

## VII. Classical Chemistry Analyses

### Methods Update Rule (MUR)

Many of the historical EPA methods for classical “wet chemistry” analyses are in the process of being deleted and replaced by EPA in the Method Update Rule (published March 12<sup>th</sup>, 2007; (40CFR Part 122, 136, 141, 143, 430, 455, 465). The corresponding Standard Methods (SM) replacements are defined in the table below. For additional information or guidance contact the laboratory.

### Methods Update Rule (MUR)

Deleted and Equivalent Methods for Clean Water Act (CWA)

| Parameter                        | Deleted Method          | Technique                   | Equivalent Methods            |
|----------------------------------|-------------------------|-----------------------------|-------------------------------|
| Acidity, as CaCO <sub>3</sub>    | EPA 305.1               | Titration                   | SM 2310 B 4(a) 18th           |
| Alkalinity, as CaCO <sub>3</sub> | EPA 310.1               | Titration                   | SM 2320 B 18th                |
| Ammonia (as N)                   | EPA 350.2               | Nesslerization              | SM 4500NH <sub>3</sub> C 18th |
| Ammonia (as N)                   | EPA 350.2               | Titration                   | SM 4500NH <sub>3</sub> E 18th |
| Ammonia (as N)                   | EPA 350.3               | Electrode                   | SM 4500NH <sub>3</sub> F 18th |
| Ammonia (as N)                   | EPA 350.3               | Electrode                   | SM 4500NH <sub>3</sub> G 18th |
| BOD                              | EPA 405.1               | Incubation, DO              | SM 5210 B 18th                |
| Bromide                          | EPA 320.1               | Titration                   | ASTM D124695 (C) 1999         |
| COD                              | EPA 410.1 and 4<br>10.2 | Titration                   | SM 5220 C 18th                |
| Chloride                         | EPA 325.3               | Titration, mercuric nitrate | SM 4500Cl C 18th              |
| Chloride                         | EPA 325.1 and 3<br>25.2 | Colorimetric, ferricyanide  | SM 4500Cl E 18th              |
| Chlorine, Total Residual         | EPA 330.1               | Amperometric, direct        | SM 4500Cl D 18th              |
| Chlorine, Total Residual         | EPA 330.3               | Iodometric, direct          | SM 4500Cl B 18th              |
| Chlorine, Total Residual         | EPA 330.2               | Back titration, ether       | SM 4500Cl C 18th              |
| Chlorine, Total Residual         | EPA 330.4               | DPD-FAS                     | SM 4500Cl F 18th              |
| Chlorine, Total Residual         | EPA 330.5               | Spectrophotometric, DPD     | SM 4500Cl G 18th              |
| Chromium VI, dissolved           | EPA 218.4               | Atomic absorption           | SM 3111 C 18th                |
| Color                            | EPA 110.1               | Colorimetric, ADMI          | SM 2120 E 18th                |
| Color                            | EPA 110.2               | Platinum-Cobalt             | SM 2120 B 18th                |
| Color                            | EPA 110.3               | Spectrophotometric          | SM 2120 C 18th                |
| Cyanide, Total                   | EPA 335.2               | Spectrophotometric, manual  | SM 4500CN E 18th              |
| Cyanide, Total                   | EPA 335.3               | Spectrophotometric, auto    | EPA 335.4 Rev. 1.0 (1993)     |
| Cyanide, Available               | EPA 335.1               | Amenable cyanide            | SM 4500CN G 18th              |
| Fluoride, Total                  | EPA 340.1               | Colorimetric, SPADNS        | SM 4500F D 18th               |
| Fluoride, Total                  | EPA 340.2               | Electrode                   | SM 4500F B 18th               |
| Fluoride, Total                  | EPA 340.3               | Automated complexone        | SM 4500F E 18th               |

