ELECTROCHEMICAL METHODS
POTENTIOMETRY – ION SPECIFIC ELECTRODES; CONDUCTIMETRY;
AMPEROMETRY – POLAROGRAPHY, ANODIC STRIPPING VOLTAMETRY

CHEMISTRY TEST METHODS

Note: Make enough copies of **Pages 1-12** 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)** **Data Analysis & 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: _____

____ **5.5.5.2.2** Do the laboratory's initial & continuing instrument calibration verifications meet the requirements in **mandated test methods & regulations** (see page 17 for acceptance criteria and the number of standards required)
Note: If it is not apparent which standard is more stringent, then the requirements of the regulation or the mandated test method are to be followed

____ **5.5.5.2.2.1(a)** Does the laboratory's **test method SOP** include or reference details of the **initial instrument calibration procedures**
Note: This includes calculations, integrations, & associated statistics
Note: If the test method is referenced for initial instrument calibration procedures, the laboratory must **have this method & make it available** for review

____ **5.5.5.2.2.1(b)** Does the laboratory retain **sufficient raw data records to permit reconstruction** of the initial instrument calibration
Note: Examples of such data records include calibration date, test method, instrument, analysis date, each analyte name, analyst initials or signature, concentration & response, calibration curve or response factor, and unique equation or coefficient used to reduce instrument responses to concentration

____ **5.5.5.2.2.1(c)** Does the laboratory **quantitate sample results** only from the **initial instrument calibration** and not from any continuing instrument calibration verifications, unless required by regulation, method, or program

____ **5.5.5.2.2.1(d)** Does the laboratory **verify all initial instrument calibrations** with a standard obtained from a **second manufacturer or lot** if the lot can be demonstrated from the manufacturer as prepared independently from other lots
Note: When commercially available, traceability shall be to a national standard

____ **5.5.5.2.2.1(e)** Has the laboratory established **criteria for the acceptance** of an initial instrument calibration
Note: Examples include linear regression correlation coefficient & response factor %RSD
Note: The acceptance criteria must be **appropriate** to the calibration technique employed

____ **5.5.5.2.2.1(f)** For purposes of establishing the **working calibration range**, is the lowest calibration standard concentration the **lower limit of quantitation**

____ **5.5.5.2.2.1(f)** Is all data reported **below the lower limit of quantitation** reported using **defined qualifiers** or flags or **explained in the case narrative**

____ **5.5.5.2.2.1(g)** Is the highest calibration standard the **highest concentration** for which **quantitative data are to be reported**

____ **5.5.5.2.2.1(g)** Is all data reported **above the highest calibration standard** reported using **defined qualifiers** or flags or **explained in the case narrative**

____ **5.5.5.2.2.1(h)** Does the laboratory report measured concentrations **outside the working calibration range** as having **less certainty** & using **defined qualifiers or flags or explained in the case narrative**

____ **5.5.5.2.2.1(h)** Is the **lowest calibration standard above the limit of detection** for each analyte

CHEMISTRY TEST METHOD EVALUATED: _____

Note: For instrument technologies (e.g., ICP, ICP/MS) with validated techniques from manufacturers or methods employing standardization with a zero point & a single-point calibration std., the following must occur:

____ **5.5.5.2.2.1(h)(1)** Prior to the analysis of samples, are the **zero point & single point calibration analyzed**, and the **linear range of the instrument established** by analyzing a series of standards, one of which must be at the lowest quantitation level
Note: Sample results within the established linear range will not require data qualifier flags

____ **5.5.5.2.2.1(h)(2)** Are the zero point & single point calibration standard analyzed **with each analytical batch**

____ **5.5.5.2.2.1(h)(3)** Is a standard corresponding to the **limit of quantitation** analyzed with each analytical batch & meet established acceptance criteria

____ **5.5.5.2.2.1(h)(4)** Is the **linearity verified** at a frequency established by the test method and/or the manufacturer

____ **5.5.5.2.2.1(i)** Does the laboratory **perform corrective actions** & reanalyze all associated samples if the initial instrument calibration results are **outside established acceptance criteria**

