

## HIGH-RESOLUTION GAS CHROMATOGRAPHY HIGH-RESOLUTION MASS SPECTROMETRY (HRMS)

**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)** **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 15 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:

- \_\_\_\_\_ **5.5.4.2.2(a)** Has the laboratory performed a **satisfactory demonstration of method capability** prior to the acceptance & institution of this test method  
**C.1**
- 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 15 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 15 for acceptance criteria
- \_\_\_ **5.1.1** Does the laboratory fulfill **additional requirements** specified in the **mandated test method or regulation**  
**Note:** See page 16 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

- \_\_\_\_\_ **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**

- \_\_\_ **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 **evaluated 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 14 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

## HIGH-RESOLUTION GAS CHROMATOGRAPHY HIGH-RESOLUTION MASS SPECTROMETRY (HRMS)

### REQUIRED REAGENTS & STANDARDS

#### EPA 613 (GC-MS or HRMS)

Methylene Chloride extraction solvent  
Sodium Sulfate drying reagent  
n-Hexane exchange solvent  
TCDD Internal Standard, isotopically labeled (EPA 613)

#### EPA 613, 1613, 1668, 8280, 8290 (GC-MS)

Isotopically labeled C-13 surrogate stds. & internal std., plus Cl-37 cleanup stds.  
Perfluorokerosene, for calibrating the resolution of the MS & for use as the lock-mass  
Methylene Chloride extraction solvent  
Sodium Chloride drying agent  
Toluene solvent for Soxhlet Dean-Stark extractions of solids & nonaqueous liquids  
1:1 Methylene Chloride / Hexane for extracting tissue samples  
Nonane (EPA 1613, 1668, 8290), Tetradecane (EPA 613), or Tridecane (EPA 8280) as final exchange solvents

#### EPA 613, 1613, 8280, 8290; EPA 3610, 3611 prior to EPA 8270

Alumina Clean-up Sorbent, conditioned with Hexane  
20% Ethyl Ether in Hexane, to elute Phthalate Esters from neutral alumina  
30% then 50% Ethyl Ether in Pentane, to elute Nitrosamines from basic alumina  
20% Methylene Chloride in Hexane, to elute Di-benzo-p-dioxins & Dibenzofurans from basic alumina  
50% Methylene Chloride in Hexane, to elute Di-benzo-p-dioxins & Dibenzofurans from acidic alumina  
Hexane eluting solvent for Base-Neutral Aliphatics in petroleum waste  
Methylene Chloride eluting solvent for Base-Neutral Aromatics in petroleum waste  
Methanol eluting solvent for Base-Neutral Polars in petroleum waste

#### EPA 1613, 1668

Florisil Clean-up Sorbent, activated by heating at 130 C overnight or deactivated by soaking in H<sub>2</sub>O for 2 hr  
Hexane or Petroleum Ether conditioning solvent  
20% Ethyl Ether in Hexane, to elute Phthalate Esters from deactivated Florisil  
15% Ethyl Ether in Pentane, to elute Diphenylamine from activated Florisil (separate from Nitrosamines);  
then 5% Acetone in Ethyl Ether, to elute Nitrosamines from activated Florisil; AND/OR  
10% Acetone in Methylene Chloride, to elute Nitroaromatics & Isophorone from activated Florisil  
6% Ethyl Ether in Hexane, to elute most Organochlorine Pesticides & PCB's from activated Florisil;  
15% Ethyl Ether in Hexane, to elute Dieldrin, Endosulfan I, & Endrin from activated Florisil; then  
50% Ethyl Ether in Hexane, to elute Endosulfan II, Endosulfan SO<sub>4</sub>, Endrin Aldehyde from Florisil  
10% Acetone in Hexane, to elute all Organochlorine Pesticides & PCB's from Florisil cartridges  
Hexane, to elute PCB's, Aldrin, DDE, & Heptachlor from Florisil cartridges;  
26% Methylene Chloride in Hexane, to elute most other Organochlorine Pesticides; then  
10% Acetone in Hexane, to elute Endosulfan II, Endrin Aldehyde, DDT, & remaining Methoxychlor  
Petroleum Ether, to elute Chlorinated Aromatics from activated Florisil; then  
6% Ethyl Ether in Petroleum Ether, to elute Haloethers from activated Florisil  
50% Methylene Chloride in Hexane, to elute 2,4,6-Trichloroaniline from activated Florisil;  
5% Isopropanol in Hexane, to elute most Aniline Derivatives; then  
5% Methanol in Hexane, to elute the remaining Aniline & Dinitroanilines  
10% Ethyl Ether in Hexane, to remove impurities from activated Florisil;  
30% Ethyl Ether in Hexane, to elute Organophosphorus Pesticides from activated Florisil; then  
40% Ethyl Ether in Hexane, to elute Tris(2,3-dibromopropyl) Phosphate  
20% Methylene Chloride in Hexane, to elute Methyl Pentachlorophenate Ester from activated Florisil;  
50%/0.35%/49.65% Methylene Chloride/Acetonitrile/Hexane, to elute most derivatized Herbicides;  
then Ethyl Ether, to elute Picloram  
Pesticide Check Solution (10 organochlorine pesticides), Herbicide Check Solution (3 chlorophenoxy methyl esters), & 2,4,5-Trichlorophenol – used to test **each batch** of activated Florisil

