

TITRIMETRIC METHODS
includes Visual & Electrometric Endpoints

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

CHEMISTRY TEST METHOD EVALUATED: _____

- _____ **5.5.4.1.2(a)** Does the laboratory have an **in-house methods manual** for each accredited **analyte** or **method**
Note: This manual may consist of copies of published or referenced test methods
- _____ **5.5.4.1.2(b)** Does the laboratory **clearly indicate** in its methods manual **any modifications** made to the referenced test method and **describe any changes or clarifications** where the referenced test method is ambiguous or provides insufficient detail

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

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

COMMENTS:

- _____ **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**

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 14 for acceptance criteria
- ___ **5.1.1** Does the laboratory fulfill **additional requirements** specified in the **mandated test method or regulation**
Note: See page 14 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 13 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

TITRIMETRIC METHODS
includes Visual & Electrometric Endpoints

REQUIRED REAGENTS & STANDARDS

Acidity – EPA 305.1; SM2310B(4a); ASTM D1067-92

Sodium Hydroxide titrant
Hydrogen Peroxide digestion reagent
Phenolphthalein indicator (colorless to red) or pH meter to detect endpoint
KHP standard

Alkalinity – EPA 310.1; SM2320B; ASTM D1067-92; USGS I-1030-85; AOAC 973.43

Sulfuric Acid or Hydrochloric Acid titrant
Bromocresol Green (green to yellow) or Methyl Orange (yellow to red) indicators,
or pH meter to detect endpoint
Sodium Carbonate or Calcium Carbonate standard

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; SM4500NH3 C (>=19th ed.), SM4500NH3 E (<=18th ed.)

Sulfuric Acid titrant
Mixed Indicator (Methyl Red + Methylene Blue) (green to lavender)

Bromide – EPA 320.1; ASTM D1246-95C; USGS I-1125-85

Phenylarsine Oxide or Sodium Thiosulfate titrant
Calcium Hypochlorite, to convert Bromide+Iodide to bromate & iodate
Bromine Water, to convert Iodide to iodate (Bromide determined by difference)
Calcium Oxide, to remove Fe, Mn, organic matter interferences

Calcium – EPA 215.2; SM3500Ca D (<=19th ed.), SM3500Ca B (20th ed.); ASTM D511-93A

EDTA titrant (Disodium Ethylenediaminetetraacetic acid)
Sodium Hydroxide to adjust sample pH to 12-13 (magnesium precipitates out)
Murexide (pink to purple) or Eriochrome Blue Black R (red to blue) indicators

**Chemical Oxygen Demand – EPA 410.1, 410.2, 410.3; SM5220B, SM5220C; USGS I-3560-85, I-3562-85;
ASTM D1252-95A; AOAC 973.46; ANSI Photo. Effluents**

Digestion Reagent (Potassium Dichromate, Silver Sulfate to oxidize aliphatics, Mercuric Sulfate to precipitate halides, Sulfamic Acid to oxidize nitrites, Sulfuric Acid) (150 C for 2 hours)
KHP standard (Potassium Hydrogen Phthalate)
Ferrous Ammonium Sulfate titrant
Ferroin Indicator (blue-green to red-brown)
Open Reflux digestion system (EPA 410.2, 410.3; SM5220B; USGS I-3562-85)
Closed Reflux digestion system (EPA 410.1; SM5220C; ASTM D1252-88A; USGS I-3560-85;
AOAC 973.46; ANSI Photo Effluents)

Chloride – EPA 9253; SM4500Cl- B; ASTM D512-89B; USGS I-1183-85

Silver Nitrate titrant
Alum (Aluminum Hydroxide) to decolorize samples
Sulfuric Acid or Sodium Hydroxide to adjust sample pH to 7-10
Potassium Chromate indicator (white precipitate to yellow precipitate)

Chloride – EPA 325.3, 9252; SM4500Cl- C; ASTM D512-89A; USGS I-1184-85; AOAC 973.51