____ **5.5.5.2.2.1(i)** When reanalysis is not possible, does the laboratory **report sample data** associated with unacceptable initial instrument calibrations **with appropriate data qualifiers**
Note: NELAC Standards 5.5.5.2.2.1(h) & (i) may need to be assessed **in conjunction with** the Quality Systems **data audit**

____ **5.5.5.2.2.1(j)** Does the laboratory have a standard operating procedure for **determining the number of points** for establishing the initial instrument calibration

____ **5.5.5.2.2.1(j)** Does the laboratory use a **minimum of two calibration standards** (not including blanks or a zero standard) for performing an initial instrument calibration
Note: This Standard applies if a reference or mandated method does not specify the number of calibration standards
Note: One of the standards must be at the limit of quantitation
Note: This Standard does not apply to instrument technologies for which it has been established by methodologies & procedures that a zero & a single point standard are appropriate for calibrations (see Section 5.5.5.2.2.1(h))

COMMENTS:

____ **5.5.5.10** Does the laboratory **verify** the validity of the initial calibration by a **continuing instrument calibration verification** with **each analytical batch, prior to sample analyses,** whenever an initial instrument calibration is not performed on the day of analysis

____ **5.5.5.10(a)** Are the **details** of the continuing instrument calibration verification **procedure, calculations, & associated statistics** included or referenced in the **test method SOP**

____ **5.5.5.10(b)** Is calibration verified **for each compound, element, or other discrete chemical species**
Note: For multi-component analytes such as Aroclors, Total Petroleum Hydrocarbons, or Toxaphene, a representative chemical related substance or mixture can be used

CHEMISTRY TEST METHOD EVALUATED: _____

____ **5.5.5.10(c)(1)** Is the instrument calibration verification performed at the **beginning & end** of **each analytical batch**

Note: Only **one** verification needs to be performed at the beginning of the analytical batch if an **internal standard** is used

____ **5.5.5.10(c)(2)** Is the instrument calibration verification performed whenever **it is expected** that the analytical system **may be out of calibration** or might not meet the verification acceptance criteria

____ **5.5.5.10(c)(3)** Is the instrument calibration verification performed if the **time period** for calibration or the most previous calibration verification **has expired**

____ **5.5.5.10(c)(4)** Is the instrument calibration verification performed for analytical systems that **contain a calibration verification requirement**

____ **5.5.5.10(d)** Does the laboratory retain **sufficient raw data records** to permit **reconstruction** of the continuing instrument calibration verification

Note: Such records include test method, instrument, analysis date, name of each analyte, concentration & response, calibration curve or response factor, or unique equations or coefficients used to convert instrument responses into concentrations

____ **5.5.5.10(d)** Does the laboratory's continuing calibration verification records **explicitly connect** the continuing verification data to the initial instrument calibration

____ **5.5.5.10(e)** Has the laboratory established **criteria for the acceptance** of a continuing instrument calibration verification (e.g. relative percent difference)

____ **5.5.5.10(e)** Does the laboratory **perform corrective actions** if the continuing instrument calibration verification results are **outside established acceptance criteria**

____ **5.5.5.10(e)** Does the laboratory perform a **new initial instrument calibration** if the routine corrective action procedures **fail to produce** a **second consecutive** (immediate) calibration **verification within acceptance criteria**

Note: Alternatively, the laboratory can demonstrate acceptable performance after correction with **2 consecutive calibration verifications**

____ **5.5.5.10(e)** If the laboratory has not verified calibration, do sample analyses **not occur** until the analytical system **is calibrated or calibration verified**

Note: For sample data associated with an **unacceptable** calibration **verification**, the results **must be flagged** but the data may be useable under the following special conditions:

- **Non-detects** for analytes in associated samples where the acceptance criteria for the continuing calibration verifications are **exceeded high**
- Any test result for an analyte that indicates **exceedence of a maximum regulatory limit** or decision level, when the acceptance criteria for the continuing calibration verification for that analyte is **exceeded low**

Any samples with test results that do not meet either of the above criteria **must be re-analyzed after** a new initial instrument calibration has been established, evaluated, & accepted