|  |           |   |  |
|--|-----------|---|--|
| <b>Hardness, Total as CaCO<sub>3</sub></b>     | EPA 130.2 | Titration                                   | SM 2340 B or C 18th  |
| <b>Hydrogen ion (pH)</b>                       | EPA 150.1 | Electrode                                   | SM 4500H+ B 18th   |
| <b>Kjeldahl Nitrogen, Total (as N)</b>         | EPA 351.3 | Digestion/<br>Distillation                  | SM 4500-<br>Norg B or C and SM 4500-<br>NH <sub>3</sub> B 18th |
| <b>Kjeldahl Nitrogen, Total (as N)</b>         | EPA 351.3 | Titration                                   | SM 4500NH <sub>3</sub> E 18th                                  |
| <b>Kjeldahl Nitrogen, Total (as N)</b>         | EPA 351.3 | Nesslerization                              | SM 4500NH <sub>3</sub> C 18th                                  |
| <b>Kjeldahl Nitrogen, Total (as N)</b>         | EPA 351.3 | Electrode                                   | SM 4500NH <sub>3</sub> F or G 18th                             |
| <b>Kjeldahl Nitrogen, Total (as N)</b>         | EPA 351.4 | Block digestion,<br>potentiometry           | ASTM 359089 (A) 2002   |
| <b>Metals, Total</b>                           | EPA 2xx.1 | FIAA  | SM 3111 B or C 18th  |
| <b>Metals, Total</b>                           | EPA 2xx.2 | GFAA  | SM 3113 B 18th   |
| <b>NitrateNitrite (as N)</b>                   | EPA 353.3 | Cd reduction,<br>manual                     | SM 4500NO <sub>3</sub> E 18th                                  |
| <b>NitrateNitrite (as N)</b>                   | EPA 353.1 | Hydrazine<br>reduction, auto                | SM 4500NO <sub>3</sub> H 18th                                  |
| <b>Nitrite (as N)</b>                          | EPA 354.1 | Spectrophotometric<br>, manual              | SM 4500NO <sub>2</sub> B 18th                                  |
| <b>Oil and Grease, total recoverable (HEM)</b> | EPA 413.1 | Gravimetric                                 | EPA 1664 A   |
| <b>Organic Carbon, Total (TOC)</b>             | EPA 415.1 | Oxidation                                   | SM 5310 B, C or D 18th   |
| <b>Orthophosphate (as P)</b>                   | EPA 365.2 | Ascorbic acid,<br>manual, single<br>reagent | SM 4500P E 18th  |
| <b>Oxygen, dissolved</b>                       | EPA 360.2 | Winkler titration                           | SM 4500O C 18th  |
| <b>Oxygen, dissolved</b>                       | EPA 360.1 | Electrode                                   | SM 4500O G 18th  |
| <b>Phosphorous, Total</b>                      | EPA 365.2 | Digestion,<br>persulfate                    | SM 4500P B.5 18th  |
| <b>Phosphorous, Total</b>                      | EPA 365.2 | Manual                                      | SM 4500P E 18th  |
| <b>Phosphorous, Total</b>                      | EPA 365.2 | Manual                                      | EPA 365.3  |
| <b>Residue, Total (TS)</b>                     | EPA 160.3 | Gravimetric                                 | SM 2540 B 18th   |
| <b>Residue, Filterable (TDS)</b>               | EPA 160.1 | Gravimetric                                 | SM 2540 C 18th   |
| <b>Residue, Nonfilterable (TSS)</b>            | EPA 160.2 | Gravimetric                                 | SM 2540 D 18th   |
| <b>Residue, Settleable</b>                     | EPA 160.5 | Imhoff cone                                 | SM 2540 F 18th   |
| <b>Sulfate (as SO<sub>4</sub>)</b>             | EPA 375.1 | Colorimetric, auto                          | EPA 375.2 Rev. 2.0 (1993)                                      |
| <b>Sulfate (as SO<sub>4</sub>)</b>             | EPA 375.3 | Gravimetric                                 | SM 4500SO <sub>4</sub> 2 C or D 18th                           |
| <b>Sulfate (as SO<sub>4</sub>)</b>             | EPA 375.4 | Turbidimetric                               | ASTM D51690 (2002)   |
| <b>Sulfide (as S)</b>                          | EPA 376.1 | Titration, iodine                           | SM 4500S 2 E 18th  |
| <b>Sulfide (as S)</b>                          | EPA 376.2 | Colorimetric,<br>methylene blue             | SM 4500S 2 D 18th  |
| <b>Sulfite (as SO<sub>3</sub>)</b>             | EPA 377.1 | Titration,<br>iodine/iodate                 | SM 4500SO <sub>3</sub> 2 B 18th                                |
| <b>Surfactants</b>                             | EPA 425.1 | MBAS  | SM 5540 C 18th   |
| <b>Temperature</b>                             | EPA 170.1 | Thermometric                                | SM 2550 B 18th   |

## Classical Wet Chemistry Parameter Relationships

| Wet Chemistry Parameter Relationships  |   |
|--|---|
| Type   | Relationship  |
| Solids   | Total solids $\geq$ TSS   |
|  | Total solids $\geq$ TDS   |
| Nutrients  | Total phosphorus $\geq$ ortho-PO <sub>4</sub>   |
|  | Total phosphorus $\geq$ organic phosphorus  |
|  | TKN $\geq$ NH <sub>3</sub>  |
|  | TKN $\geq$ Total organic nitrogen   |
|  | NO <sub>3</sub> /NO <sub>2</sub> $\geq$ NO <sub>3</sub>   |
| Cyanide  | NO <sub>3</sub> /NO <sub>2</sub> $\geq$ NO <sub>2</sub>   |
|  | Total cyanide $\geq$ Free cyanide   |
|  | Total cyanide $\geq$ Amenable cyanide   |
| Demands  | Total cyanide $\geq$ Reactive cyanide   |
|  | COD $\geq$ 1.5 x BOD  |
| Minerals   | COD $\geq$ TOC (COD $\sim$ 2.5 x TOC)   |
|  | Total alkalinity $\geq$ carbonate alkalinity  |
|  | Total alkalinity $\geq$ bicarbonate alkalinity  |
| Others   | Total alkalinity $\geq$ hydroxide alkalinity  |
|  | Total [x] $\geq$ Dissolved [x]  |
|  | Cr $\geq$ Cr+6  |
|  | Total sulfide $\geq$ Reactive sulfide   |
|  | TDS $\div$ Conductivity $\sim$ 0.55 to 0.81   |
|  | TDS $\geq$ Total alkalinity   |
|  | TDS $\geq$ Hardness   |
|  | TDS $\geq$ Chloride   |
|  | TDS $\geq$ Sulfate  |
|  | If TDS = ND, metals should be ND  |
|  | If TOC = ND, organic results should be very low level   |
|  | If a sample flashes, BTU $\geq$ 1000  |
|  | Cation check <sup>1</sup> :<br>(Ca + Mg + Na) $\div$ Conductivity = 0.009 to 0.0124<br>• If this does not check out, check for other cations at high levels or low pH |
|  | Anion check <sup>1</sup> :<br>(Bicarbonate + carbonate + Cl + SO <sub>4</sub> ) $\div$ Conductivity = 0.009 to 0.0124   |
|  | Ion balance check <sup>1</sup> :<br>(Anions – Cations) $\div$ (Anions + Cations) < .075   |
| <sup>1</sup> Applicable to clean samples with conductivity readings between 200 – 5,000 umhos/cm. Low conductivity, high viscosity, colored samples, or high NH <sub>3</sub> content will not work for the cation, anion and ion balance checks. |   |

## Color , EPA Method 110.2/SM 2120 B

**METHOD SUMMARY:** Color is measured by visual comparison of the sample with platinum-cobalt standards. One unit of color is that produced by 1 mg/L platinum in the form of the chloroplatinate ion.