**EPA 613, 1613, 1668, 8280, 8290**

Silica Gel Clean-up Sorbent, activated at 130 C for 16 hours, conditioned with Pentane solvent  
 40% Methylene Chloride in Pentane, to elute Polynuclear Aromatic Hydrocarbons from silica gel  
 20% Benzene in Hexane or 100% Hexane, to elute Dibenzo-p-dioxins & Dibenzofurans from silica gel  
 15% Toluene in Hexane, to elute derivatized Pentachlorophenol from silica gel;  
     40% then 70% Toluene in Hexane, to elute most Derivatized Phenols from silica gel; then  
     15% Isopropanol in Toluene, to elute the derivatized Nitrophenols  
 25% Toluene in Hexane, to elute Derivatized Phenols from silica gel cartridge  
 Hexane, to elute PCB's, Heptachlor, Aldrin, & DDE from silica gel or silica gel cartridge; then  
 Methylene Chloride, to elute remaining Organochlorine Pesticides from silica gel; or  
 50% Ethyl Ether in Hexane, to elute remaining Organochlorine Pesticides from silica gel cartridge

**EPA 613, 625, 1613, 1625, 1668, 8280, 8290; EPA 3650 prior to EPA 8270**

Sodium Hydroxide, to remove water-soluble Organic Acids & Phenols from extract into aqueous phase  
 Sulfuric Acid, to remove water-soluble Amines & Anilines from Dioxin extracts into aqueous phase  
 Sulfuric Acid, to facilitate re-extraction of Organic Acids & Phenols into organic phase

**EPA 1613, 1668; EPA 3640 prior to EPA 8270**

Gel Permeation Chromatography system with GPC Bio-Beads, UV Detector  
 GPC Calibration Solution (Corn Oil, Bis(2-ethylhexyl) Phthalate, Methoxychlor, Perylene, Sulfur)  
     (store at 4 C, replace every 6 months)  
 Methylene Chloride eluting solvent  
 Semivolatile Organics collected within the Phthalate, Methoxychlor, & Perylene elution times  
 Organochlorine Pesticides & PCB's collected within the Methoxychlor & Perylene elution times

**EPA 1613, 1668, 8280, 8290**

Activated Carbon Clean-up Sorbent  
 Conditioning Reagents (5% Toluene & 20% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Cyclohexane, & Hexane)  
 Hexane, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Cyclohexane, & 5% Toluene/20% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>, to elute impurities  
 Toluene, reverse-flow, to elute Dibenzo-p-dioxins & Dibenzofurans

**HOLDING TIME, SAMPLE CONTAINER, & SAMPLE PRESERVATION REQUIREMENTS****7 Days to Extract Sample, Analyze Extract Immediately; glass container with Teflon-lined cap; 4 C**

Dibenzo-p-dioxins & Dibenzofurans (solids, mixed-phase, & tissues for CWA)

**7 Days to Extract Sample, 40 Days to Analyze Extract; glass container with Teflon-lined cap; 4 C**

PCB's

**30 days to Extract Sample, 45 Days to Analyze Extract; glass container with Teflon-lined cap; 4 C; 0.008% Sodium Thiosulfate**

Dibenzo-p-dioxins & Dibenzofurans (RCRA aqueous-phase samples)

**1-Year Holding Time, glass container with Teflon-lined cap, 4 C, 0.008% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**

Dibenzo-p-dioxins & Dibenzofurans (aqueous-phase samples for CWA)

**1-Year Holding Time, glass container with Teflon-lined cap, frozen <-10 C**

Dibenzo-p-dioxins & Dibenzofurans (solids, mixed-phases, & tissues for CWA)

**EPA REGULATORY LEVELS REQUIRING SPECIFIC DETECTION LIMITS****SDWA MAXIMUM CONTAMINANT LEVELS**

2,3,7,8-TCDD (Dioxin)                      30 pg/L

## **INITIAL INSTRUMENT CALIBRATION ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS**

### **3 standards + blank**

EPA 613, 7.1, response factors (if used) < 10% RSD

### **5 standards + blank**

EPA 8280, 7.13.3.1-7.13.3.4, relative response factors < 15% RSD

EPA 8290, 7.7, response factors < 20% RSD relative to internal stds., internal stds. < 30% RSD relative to Surrogate stds.