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 17 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 17 for acceptance criteria
____	**5.1.1**	Does the laboratory fulfill **additional requirements** specified in the **mandated test method** or **regulation** **Note:** See page 18 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 18 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

ELECTROCHEMICAL METHODS
POTENTIOMETRY – ION SPECIFIC ELECTRODES; CONDUCTIMETRY; AMPEROMETRY – POLAROGRAPHY, ANODIC STRIPPING VOLTAMETRY

REQUIRED REAGANTS & STANDARDS

Ammonia Distillation – SM4500NH3 B (required unless comparability data for representative effluents proves otherwise)
- Sodium Hydroxide distillation reagent
- Indicating Boric Acid receiver solution

Ammonia – EPA 350.2, 350.3; SM4500NH3 D, SM4500NH3 E (both >=19th ed.); ASTM D1426-98B; SM4500NH3 F, SM4500NH3 G (both <=18th ed.)
- Ammonia membrane electrode & filling solution
- Sodium Hydroxide to adjust pH above 11 (immerse electrode in solution FIRST)
- **SM4500NH3 G (<=18th ed.) & SM4500NH3 E (>=19th ed.)**: standard additions methods for NH3

Ammonia – Technicon 378-75WE
- Autoanalyzer with Ammonia sensitive electrode detector

Arsenic – EPA 7063
- Gold metal film deposited on glassy carbon electrode (+145 mv applied potential vs. SCE)
- Saturated Calomel reference electrode (SCE)
- Hydrochloric Acid, to acidify sample (2 M)

Biochemical Oxygen Demand – EPA 405.1; SM5210B; USGS I-1578-78; AOAC 973.44; ANSI Photo. Effluents
- Oxygen Membrane Electrode
- Glucose-Glutamic Acid standard
- Sulfuric Acid or Sodium Hydroxide to adjust sample pH to 6.5-7.5 (if sample pH not 6.0-8.5 prior to testing)
- Sodium Sulfite (prepared fresh daily) to remove residual Cl2 if present (starch-iodine titrimetric endpoint)
- Phosphate Buffer, Calcium Chloride, Ferric Chloride, & Magnesium Sulfate for dilution water
- Seed (if chlorinated effluents are analyzed)

Carbonaceous Biochemical Oxygen Demand – SM5210B
- Same reagents as for BOD above, plus:
- Nitrification Inhibitor, added to all samples & quality control items (2-Chloro-6-(trichloromethyl)pyridine)

Bromide – EPA 9211
- Bromide Specific Electrode
- Sulfuric Acid, to raise sample pH to 4 (eliminate cyanide, sulfide, ammonia interferences)
- EDTA, to remove interferences from multivalent metal ions
- Phosphoric Acid, to remove Fe interference
- Sodium Nitrate, ionic strength adjustment reagent

Cadmium – ASTM D3557-95C; SM3130B
- Hanging drop Hg electrode & Calomel ref. electrode (-0.8 v to deposit Cd onto Hg, re-oxidized at –0.6 v)
- Nitric Acid digestion solution
- Ammonium Citrate buffer, to adjust sample pH to 3.0
- Hydroxylamine, to reduce interfering Fe(III) to Fe(II)

Chloride – EPA 9212
- Chloride Specific Electrode
- EDTA, to remove interferences from polyvalent cations
- Sulfuric Acid, to adjust sample pH to 4 (eliminate sulfide, cyanide, ammonia interferences)
- Potassium Bromate, to remove interferences from bromide & iodide
- Sodium Nitrate, ionic strength adjustment reagent

Chlorine – SM4500CL I

Platinum & Iodide Selective Electrodes
Potassium Iodate standard
Potassium Iodide, to release iodine upon reaction with chlorine
Acetate Buffer to adjust sample pH to 4-5

Chlorine – Orion 97-70 instruction manual

Chlorine membrane electrode

Chromium(VI) – EPA 7198

Dropping Hg electrode & Ag/AgCl reference electrode (Cr(VI) reduces to Cr(III) at -0.250 v)
Ammonia Buffer, as supporting electrolyte (also reduces Cu(II) interference)