Mercuric Nitrate titrant

Mixed Indicator (Diphenylcarbazone, Nitric Acid, Xylene Cyanol FF for low-Cl- samples)
(blue-green to purple)

Mixed Indicator (Diphenylcarbazone, Bromphenol Blue for high-Cl- samples; add Nitric Acid to pH 2.5
(purple to yellow), then titrate (yellow to purple))

Chloride – SM4500Cl- D

Silver Nitrate titrant

Glass & Ag/AgCl Electrodes for potentiometric endpoint

Chlorine – EPA 330.1; SM4500CL D, SM4500CL E (low-level free chlorine); ASTM D1253-92

Phenylarsine Oxide titrant

Phosphate Buffer to adjust sample pH to 6.5-7.5

Platinum Electrode & Amperometric Detection System

Chlorine – EPA 330.2; SM4500CL C

Iodine or Potassium Iodate titrant

Phenylarsine Oxide or Sodium Thiosulfate

Potassium Iodide & Starch Indicator (colorless to blue), or amperometric detection

Chlorine – EPA 330.3; SM4500CL B

Phenylarsine Oxide or Sodium Thiosulfate titrant

Potassium Iodide reagent (iodine liberated upon reaction with chlorine)

Potassium Bi-iodate or Potassium Dichromate primary standard

Starch indicator (blue to colorless)

Chlorine – EPA 330.4; SM4500CL F

Ferrous Ammonium Sulfate titrant

DPD Indicator (N,N-Diethyl-p-phenylenediamine) (red to colorless)

Potassium Dichromate primary standard

Potassium Iodide, to convert monochloramine & dichloramine to chlorine

Glycine, to determine bromine+iodine & subtract from the total halogen result

Total Chlorine – EPA 9076

Silver Coulometric Titration Cell

Chlorobenzene standard

Total Chlorine – EPA 9077

Metallic Sodium, Naphthalene, & Diglyme (converts organic halogens to sodium halides)

Mercuric Nitrate titrant

Diphenylcarbazone indicator (yellow to violet)

Chlorine Dioxide – SM4500ClO2 D

Ferrous Ammonium Sulfate titrant

DPD Indicator

Glycine, to suppress the response due to free chlorine

Chlorine Dioxide – SM4500ClO2 E

Sodium Thiosulfate or Phenylarsine Oxide titrant

Platinum Electrode & Amperometric detection system

Potassium Iodide, to release iodine upon reaction with chlorine

Phosphate Buffer, to adjust sample to pH 7 for residual chlorine determination

Hydrochloric Acid, for chlorite determination (chlorine dioxide by difference)

Cyanide Distillation – EPA 335.4, 9010; SM4500CN- C

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

Total Cyanide – EPA 9014; SM4500CN- D; ANSI Photo. Effluents

Silver Nitrate titrant
p-Dimethylaminobenzalrhodanine Indicator (yellow to salmon)
Sodium Chloride, to standardize titrant

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

Hardness – EPA 130.2; SM2340C; ASTM D1126-86(92); USGS I-1338-85; AOAC 973.52B

EDTA titrant (Disodium salt of Ethylenediaminetetraacetic Acid)
Calcium Carbonate standard
Eriochrome Black T or Calmagite indicators (red to blue)
Sodium Cyanide, Sodium Sulfide, or CDTA inhibitors (to sharpen titration endpoints if necessary)
Ammonia Buffer to adjust sample pH to 10.0-10.1

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 C (>=19th ed.), SM4500NH3 E (<=18th ed.); ASTM D3590-89A; AOAC 973.48; PAI-DK01

Sodium Hydroxide distillation reagent
Indicating Boric Acid receiver solution
Sulfuric Acid titrant
Mixed Indicator (Methyl Red + Methylene Blue) (green to lavender)

Organic Halogens – EPA 1650, 9020, 9021, 9022, 9023; SM5320B

Granular Activated Column adsorbent for TOX (EPA 1650, 9020, 9022)
Trichlorophenol or Chloroform standards (instrument calibration, adsorption efficiency checks)
Potassium Nitrate acid wash solution
Sodium Chloride, for coulometric titration cell testing & inorganic halide std.
Ethyl Acetate extraction solvent (EPA 9023)