**DETECTION LEVEL:** 10 PtCo units, lower upon request.

**PRESERVATIVE:** Refrigerate at 4 °C.

**SAMPLING:** A minimum of 100 mL is required for the analysis.

**HOLDING TIME:** 48 hours.

### COMMENTS

The Platinum-Cobalt method is useful for measuring color of water derived from naturally occurring material, i.e., vegetable residues such as leaves, barks, roots, humus and peat materials. The method is not applicable to color measurement on waters containing highly colored industrial wastes.

**PREFERRED SAMPLING CONTAINER:** 500 mL plastic or glass.

## Specific Conductance , EPA Method 120.1

**METHOD SUMMARY:** The specific conductance of a sample is measured by the use of a self-contained conductivity meter. Temperature compensation is automatically performed by the meter.

**DETECTION LEVEL:** 1 mmho/cm

**SAMPLING:** A minimum of 100 mL of sample is required for analysis.

**PRESERVATIVE:** Refrigerate at 4°C.

**HOLDING TIMES:** 28 days.

**COMMENTS:**

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes, and acid rain (atmospheric deposition).

**PREFERRED SAMPLING CONTAINER:** Small plastic or glass container.

## **Total Hardness (as CaCO<sub>3</sub>), EPA Method 130.2/SM 2340 B or C**

**METHOD SUMMARY:** Calcium and magnesium ions are chelated by the addition of disodium ethylene diamine tetra acetate (Na<sub>2</sub>EDTA). The end point of the reaction is detected by means of an indicator, Eriochrome Black T indicator or Calmagite which has a red color in the presence of Ca and Mg at a pH of 10.0 +/- 0.01. This solution turns from wine red to blue at the endpoint of the titration.

**DETECTION LEVEL:** 1 mg/L for liquid samples and 3 mg/Kg for soil samples

**SAMPLING:** A minimum of 100 mL for liquids and 50 g for soil is required for analysis.

**PRESERVATIVE:** Add HNO<sub>3</sub> to a pH 2.0, refrigerate at 4°C.

**HOLDING TIMES:** 6 months with preservative.

**COMMENTS:**

This method is applicable to drinking, surface, and saline waters, as well as domestic and industrial wastes.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container.

**Threshold Odor , EPA Method 140.1  
(Consistent Series)**

**METHOD SUMMARY:** The sample of water is diluted with odor-free water until a dilution that is of the least definitely perceptible odor to each tester is found. The resulting ratio by which the sample has been diluted is called the "threshold odor number" (T.O.N.). People vary widely as to odor sensitivity, and even the same person will not be consistent in the concentrations they can detect from day to day. To minimize this variation, a panel of six individuals is used to measure the detectable odor.

**DETECTION LEVEL:** 1 T.O.N.

**PRESERVATIVE:** Refrigerate at 4 °C.

**SAMPLING:** A minimum of 500 mL is required for the analysis.

**HOLDING TIME:** 24 hours.

**COMMENTS:**

This method is applicable to the determination of threshold odor of drinking, surface, and saline waters, domestic and industrial wastes. Highly odorous samples are reduced in concentration proportionately before being tested. Thus, the method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold odor numbers in the thousands.

**PREFERRED SAMPLING CONTAINER:**A glass container with Teflon lined cap is required. Plastics are not reliable for odor samples.

## **pH , EPA Method 150.1/9040/9045/SM 4500 H+B**

**METHOD SUMMARY:** Approximately 50 mL of a liquid sample (or sample/DI slurry) is placed in a beaker and the pH is determined electrometrically using a combination electrode. Temperature effects are automatically compensated.

**DETECTION LEVEL:** N/A

### **SAMPLING:**

Samples that are not at equilibrium with the atmosphere are subject to change when exposed to the atmosphere. Therefore sample containers should be filled completely and kept sealed prior to analysis.

**PRESERVATIVE:** None required

**HOLDING TIME:** Immediate (within 15 minutes of sampling)

### **COMMENTS:**

Samples should be analyzed as soon as possible, preferably in the field at the time of sampling.

For characterization purposes, pH paper may be used as a qualitative indicator, but cannot be used in instances where true measurement is required.

Soils are prepared by creating a slurry of the sample with de-ionized water (1:1 ratio). pH of the slurry is measured while the sample is mechanically stirred.

**PREFERRED SAMPLING CONTAINER:** 8 oz glass - water or soil, minimal headspace.

## **Total Dissolved Solids , EPA Method 160.1/SM 2540 C**

**METHOD SUMMARY:** A well-mixed pre-measured aliquot of sample is filtered to remove suspended matter. The filtrate is transferred to a pre-weighed crucible. The liquid is evaporated and the remaining residue dried at 180°C until a constant crucible weight is obtained.

**DETECTION LEVEL:** 2 mg/L

**PRESERVATIVE:** Refrigerate at 4 °C.

**SAMPLING:** A minimum of 100 mL is required for the analysis.

**HOLDING TIME:** 7 days.

**COMMENTS:** This method is applicable to drinking, surface, and saline waters, as well as domestic and industrial waste.