Cyanide Distillation – EPA 335.4, 9010; SM4500CN- C

Sulfuric Acid, added to liberate HCN
Sodium Hydroxide, scrubber solution to trap HCN
Magnesium Chloride Hexahydrate, catalyst for the distillation
Lead Carbonate, added to scrubber solution to precipitate sulfides
Sulfamic Acid, added to distillation solution to eliminate nitrate & nitrite interferences
Bismuth Nitrate, added to distillation solution to precipitate sulfides
Sodium Arsenite, to remove chlorine & other oxidizing agents (that decompose cyanides)

Total Cyanide – EPA 9213; SM4500CN- F

Cyanide Specific Electrode with Potassium Nitrate filling solution
Lead Carbonate, to remove sulfide interference
Sodium Hydroxide, ionic strength adjustment reagent

Total Cyanide – OIA 1677

Autoanalyzer with Cyanide Specific Electrode
Gas-diffusion membrane into proprietary receiver solution

Cyanide Amenable to Chlorination – EPA 335.1, 9010, 9012; SM4500CN- G; ASTM D2036-98B

Calcium Hypochlorite, to generate excess chlorine
Sodium Arsenite or Ascorbic Acid, to remove excess chlorine after the 1-hour reaction time
Same reagents for Cyanide Distillation & for Total Cyanide

Fluoride Distillation – SM4500F- B (required unless comparability data for rep. effluents shows otherwise)

Sulfuric Acid, to liberate HF & Fluosilicic Acid
Soft Glass boiling beads, to convert HF to Fluosilicic Acid
Silver Sulfate, to eliminate chloride interference if necessary

Fluoride – EPA 340.2, 9214; SM4500F- C; ASTM D1179-93B; USGS I-4327-85 & Technicon 380-75WE (automated)

Fluoride Specific Electrode
Ionic Strength Adjustment Buffer (Acetic Acid, Sodium Chloride, Cyclohexylenediaminetetraacetic Acid)

pH – EPA 150.1, 9040, 9045; SM4500H+ B; ASTM D1293-95A, D1293-95B; USGS I-1586-85; AOAC 973.41

pH Glass Electrode
pH Standard Buffers
SW-846: Use EPA 9040 if Aqueous Phase > 20% of sample; otherwise, must use EPA 9045

pH – EPA 150.2; Technicon 378-75WA

pH Glass Electrode
Autoanalyzer or continuous readout flow cell
pH Standard Buffers

Kjeldahl Nitrogen Digestion – EPA 351.2; SM4500Norg B, SM4500Norg C; ASTM D3590-89B; USGS I-4515-91

Digestion reagent (Sulfuric Acid; Potassium Sulfate; Mercuric Sulfate, Copper Sulfate, or Selenium)

Kjeldahl Nitrogen – EPA 351.3; SM4500NH3 D, SM4500NH3 E (both >=19th ed.);
SM4500NH3 F, SM4500NH3 G (<= 18th ed.)

Sodium Hydroxide distillation reagent
Indicating Boric Acid receiver solution
Ammonia membrane electrode & filling solution
Sodium Hydroxide to adjust pH above 11 (immerse electrode in solution FIRST)
SM4500NH3 G (<=18th ed.) & SM4500NH3 E (>=19th ed.): standard additions methods for NH3

Kjeldahl Nitrogen – EPA 351.4; ASTM D3590-89A

Ammonia membrane electrode & filling solution
Sodium Hydroxide, EDTA, & Sodium Iodide to adjust pH above 11 (immerse electrode in solution FIRST)

Lead – ASTM D3559-95C; SM3130B

Hanging drop Hg electrode & Calomel ref. electrode (-0.8 v to deposit Pb onto Hg, re-oxidized at –0.45 v)
Nitric Acid digestion solution
Ammonium Citrate buffer, to adjust sample pH to 3.0
Hydroxylamine, to reduce interfering Fe(III) to Fe(II)

Mercury – EPA 7472

Gold metal film deposited on glassy carbon electrode (+500 mv applied potential vs. SCE)
Saturated Calomel reference electrode (SCE)
Hydrochloric Acid or Sodium Chloride, to adjust all samples & stds. to 0.1 M chloride