Dissolved Oxygen – EPA 360.2; SM4500O C; ASTM D888-92A; USGS I-1575-78; AOAC 973.45B

Manganous Sulfate
Alkali-Iodide-Azide reagent (Sodium or Potassium Hydroxide, Sodium Iodide, Sodium Azide)
Sodium Thiosulfate titrant (Winkler titration)
Starch indicator (blue to colorless)
Potassium Bi-iodate primary standard

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 376.1, 9031, 9034; SM4500S= E (<=18th ed.), SM4500S= F (>=19th ed.); USGS I-3840-85
Sodium Thiosulfate or Phenylarsine Oxide titrant
Iodine reagent & Starch indicator (blue to colorless)
Potassium Bi-iodate primary standard

Sulfite – EPA 377.1; SMSM4500SO3= B
Potassium Iodide & Potassium Iodate titrant
Starch Indicator (colorless to blue)
EDTA fixing solution
Sulfamic Acid, to eliminate nitrite interference

Waste Reactivity Distillation – Section 7.3 of the SW-846 Manual
Sulfuric Acid, to release reactive gases (30-minute test period, no heating, constant stirring)
Sodium Hydroxide, scrubber solution to collect reactive gases

HOLDING TIME, SAMPLE CONTAINER, & SAMPLE PRESERVATION REQUIREMENTS

Analyze Immediately in the field or upon arrival at the laboratory, plastic or glass containers
Total Residual Chlorine, Sulfite, Chlorine Dioxide

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

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
Acidity, Alkalinity

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

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

28-Day Holding Time, glass container (only), 4 C, Sulfuric Acid to pH<2
TOX (must have Teflon-lined cap)

6-Month Holding Time, plastic or glass containers, Nitric or Sulfuric Acid to pH<2
Hardness

EPA REGULATORY LEVELS REQUIRING SPECIFIC DETECTION LIMITS

SDWA MAXIMUM CONTAMINANT LEVELS

Cyanide	0.2 mg/L
Chlorine	4.0 mg/L as Cl ₂
Chloramine	4.0 mg/L as Cl ₂
Chlorine Dioxide	0.8 mg/L as ClO ₂

QUALITY CONTROL ACCEPTANCE CRITERIA FOR MANDATED TEST METHODS

QC Check Sample Recoveries & Matrix Spike Recoveries within 80-120%
PAI-DK01

QC Check Sample Recoveries within 85-115%
EPA 9010/9014, 8.3

External QC Check Sample Recoveries within 90-110%
PAI-DK01

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.

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 Spikes analyzed every 10 samples
EPA 9020, 8.5 & EPA 9021, 8.4
EPA 1650, 9.3

Matrix Spike & Sample Duplicate every 20 samples
EPA 9253, 8.4, or batch
EPA 9010/9014, 8.4 & 8.5

Matrix Spike & Matrix Spike Duplicate
EPA 5050, 9023, 9076, 8.3, for oxidative combustion & bomb preparations of solid waste for EOX & Cl2

Independent Quality Control Check Samples analyzed every 15 samples
EPA 9021, 8.3

Method Blank analyzed every 20 samples or each 8 or 12-hour work shift, per matrix
EPA 9021, 8.2
EPA 9253, 8.3

Spike Duplicate analyzed every 10 samples
EPA 9022, 8.6

All Samples analyzed in Duplicate
EPA 9020, 8.2 & 9021, 8.5

Calibration Verification & Method Blank analyzed every 5 samples
EPA 9020, 7.2.2-7.2.3, since Nitrate-wash blanks & CCV repeated every 10 pyrolysis determinations

Calibration Verification every 15 samples
EPA 9022, 8.5, second-source std.

Reagent Blank analyzed every 8 samples
EPA 9020, 8.3