Large floating particles are excluded prior to analysis.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container required.

**Total Suspended Solids, EPA Method 160.2/SM 2540 D  
(Gravimetric at 103°C)**

**METHOD SUMMARY:** A well mixed pre-measured aliquot of sample is passed through a pre-weighed filter to isolate suspended solids from the liquid. The filter is dried and weighed to determine the mass of suspended matter.

**DETECTION LEVEL:** 2 mg/L

**SAMPLING:** A minimum of 100 mL is required for analysis.

**PRESERVATIVE:** Refrigerate at 4 °C.

**HOLDING TIMES:** 7 days.

**COMMENTS**

This method is applicable to drinking, surface, and saline waters, as well as domestic and industrial waste.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container.

**Total Solids, EPA Method 160.3/SM 2540 B  
(Gravimetric at 103 °C)**

**METHOD SUMMARY:** A well mixed aliquot of unfiltered sample is transferred to a pre-weighed crucible and evaporated to dryness in an oven at 103 °C.

**DETECTION LEVEL:** 2 mg/L

**SAMPLING:** A minimum of 100 mL is required for analysis.

**PRESERVATIVE:** Refrigerate at 4 °C.

**HOLDING TIMES:** 7 days.

**COMMENTS:**

This method is applicable to drinking, surface, and saline waters, as well as domestic and industrial waste.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container.

**TFS & TVS, EPA Method 160.4**  
**Fixed, and Volatile Solids in Solid and Semisolid Samples**

**METHOD SUMMARY:** A well-mixed aliquot of sample is transferred to a pre-weighed crucible and evaporated to dryness at 550 °C.

**DETECTION LEVEL:** 2 mg/L

**PRESERVATIVE:** Refrigerate at 4 °C.

**SAMPLING:** A minimum of 100 mL is required for the analysis.

**HOLDING TIME:** 7 days.

**COMMENTS**

The determination of both total and volatile solids in these materials is subject to negative error due to loss of ammonium carbonate and volatile organic matter during drying. Sludge and sediment samples require a longer heating time. Observe specified ignition time and temperature to control losses of volatile inorganic salts. Weigh sample promptly for wet sample will evaporate and therefore lose weight.

**PREFERRED SAMPLING CONTAINER:** Glass with a Teflon-lined lid is required for this analysis.

## **Turbidity, EPA Method 180.1 (Nephelometric)**

**METHOD SUMMARY:** The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer. A standard suspension of Formazin, prepared under closely defined conditions, is used to calibrate the instrument.

**DETECTION LEVEL:** 0.1 NTU

**PRESERVATIVE:** Refrigerate at 4°C.

**SAMPLING:** A minimum of 100 mL is required for the analysis.

**HOLDING TIME:** 48 hours.

### **COMMENTS:**

The presence of floating debris and coarse sediments that settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner. The presence of true color, that is the color of water which is due to dissolved substances which absorb light, will cause turbidity to be low, although this effect is generally not significant with finished waters. This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). Higher values may be obtained with dilution of the sample.

**PREFERRED SAMPLING CONTAINER:** 250 mL, Plastic or glass

## Hexavalent Chromium, SM #3500 Cr-D

**METHOD SUMMARY:** Hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution. 100 mL of sample is filtered through a 0.45 micron filter, then diphenylcarbazide is added. Fifteen minutes is allowed for color development before it is read on the HACH DR2000 at 540 nm.

**DETECTION LEVEL:** 0.02 mg/L or 0.1 mg/Kg

**SAMPLING:** A minimum of 300 mL or 50 g is required for analysis.

**PRESERVATIVE:** Refrigerate at 4° C.

**HOLDING TIMES:** 24 hours.

**COMMENTS;**

This method is applicable to water, wastewater, and soils with a slight modification.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass containers

**IC, EPA Method 300.0 / SW-846 Method 9056**  
**Inorganic Anions via Ion Chromatography**

|          |                   |
|----------|-------------------|
| Bromide  | Nitrite           |
| Chloride | Fluoride          |
| Nitrate  | Ortho-Phosphate-P |
| Sulfate  |                   |

**METHOD SUMMARY:** A small volume of aqueous sample is injected into a closed liquid chromatography system. Anions are resolved from one another based on their interactions with the anion chromatography column. The anions are subsequently detected with a conductivity detector.

**DETECTION LEVEL:** 0.01-1 mg/L or 0.1-10 mg/Kg (component specific)

**SAMPLING:** Aqueous samples can be collected in 250-mL plastic or glass containers. Samples should be iced or refrigerated at 4°C from the time of collection until analysis. Soil samples should be collected in 2-4 oz glass jars.

**PRESERVATIVE:** Refrigerate at 4C from time of collection.

**HOLDING TIMES:**

- Nitrate, Nitrite, Orthophosphate : 48 hours
- Fluoride, Chloride, Bromide and Sulfate : 28 days

**PREFERRED SAMPLING CONTAINER:**

Aqueous: 250 mL plastic  
Soils: 2 oz glass jar

**Acidity, EPA Method 305.1/SM 2310 B**  
**(Titrimetric, pH 8.2)**

**METHOD SUMMARY:** The pH of the sample is determined and a measured amount of standardized acid is added to lower the pH to 4.0. Hydrogen peroxide is added, the solution is boiled for several minutes, cooled and titrated electrometrically with sodium hydroxide to a pH of 8.2.

