix duplicates performed on **replicate aliquots of actual samples**

____ **D.1.1.3.2(d)** Does the laboratory **document the calculations for relative percent difference** or other statistical treatments

____ **D.1.1.3.2(d)** Are the individual analyte duplicate precisions **compared to the acceptance criteria** published in the mandated test method

____ **D.1.1.3.2(d)** If there is no established criteria, has the laboratory **determined internal criteria & documented the method** used to establish the limits

____ **D.1.1.3.2(d)** Are **all samples** associated with duplicate precisions **outside established criteria** documented with corrective actions or **reported** with appropriate **data qualifying codes**

____ **D.1.1.3.3(b)** Does the laboratory add **surrogate compounds** to all **samples, standards, & blanks** for all **appropriate test methods**
Note: This Standard does not apply if the sample matrix precludes the use of surrogates or when a surrogate is not commercially available

____ **D.1.1.3.3(c)** Do the surrogates **represent the various chemistries** of the method's target analytes & deliberately chosen for **being unlikely to occur** as an environmental contaminant

____ **D.1.1.3.3(d)** Are the surrogate recoveries **compared to the acceptance criteria** in the mandated test method

____ **D.1.1.3.3(d)** Does the laboratory evaluate surrogate recoveries outside acceptance limits for **the effect indicated** for the individual sample results

____ **D.1.5(a)** Has the laboratory **evaluated selectivity** by following the checks established within the method
Note: These evaluations may include mass spectral tuning, second-column confirmation, chromatography retention time windows, ICP inter-element interference checks, sample blanks, spectrochemical absorption or fluorescence profiles, co-precipitation evaluations, & electrode response factors.

____ **D.1.5(b)** Does the laboratory perform confirmations to **verify compound identification** when positive results are detected on a **sample from a location** that has **not been previously tested** by the laboratory
Note: These confirmations are performed on pesticides, herbicides, acid extractables, or other organic tests, or when recommended by the analytical test method
Note: Confirmation is not required when the analysis involves the use of a mass spectrometer
Note: Confirmation is required unless stipulated in writing by the client

____ **D.1.5(b)** Does the laboratory **document all confirmations** of compound identity

____ **D.1.5(c)** If a mass spectrometer is used, has the laboratory documented **acceptance criteria for mass spectral tuning**

CHEMISTRY TEST METHOD EVALUATED: _____

____ **D.1.2** Does the laboratory **document all procedures & retain all supporting data** in determining & verifying limits of detection & limits of quantitation

____ **D.1.2.1** Does this test method **provide limits of detection (LOD's)** that are **appropriate & relevant** for the intended use of the data

____ **D.1.2.1** Has the laboratory **determined the limit(s) of detection** by the **protocol** in the mandated **test method** or applicable **regulation**

Note: If the protocol for determining LOD's is not specified, the laboratory must **still determine the LOD's** but according to a procedure that **reflects instrument limitations & intended application** of the test method

Note: In the absence of regulatory or client requirements, an LOD **is not required** when test results are **not reported outside of the calibration range**

____ **D.1.2.1(a)** Has the laboratory **initially determined the detection limits** for the **compounds of interest** in this test method **in a quality system matrix** in which there are **no target analytes or interferences** at a concentration that would impact the results

Note: If this is not possible, the laboratory must determine these detection limits **in the quality system matrix of interest**

____ **D.1.2.1(b)** Does the laboratory determine LOD's **each time** there is a **change** in the test method that **affects how the test is performed** or when a **change in instrumentation** occurs that **affects the sensitivity of the analysis**

____ **D.1.2.1(c)** Does the laboratory have **established procedures** to relate **LOD's with Limits of Quantitation (LOQ's)**

____ **D.1.2.1(d)** Has the laboratory **verified the LOD annually** for each quality system matrix, test method, & analyte

Note: All sample processing steps of the analytical method must be included in the determination of the LOD

Note: Validity of the LOD is confirmed by **qualitative identification** of the analyte(s) in a quality control sample in each quality system matrix containing the analyte at **no more than 2-3x** the LOD for single-analyte tests and **1-4x** the LOD for multiple analyte tests

Note: LOD verification must be performed **on every instrument that is to be used** for analysis of samples & reporting of data

Note: A LOD study is not required for any component for which spiking solutions or quality control samples are not available (e.g., Temperature), or when test results are **not to be reported to the LOD** (versus the Limit of Quantitation or working range of instrument calibration according to Appendices D.1.2, D.4.5, D.5.4, and D.6.6 to NELAC Chapter 5).