Nitrate – EPA 9210; SM4500NO3- D; Orion 601

Nitrate Specific Electrode with Ammonium Sulfate filling solution
Buffer Solution (Aluminum Sulfate, Silver Sulfate, Boric Acid, Sulfamic Acid, Sodium Hydroxide to pH 3)

Dissolved Oxygen – EPA 360.1; SM4500O G; ASTM D888-92B; USGS I-1576-78

Specific Oxygen Uptake Rate – SM2710B

Oxygen Membrane Electrode

Potassium – SM3500K E (<=19th ed.), SM3500K C (20th ed.)

Potassium Ion Specific Electrode
Sodium Chloride ionic strength adjustment solution & reference electrode filling solution

Salinity – SM2520B

Synthetic Seawater samples of known Salinity, to calibrate Conductivity Meter

Specific Conductance – EPA 120.1, 9050; SM2510B; ASTM D1125-95A; USGS I-1780-85; AOAC 973.40

Sodium Chloride or Potassium Chloride standards (Wheatstone Bridge with platinum electrodes)

Sulfide Distillation – EPA 9030

Sulfuric Acid for Acid-soluble Sulfides (EPA 9030)
Zinc Acetate & Formaldehyde gas washing solutions
Tin(II) Chloride & Hydrochloric Acid for Acid-insoluble Sulfides (EPA 9031)

Sulfide – EPA 9215

Sulfide Specific Electrode
Silver Nitrate & Sodium Chloride, to standardize Sulfide standards
Anti-oxidant Buffer (Sodium Salicylate & Ascorbic Acid)

HOLDING TIME, SAMPLE CONTAINER, & SAMPLE PRESERVATION REQUIREMENTS

Analyze Immediately in the field or upon arrival at the laboratory, plastic or glass containers
Total Residual Chlorine, pH (CWA & SDWA)

Analyze Immediately in field or upon arrival at the laboratory, glass bottle & top
Dissolved Oxygen (electrode method), Salinity (6-mo hold if wax seal is used)

8-Hour Holding Time, glass bottle & top, fix on-site & store in the dark
Dissolved Oxygen (Winkler Titration)

24-Hour Holding Time, plastic or glass containers, 4 C
Chromium(VI), pH (RCRA)

48-Hour Holding Time, plastic or glass containers, 4 C, unpreserved
Biochemical Oxygen Demand, Carbonaceous Biochemical Oxygen Demand, Nitrate

7-Day Holding Time, plastic or glass container, 4 C, Zinc Acetate & NaOH to pH>9
Sulfide (analyze immediately if sample unpreserved)

14-Day Holding Time, plastic or glass containers, 4 C
Nitrate (SDWA chlorinated samples)

14-Day Holding Time, plastic or glass containers, 4 C, NaOH to pH>12
Total & Amenable Cyanide (24-Hour Holding Time if Sulfide is present)
(Add $NaAsO_2$ or Ascorbic Acid if oxidizing agents present (RCRA))

28-Day Holding Time, plastic or glass containers, 4 C
Bromide, Chloride, Specific Conductance

28-Day Holding Time, plastic container (only)
Fluoride

28-Day Holding Time, plastic or glass containers, 4 C, Sulfuric Acid to pH<2
Ammonia, Total Kjeldahl Nitrogen, Organic Nitrogen

28-Day Holding Time, plastic or glass containers, 4 C, Nitric Acid to pH<2
Mercury

6-Month Holding Time, plastic or glass containers, Nitric Acid to pH<2
Metals (except Cr(VI) & Hg; add HNO_3 if sample unpreserved & let stand prior to analysis)

INITIAL INSTRUMENT CALIBRATION ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS

3 standards + blank

SM1020B, 5, applies to all SM methods unless more stringent requirements are found in individual mtds
EPA 350.2, 7.4
EPA 350.3, 7.2
EPA 351.3, 8.4
EPA 351.4, 8
D1426-93B, 21.1, to calibrate NH3 electrode
OIA1677, 10.3, CF (if used) < 10% RSD

