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: ________________________________

5.5.2.2 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

5.5.2.2.1(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

5.5.2.2.1(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

5.5.2.2.1(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

5.5.2.2.1(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

5.5.2.2.1(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

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

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

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

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

5.5.2.2.1(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

5.5.2.2.1(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 show that a demonstration of capability is not required

**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)**_ 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)**_ 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)**_ 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 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) 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:
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

Are matrix duplicates performed on **replicate aliquots of actual samples**

Does the laboratory **document the calculations for relative percent difference** or other statistical treatments

Are the individual analyte duplicate precisions **compared to the acceptance criteria** published in the mandated test method

If there is no established criteria, has the laboratory **determined internal criteria & documented the method** used to establish the limits

Are **all samples** associated with duplicate precisions **outside established criteria** documented with corrective actions or **reported** with appropriate **data qualifying codes**

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

Do the surrogates **represent the various chemistries** of the method’s target analytes & deliberately chosen for being unlikely to occur as an environmental contaminant

Are the surrogate recoveries **compared to the acceptance criteria** in the mandated test method

Does the laboratory evaluate surrogate recoveries outside acceptance limits for **the effect indicated** for the individual sample results

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.

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

Does the laboratory **document all confirmations** of compound identity

If a mass spectrometer is used, has the laboratory documented **acceptance criteria for mass spectral tuning**
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 evaluated at the LOQ.

Note: The LOQ verification 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.
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REQUIRED REAGENTS & 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 Nitrates, 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 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)
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 NaAsO2 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 HNO3 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