**DETECTION LEVEL:** 2 mg/L or 6 mg/Kg

**SAMPLING:** A minimum of 100 mL or 50 g of sample is required for analysis.

**PRESERVATIVE:** Refrigerate at 4° C.

**HOLDING TIMES:** 14 days.

**COMMENTS:**

This method is applicable to surface water, sewage, and industrial wastes and with modifications, soils.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or 8 oz. glass container.

**Alkalinity, EPA Method 310.1/SM 2320 B  
(Titrimetric, pH 4.5)**

**METHOD SUMMARY:** An unaltered sample is titrated using a standardized H<sub>2</sub>SO<sub>4</sub> solution to an electrochemically determined endpoint of pH 4.5.

**DETECTION LEVEL:** 2 mg/L or 6 mg/Kg

**SAMPLING:** A minimum of 200 mL or 50 g of sample is required for analysis.

**PRESERVATIVE:** Refrigerate at 4 °C.

**HOLDING TIMES:** 14 days.

**COMMENTS:**

This method is applicable to drinking, surface, and saline waters, as well as domestic and industrial wastes, and with modifications, soils.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic container.

**Chloride, EPA Method 325.3/SM 4500 Cl-C  
(Titrimetric, Mercuric Nitrate)**

**METHOD SUMMARY:** An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone bromophenol blue indicator. The end-point of the titration is the formulation of the blue-violet complex.

**DETECTION LEVEL:** 1 mg/L or 3 mg/Kg

**SAMPLING:** A minimum of 200 mL or 50 g of sample is required for analysis.

**PRESERVATIVE:** Refrigerate at 4 °C.

**HOLDING TIMES:** 28 days.

**COMMENTS**

This method is applicable to drinking, surface, and saline waters, and domestic and industrial wastes, and with modifications, soils.

**PREFERRED SAMPLING CONTAINER:** 500 mL plastic or 8 oz amber glass container.

## Total Halides, SW-846 Method 5050/9253

**METHOD SUMMARY:** The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples. The bomb combustate solution can then be analyzed for halides (as chlorides) by SW-846 Method 9252.

**DETECTION LEVEL:** 500 mg/Kg

**SAMPLING:**

A minimum of 50 mL or 50 g of sample is required for analysis.

**PRESERVATIVE:** Refrigerate at 4° C.

**HOLDING TIMES:** Not Specified

**COMMENTS:**

If the sample is not readily combustible, other non-volatile, chlorine-free combustible diluent such as white oil may be employed. However, the combined weight of sample and non-volatile diluent shall not exceed 1 gram. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

This method is typically used as a screening tool in solids and wastes for halogenated components. However, if the constituents of concern are volatile (chlorinated solvents such as tetrachloroethene or trichlorethene) or are in an aqueous matrix, other methods of analysis should be considered. If halogenated volatiles are suspected, the methods 8021 or 8260 should be used. If the matrix is aqueous and the constituents of concern are not volatile, the SW-846 Method 9020 should be used.

This method does not discriminate between organic and inorganic halides (ex: chloride present as a salt could yield the same results as the chloride present as a combustion byproduct of PCB's!)

**PREFERRED SAMPLING CONTAINER:** 500 mL plastic or glass.

## Chlorine, Total Residual, EPA Method 330.5/SM 4500 Cl- G

**METHOD SUMMARY:** Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less. The liberated iodine reacts with N,N-diethyl-p-phenylene diamine (DPD) to produce a red colored solution. The solution is spectrophotometrically compared to a series of standards to determine the concentration present in the sample.

**DETECTION LEVEL:** 0.1 mg/L

**PRESERVATIVE:** Refrigerate at 4° C.

**SAMPLING:** A minimum of 100 mL is required for the analysis.

**HOLDING TIME:** Analyze immediately (within 15 minutes of collection).

### COMMENTS:

Any oxidizing agents, such as peroxides or some metal species may cause interferences. Turbidity and natural colors will interfere with the colorimetric analysis. Due to the holding time requirement, this procedure is typically performed as a field measurement. Care must be taken when performing to measure and properly account for the presence of interferences from the reagents used, the sample's color or turbidity, and any other coincident interferences. When positive results are obtained, it is good practice to obtain another sample, treat with a dechlorinating solution such as sodium thiosulfate, and determine the remaining residual chlorine. If positive results are still obtained after treating with sodium thiosulfate, the result as obtained is probably not residual chlorine.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass container required for this analysis.

## Cyanide, EPA Method 335.2/SM 4500 CN-E

**METHOD SUMMARY:** This method incorporates UV digestion and distillation of the sample whereby all complexes of cyanide are converted to simple cyanides. Upon acidification this forms hydrogen cyanide, which is, theoretically, converted to cyanogen chloride by reaction with chloramine-T. This in turn reacts with pyridine-barbituric acid to generate a reddish-violet colored complex that is measured colorimetrically at 570 nm.

**DETECTION LEVEL:** 10 mg/L or 100 mg/Kg.

**PRESERVATIVE:** Refrigerate at 4 °C, add NaOH to a pH > 12.

**SAMPLING:** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 14 days.

### COMMENTS:

Sulfides will distill over with cyanide and create a false negative absorbance (remove by classical distillation and treatment with cadmium nitrate to precipitate out the sulfides). Carbonate in high concentrations will affect pH of sample. Use hydrated lime to stabilize the pH > 12.0. Nitrates and nitrites at a concentration of 100 mg/L or higher may interfere. The manual method for cyanides (EPA 335.2) may be used as an alternate test method, depending on sample matrix and in-house sample load.