EPA 1613, 10.5-10.6, relative response factor (if used) < 20% RSD relative to the isotope-labeled analog, < 35% RSD relative to sample matrix internal standard

EPA 1668, 10.4, labeled compound calibration factor (if used) < 20% RSD

EPA 680, 7.14 & 9.2.8, relative response factors < 20% RSD

## **CALIBRATION VERIFICATION ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS**

### **Recovery 70-130%**

EPA 8280, 7.13.3.6

### **Recovery 80-120%**

EPA 680, 9.3.7

EPA 8290, 7.7, plus 70-130% recovery for internal standards

### **Recovery 85-115%**

EPA 613, 7.1.3

### **Recovery within the Test Method QC Acceptance Criteria**

EPA 1613, 1668, 15.3

## **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**

EPA 613, 8.1.1

EPA 1613, 1668, 9.2

EPA 8000, 8.6, applicable to all EPA 8000-series methods

## **QUALITY CONTROL ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS**

### **QC Check Sample or Matrix Spike Recoveries within the Test Method QC Acceptance Criteria for each Analyte**

EPA 1613, 15.5

EPA 1668, 9.3

### **Duplicate Precisions within 20%**

EPA 8290, 8.3.6, precision within 25% for sample duplicate rather than Matrix Spike duplicate

### **Internal Standards Responses**

EPA 680, 9.3.6, decrease < 30% from last Calib. Verification & < 50% from last Initial Calibration

EPA 1613, 9.3, serves as Matrix Spike since labeled stds. added to each sample, acceptance criteria in Table

## ADDITIONAL REQUIREMENTS

### All samples spiked with Isotopically Labeled Compounds

EPA 1613, 1668, 9.3

### Matrix Spike & Matrix Spike Duplicate each batch of 20 samples or fewer

EPA 680, 10.7

EPA 8000, 8.5, applies to all 8000-series Organics mtds., may use sample dup. in place of MSD

### Matrix Spike & Quality Control Check Samples analyzed every 10 samples

EPA 613, 8.1.4 & 8.4

### Both Matrix Spike Duplicates & Sample Duplicates analyzed each sample batch

EPA 8290, 8.3.5-8.3.6

### Method Blank analyzed every 20 samples or each 8 or 12-hour work shift, per matrix

EPA 1613, 9.5

EPA 8280, 7.1-7.2

EPA 8290, 8.2

### GC Injector Port Degradation < 10% for Endrin & < 5% for DDT

EPA 680, 9.2.5.1 & 9.2.5.3, when Pesticides are determined

### GC Retention Time Windows established for each analyte

EPA 680, 9.2.9, within 10 sec between analyses

EPA 1613, 15.4.1, acceptance limits for each target analyte given in Table

EPA 1668, 10.1.2

EPA 8000, 7.6

### Chromatographic Resolution Checks

EPA 1613, 15.4.2, Tetra-dioxin & Tetra-furan isomers

EPA 8280, 7.12; 2,3,7,8-TCDD & 1,2,3,4-TCDD

EPA 8290, 8.2.1; 2,3,7,8-TCDD & all other TCDD's

### Mass Spectrometer Resolution > 10000

EPA 1613, 10.1.2 & EPA 8290, 8.2.2

EPA 1668, 10.2

### GPC Column Calibration Acceptance Criteria (EPA 3640) (performed weekly)

Retention time shift < 5% compared with the previous calibration

Symmetrical peaks observed for all compounds

Resolution between Corn Oil, Bis(2-ethylhexyl) Phthalate, Methoxychlor, & Perylene peaks all > 85%

Resolution between Perylene & Sulfur peaks > 90% & neither peak is saturated in response

### Criteria for Qualitative Identification of Dibenzo-p-dioxins & Dibenzofurans (EPA 1613, 1668, 8280, 8290)

GC retention times for target analytes agree match the retention times for the isotopically labeled analogs

GC retention times for target analytes in samples match the retention times in the CCV std.

GC retention times for target analytes in calibration verification std. match the retention times in the GC column performance check solution

MS ion current responses for both quantitation mass ions of target analyte reach maximum simultaneously

MS ion current responses for both quantitation mass ions of each isotopically labeled std. reach maximum simultaneously

Integrated peak areas for both quantitation mass ions meet isotope abundance ratio criteria

Signal-to-noise ratio for GC peaks exceeds 2.5 (10 for EPA 1613)

No GC peaks due to polychlorinated diphenyl ethers are observed