4 standards

SM3500K E (<=19th ed.), 4

5 standards + blank

EPA 7063, 7.7
EPA 7472, 7.8

CALIBRATION VERIFICATION ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS

Recovery 90-110%

EPA 7063, 7472, 8.1 & 8.2, also **every 10 samples & end of run**
EPA 9210, 9211, 9212, 9213, 9214, 9215, 8.2-8.3, plus after **every 10 samples & end of run**, calibration blank analysis also required each time

PRECISION & ACCURACY ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS (INITIAL DEMONSTRATION OF CAPABILITY)

Average Recovery & Standard Deviation of Recovery compared to Acceptance Criteria in Table of Test Method

OIA1677, 9.2

QUALITY CONTROL ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS

Matrix Spike Recoveries within 75-125%

EPA 7063, 7472, 9210, 9211, 9212, 9213, 9214, 9215, 8.5, analyzed every 20 samples or batch

Duplicate Precisions within 20%

EPA 7063, 7472, 9210, 9211, 9212, 9213, 9214, 9215, 8.5, MSD or sample dup. analyzed every 20 samples or batch

Analyte Concentrations in Blank

EPA 9210, 8.4, < 1.0 mg/L Nitrate
EPA 9211, 8.4, < 0.3 mg/L Bromide
EPA 9212, 8.4, < 1.0 mg/L Chloride
EPA 9213, 8.4, < 0.03 mg/L Cyanide
EPA 9214, 8.4, < 0.1 mg/L Fluoride
EPA 9215, 8.4, < 0.05 mg/L Sulfide

BOD Results 198 +/- 30.5 mg/L for 300 mg/L Glucose-Glutamic Acid Solution

SM5210B, 6a, can adjust amount of seed added to blanks & samples such that corresponding GGA results will achieve criteria (NOTE: EPA allows CBOD results to be independently evaluated by the laboratory with at least 20 replicate determinations if these control limits are not within 198 +/- 30.5 mg/L; value must be above 150 mg/L & precision must be below +/- 26 mg/L)

EPA REGULATORY LEVELS REQUIRING SPECIFIC DETECTION LIMITS

SDWA MAXIMUM CONTAMINANT LEVELS

Nitrate	10.0 mg/L as N
Cyanide	0.2 mg/L
Fluoride	4.0 mg/L
Chlorine	4.0 mg/L as Cl2

RCRA TOXICITY CHARACTERISTICS

Arsenic	5.0 mg/L
Cadmium	1.0 mg/L
Lead	5.0 mg/L
Mercury	0.2 mg/L

ADDITIONAL REQUIREMENTS

Matrix Spikes, Control Standards, & Duplicates at least 15% of workload for any parameter
USGS Bk. 5, Ch. A1, p.7, applies to all USGS Metals & General Chemistry mtds.

Method of Standard Additions required to quantitate Metal analytes
EPA 7198, 8.3 (Cr(VI) by differential pulse polarography)
ASTM D3557-95C, 32 (Cd by ASV)
ASTM D3559-96C, 33 (Pb by ASV)

Matrix Spike every 10 samples, or Matrix Spike & Duplicate every 20 samples
SM1020B, 2 (applies to all SM methods unless more stringent requirements appear elsewhere)

Duplicate every 10 samples or analytical batch
SM2020 (applies to all SM2000-series methods)

Matrix Spike & Matrix Spike Duplicate every 10 samples
OIA1677, 9.3

Matrix Spike & Matrix Spike Duplicate each batch of 20 samples or fewer
EPA 7063, 7472, 8.5, may use sample dup. in place of MSD

Calibration Verification every 10 samples
OIA1677, 9.5

Calibration Verification every 15 samples
EPA 7198, 8.4, second-source std.

Calibration Verification every 3 hours
D1426-93B, 21.2.1, for NH3 by electrode

BOD & CBOD Calculation Criteria
SM5210B, 5, only sample dilutions with at least 2.0 mg/L oxygen depletion after 5 days incubation at 20 C, with at least 1.0 mg/L dissolved oxygen remaining in that dilution, used to calculate results

Duplicate Readings until successive results agree within 0.1 pH units
EPA 9040, 7.2