**PREFERRED SAMPLING CONTAINER:** Amber glass container is preferred for this analysis.

**Fluoride, EPA Method 340.2/SM 4500 F-B  
(Ion Selective Electrode)**

**METHOD SUMMARY:**

A fluoride electrode used with a standard reference electrode measures the ion activity in a solution. This activity is dependent upon the solution's ionic strength and pH on fluoride-complexing species. Adding an appropriate buffer (TISAB - Total Ionic Strength Adjusting Buffer) provides a uniform ionic background strength, adjusts pH and breaks up complexes so that the electrode measures concentration.

**DETECTION LEVEL:** 1 mg/L or 3 mg/Kg

**SAMPLING:** A minimum of 300 mL or 50 g of sample is required for analysis.

**PRESERVATIVE:** None required

**HOLDING TIMES;** 28 days.

**COMMENTS;**

This method is applicable to drinking waters. With distillation, wastes and wastewaters can be analyzed. Soil can be analyzed utilizing a leachate extraction.

**PREFERRED SAMPLING CONTAINER:** 500 mL plastic container.

## Nitrogen

### An Overview of the Nitrogen Series

- Introduction:** In waters and waste waters, the forms of Nitrogen of greatest interest are, in order of decreasing oxidation states, Nitrate ( $\text{NO}_3\text{-N}$ ), Nitrite ( $\text{NO}_2\text{-N}$ ), Ammonia ( $\text{NH}_3\text{-N}$ ) and Organic Nitrogen (Organic N). All of these forms of nitrogen are biochemically interconvertible and are components of the *nitrogen cycle*.
- Nitrate/Nitrite:** Total oxidized nitrogen is the sum of [ $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ ] which is referred to as the  $\text{NO}_x$  value
- Nitrate ( $\text{NO}_3$ ):** Nitrate generally occurs in trace quantities in surface water but may achieve high levels in some ground waters. Nitrate is found only in small amounts in fresh domestic waste water but in the effluent of nitrifying biological treatment plants, nitrate concentrations up to 30 parts per million as  $\text{NO}_3\text{-N}$  may be found. Nitrate is an essential nutrient for many photosynthetic autotrophs (organisms that don't require nutrients supplied from external sources; for example, photosynthetic algae) and in some cases has been identified as the growth-limiting nutrient. This is best exemplified by the frequent occurrences of algal blooms in nitrate-rich lakes in many nitrate-limited watersheds. Agricultural run-off (nitrate-rich fertilizers) makes up the vast majority of the non-naturally occurring nitrates introduced into such areas. A limit of 10 parts per million as  $\text{NO}_3\text{-N}$  has been imposed on drinking waters.
- Nitrite ( $\text{NO}_2$ ):** Nitrite, an intermediate oxidation state of nitrogen, can form from the reduction of ( $\text{NO}_3\text{-N}$ ) nitrate and oxidation of ( $\text{NH}_3\text{-N}$ ) ammonia. Such reduction and oxidation may occur in wastewater treatment plants, water distribution systems, and natural waters. Nitrite can enter a water supply system through its use as a corrosion inhibitor in industrial processed waters. It should also be noted that nitrites form nitrous acids and the resulting complexes form nitrosamines, many of which are known carcinogens. Nitrosamines are also found in hot dogs and processed lunch meats (yumm!!)
- Ammonia ( $\text{NH}_3$ ):** Ammonia is present naturally in surface and wastewaters. Its concentration in ground water is generally low because it adheres to soil particles and clays and is not leached readily from soils. It is produced largely by oxidation of organic nitrogen compounds and by hydrolysis of urea and uric acid (waste products from animals). Ammonia concentrations range from less than 10 parts per billion in some natural surface and ground waters to greater than 30 parts per million in some waste waters.

## An Overview of Nitrogen (cont.)

**Organic Nitrogen:** Organic nitrogen is defined as organically bound nitrogen in the (Organic-N) tri-negative oxidation state. Analytically, organic nitrogen and ammonia are determined together and are referred to as TKN (Total Kjeldahl [pronounced "kel'-dall"] Nitrogen). Organic nitrogen ranges from 200 parts per billion in some lakes to greater than 20 parts per million in raw sewage.

### Nitrogen Family Relationships

|                               |                            |                               |                            |                               |                            |                     |
|-------------------------------|----------------------------|-------------------------------|----------------------------|-------------------------------|----------------------------|---------------------|
| Nitrate<br>NO <sub>3</sub> -N | <oxidation<<br>>reduction> | Nitrite<br>NO <sub>2</sub> -N | <oxidation<<br>>reduction> | Ammonia<br>NH <sub>3</sub> -N | <oxidation<<br>>reduction> | Organic<br>Nitrogen |
|-------------------------------|----------------------------|-------------------------------|----------------------------|-------------------------------|----------------------------|---------------------|

### Important Relationships

- A.  $NO_x = (NO_3-N) + (NO_2-N)$
- B.  $NO_3-N = (NO_x) - (NO_2-N)$
- C. Total Nitrogen(TN) = TKN + (NO<sub>x</sub>)
- D. TKN <sup>3</sup> NH<sub>3</sub>-N (always)
- E.  $TKN = (Organic\ N) + (NH_3-N)$
- F.  $Organic\ N = TKN - (NH_3-N)$

### Oxidation States of Nitrogen in the following compounds:

- 1. NO<sub>3</sub>-N +5
- 2. NO<sub>2</sub>-N +3
- 3. NH<sub>3</sub>-N 0
- 4. Organic Nitrogen -3

## Ammonia, EPA Method 350.1

**METHOD SUMMARY:** The automated procedure for the determination of ammonia utilizes the Berthelot reaction, in which the formation of a blue colored compound occurs when the solution of an ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite. A final solution of EDTA is added to the sample stream to eliminate the precipitation of the hydroxides of calcium and magnesium. Sodium nitroprusside is added to intensify the blue color.