CHEMISTRY TEST METHOD EVALUATED: _____

____ **D.1.2.2(a)** Are **all established LOQ's above** the LOD's for each analyte

____ **D.1.2.2(b)** Has the laboratory **verified the LOQ annually** for each quality system matrix, test method, & analyte

Note: The LOQ study is not required for any component or property for which spiking solutions or quality control samples are not commercially available or otherwise inappropriate (e.g., pH).

Note: The **validity of the LOQ** is confirmed by **successful analysis** of a quality control sample, containing the analytes of concern in each quality system matrix at **1-2 times** the claimed LOQ

Note: A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy.

Note: This single analysis is not required if the **bias & precision** of the measurement system are e**valuated at the LOQ**

Note: The LOQ verification is not required is not required if the LOD is re-evaluated or verified

____ **5.1.1** Do the laboratory's limits of detection **fulfill the requirements** of **mandated test methods** or **regulations**

Note: US EPA's Safe Drinking Water Act (SDWA) & Clean Water Act (CWA) regulations require determination of Method Detection Limits according to the procedures & criteria in 40 CFR Part 136, Appendix B

Note: See page 10 for SDWA Maximum Contaminant Levels & RCRA Toxicity Characteristics, which the LOD, LOQ, or the lowest-concentration calibration standard must be reliably & consistently below

Note: Other regulations (including state regulations) & permits may contain additional requirements for **Reporting Limits, Minimum Levels, Lower Limits of Detection,** & other criteria

COMMENTS: List analytes for which the above requirements for measurement sensitivity have not been fulfilled

GRAVIMETRIC (PRECIPITATION) METHODS

REQUIRED REAGANTS & STANDARDS

Magnesium – SM3500Mg D (<=19th ed.); ASTM D511-77A

Diammonium Hydrogen Phosphate precipitating reagent (as MgNH4PO4, ignited to Mg2P2O7)

Oil & Grease – EPA 413.1, 9070, 9071; SM5520B, SM5520D, SM5520E, SM5520F

Trichlorotrifluoroethane Extraction Solvent (1,1,2-Trichloro-1,2,2-trifluoroethane)
Sodium Sulfate drying agent
Corn Oil, or Isooctane/Hexadecane/Benzene mixture, as Oil & Grease standard
EPA 413.1, 9070, SM5520B, SM5520F: Separatory funnel extraction
EPA 9071, SM5520D, SM5520E: Soxhlet extraction
SM5520E: Magnesium Sulfate Monohydrate, to dehydrate sludge
SM5520F: Silica Gel cleanup sorbent, to quantitate Oil & Grease as "Hydrocarbons"

Oil & Grease; Total Petroleum Hydrocarbons – EPA 1664

n-Hexane extraction solvent
Sodium Sulfate drying agent
Silica Gel, to remove aromatics & polars & vegetative matter (to determine Total Petroleum Hydrocarbons)
Stearic Acid & Hexadecane standard
2-mg and 1000-mg Class S weights to calibrate analytical balance

Potassium – SM317B (14th ed.)

Cobaltinitrite precipitating reagent (potassium precipitates as NaK2Co(NO2)6)
Potassium Dichromate oxidizing agent (excess measured at 425 nm)

Total Residue (TS) – EPA 160.3; SM2540B; USGS I-3750-85
Filterable Residue (TDS) – EPA 160.1; SM2540C; USGS I-1750-85
Nonfilterable Residue (TSS) – EPA 160.2; SM2540D; USGS I-3765-85

Volatile Residue – EPA 160.4; SM2540E; USGS I-3753-85

Glass fiber filter, ignition of volatile matter at 500-600 degrees Celsius

Settleable Residue – EPA 160.5; SM2540F

Volumetric (Imhoff Cone) or gravimetric method

Total, Fixed, & Volatile Solids – SM2540G

Ignition of voltatile residue from sludge 450-550 degrees Celsius

Silica as SiO2 – SM4500Si C (<=19th ed.)

Perchloric Acid or Hydrochloric Acid as dehydrating agents, sample evaporated to dryness
Hydrofluoric & Sulfuric Acids, to volatilize SiO2 as SiF4
Platinum crucibles, to hold SiO2 residue when dried at 110 C and ignited at 1200 C

Sulfate – EPA 375.3; SM4500SO4= C, SM4500SO4= D; AOAC 925.54

Barium Chloride precipitating agent (digest at 80-90 C for 2 hours)
Precipitate dried in 105 C oven (EPA 375.3; SM4500SO4= D)
Precipitate ignited at 800 C for 1 hour (SM4500SO4= C)