**DETECTION LEVEL:** 0.03 mg/L or 0.15 mg/kg

**PRESERVATIVE:** Refrigerate at 4 °C, add H<sub>2</sub>SO<sub>4</sub> to a pH < 2.0.

**SAMPLING:** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 28 days with preservative.

**COMMENTS:**

Excessive amounts of calcium or magnesium, turbidity and color may interfere with this analysis.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass containers are acceptable for this analysis.

## Total Kjeldahl Nitrogen, EPA Method 351.2

**METHOD SUMMARY:** The determination of nitrogen is based on a colorimetric method in which an emerald-green color is formed by the reaction of ammonia, sodium salicylate, sodium nitroprusside and sodium hypochlorite (chlorine source) in a buffered alkaline solution at a pH of 12.8-13.0. The ammonia salicylate complex is read at 660 nm. Samples are prepared by block digestion prior to analysis.

**DETECTION LEVEL:** 0.04 mg/L or 1.6 mg/kg

**PRESERVATIVE:** Refrigerate at 4 °C, add H<sub>2</sub>SO<sub>4</sub> to a pH < 2.0.

**SAMPLING:** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 28 days with preservative.

**COMMENTS:**

Nitrate causes negative interferences. Inorganic salts and solids can cause pyrolytic loss of nitrogen.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass containers are acceptable for this analysis.

## Nitrate/Nitrite, EPA Method 353.1/SM 4500 NO3-H

**METHOD SUMMARY:** The automated procedure for the determination of nitrate utilizes the reaction whereby nitrate is reduced to nitrite by an alkaline solution of hydrazine sulfate containing a copper catalyst. The stream is then treated with sulfanilamide/NED reagent under acidic conditions to form purple dye, which is measured colorimetrically at 520 nm. The final product measured represents the nitrite ion originally present plus that formed from the nitrate. In order to determine nitrate levels, the nitrite alone must be subtracted from the total (nitrate + nitrite). This can be achieved by substituting distilled water for the hydrazine sulfate line on the manifold. Separate calibration curves are determined for nitrate plus nitrite and for nitrite alone.

**DETECTION LEVEL:** 0.02 mg/L or 0.10 mg/kg

**PRESERVATIVE:** Refrigerate at 4° C, add H<sub>2</sub>SO<sub>4</sub> to a pH < 2.0 for Nitrate/Nitrite  
Refrigerate at 4° C for Nitrite.

**SAMPLING** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 28 days for Nitrate/Nitrite if preserved, 48 hours for Nitrite.

**COMMENTS:**

Chloride, sulfide, ferric, and phosphate ions interfere.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass containers are suitable for these analyses.

**Nitrates, EPA Method 353.3  
(Cadmium Reduction Column)**

**METHOD SUMMARY:** The sample is pH adjusted to 8.0, vacuum-filtered then diluted and passed through a cadmium reduction column where  $\text{NO}_3$  is converted to  $\text{NO}_2$ . Sulfanilamide (SAN) and N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) indicator are added and the violet color absorbance is measured on the HACH DR2000 at 543 nm. This is compared with standards to determine the concentration present in the sample.

**DETECTION LEVEL:** 0.02 mg/L or 0.20 mg/Kg

**SAMPLING:** A minimum of 200 mL or 50 g of sample is required for analysis

**PRESERVATIVE:** Add  $\text{H}_2\text{SO}_4$  to pH < 2.0 and refrigerate at 4 °C.

**HOLDING TIMES:** 28 days.

**COMMENTS:**

This method is applicable to the analysis of drinking, surface, and saline waters, as well as domestic and industrial wastes. Modification enables the analysis of soils.

**PREFERRED SAMPLING CONTAINER:** 500 mL plastic or amber glass container.

## Nitrite, EPA Method 354.1/SM 4500 NO2-H

**METHOD SUMMARY:** Sulfanilamide (SAN) and N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) is added to a 50 mL portion of the sample. After 15 minutes, the violet color absorbance is read at 543 nm on the Hach DR2000.

**DETECTION LEVEL:** 0.02 mg/L or 0.2 mg/Kg

**SAMPLING:** A minimum of 100 mL or 50 g of sample is required for analysis.

**PRESERVATIVE:** Refrigerate at 4 °C.

**HOLDING TIMES:** 48 hours.

**COMMENTS:**

This method is applicable to the analysis of drinking, surface, and saline waters, as well as domestic and industrial wastes. Modification enables analysis of soils.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container.

## Orthophosphate, EPA Method 365.1

**METHOD SUMMARY:** The determination of orthophosphate is based on the colorimetric method in which a blue color is formed by the reaction of orthophosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid at an acidic pH. The resulting phosphomolybdenum complex is read at 660 nm.

**DETECTION LEVEL:** 0.02 mg/L or 0.20 mg/kg

**PRESERVATIVE:** Refrigerate at 4 °C.

**SAMPLING:** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 48 hours.

**COMMENTS:**

Arsenate and high concentrations of silica cause false positive results.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container.

## Total Phosphorus, EPA Method 365.4

**METHOD SUMMARY:** Total phosphorus in water and wastewater is first converted to orthophosphate by hydrolysis (digestion) with sulfuric acid. The determination of orthophosphate is then based on the colorimetric method in which a blue color is formed by the reaction of ortho-phosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid at an acidic pH. The intensity of the phosphomolybdenum complex is determined on a spectrophotometer at 660 nm.

**DETECTION LEVEL:** 0.02 mg/L or 4.0 mg/kg

**PRESERVATIVE:** Refrigerate at 4°C, add H<sub>2</sub>SO<sub>4</sub> to a pH < 2.0.

**SAMPLING:** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 28 days.

**COMMENTS:**

High levels of silica can yield false positive results.

**PREFERRED SAMPLING CONTAINER:** 250 mL plastic or glass container.

**Sulfate, EPA Method 375.4/ASTM D516-90  
(Turbidimetric)**

**METHOD SUMMARY:** A portion of sample is placed in a 250 mL beaker. While mixing the sample, a conditioner and BaCl is added to complex with the sulfate. While mixing the suspension, absorbance is measured on the Hach DR2000 at 420 nm once each minute for 5 minutes. These absorbances are compared with standards to determine sulfate concentrations.

**DETECTION LEVEL:** 1.0 mg/L or 3 mg/Kg.

**SAMPLING:** A minimum of 200 mL or 50 g of sample is required for analysis.

**PRESERVATIVE;** Refrigerate at 4 °C.

**HOLDING TIMES:** 28 days.

**COMMENTS:**

This method is applicable to the analysis of drinking and surface waters, as well as domestic and industrial wastes. Dilutions must be used for concentrations higher than 40 mg/L. Soils can be analyzed by this procedure following the appropriate preparation procedure.

**PREFERRED SAMPLING CONTAINER:** 500 mL plastic or glass container.

**BOD, EPA Method 405.1/SM 5210 B**  
**Biochemical Oxygen Demand**

**METHOD SUMMARY:** This method consists of filling a sample in a full, airtight bottle and incubating the bottle under specified conditions for a specified amount of time. The dissolved oxygen (DO) concentration of the sample is measured initially and after incubation. BOD is computed from the difference between the initial and final DO concentrations.

**DETECTION LEVEL:** 2 mg/L

**PRESERVATIVE:** Refrigerate at 4 °C.

**SAMPLING:** 1 Liter of sample is required for this analysis.

**HOLDING TIME:** 48 hours.

**COMMENTS:**

Samples containing caustic alkalinity or acidity must be neutralized. The pH of the sample should be adjusted to pH ~ 5 to 7.5 with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or sodium hydroxide (NaOH). Samples containing residual chlorine must be dechlorinated. Residual chlorine can be eliminated by using sodium thiosulfate. Samples must be brought to 20 +/- 1 degrees Celsius before making dilutions. Nitrification inhibition may be required for some samples such as biologically treated effluents, samples seeded with biologically treated effluents, and river waters. Note the use of nitrogen inhibition in reporting results; in such cases that this inhibitor is used the results are reported as carbonaceous biochemical demand, or CBOD.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass containers are suitable for this analysis.

**COD, EPA Method 410.4/SM 5220 C**  
**Chemical Oxygen Demand**

**METHOD SUMMARY:** A 2 mL aliquot of sample is transferred into a COD vial already containing all necessary reagents. It is then placed in the COD reactor for two hours at 150 °C, cooled, and read on the HACH DR2000.

**DETECTION LEVEL:** 5 mg/L or 10 mg/Kg

**SAMPLING:** A minimum of 40 mL or 10 g is required for analysis.

**PRESERVATIVE:** H<sub>2</sub>SO<sub>4</sub> to pH < 2.0, refrigerate at 4°C.

**HOLDING TIMES:** 28 days.

**COMMENTS:**

COD is used to measure the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation. This organic matter content is also measurable by such parameters as Total Organic Carbon (TOC) and Biochemical Oxygen Demand (BOD).

**PREFERRED SAMPLING CONTAINER:** 100 mL plastic or glass container.

**EPA Methods 413.1 & 413.2/ SW-846 Methods 9070 & 9071**  
**Oil & Grease**

**METHOD SUMMARY:** A 1 liter water sample or 30 g solid sample is extracted with fluorocarbon-113. The extract is dried and the residue weighed (413.1, 9070, 9071) or measured via FTIR (413.2) to determine Oil & Grease concentrations.

**DETECTION LEVEL:** 1 mg/L in water, 5 mg/Kg in solids

**SAMPLING:** For waters, a minimum of 2 liters should be collected in glass jars. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Samples should be taken directly into the sample container to minimize such losses. Solids should be collected in amber glass containers.

**PRESERVATIVE:** Refrigerate at 4 °C, add H<sub>2</sub>SO<sub>4</sub> to pH < 2 for aqueous samples.  
Refrigerate at 4 °C for soils.

**HOLDING TIMES:** 28 days.

**COMMENTS:**

This method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70 °C (the concentration bath temperature). Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation. Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not readily soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

Due to increasing pressures to eliminate the uses of chlorofluorocarbons, the EPA has developed an alternative procedure (EPA Method 1664a - Hexane Extractable Material). This procedure does yield different concentrations versus the freon based methods, and this variation can result in higher or lower results depending upon the types of contamination present.

SW-846 Method 9071 currently offers two versions: 9071a is a Freon-based extraction, while 9071b is a hexane based. Please specify method version when submitting samples. Also note that many of the same caveats that apply to the 1664a method also apply to the 9071b procedure.

**PREFERRED SAMPLING CONTAINER:** 2x1 Liter amber glass with Teflon lined cap for liquid samples and 500 mL amber glass jar with Teflon lined cap for soils.

**HEM & SGT-HEM, EPA 1664a**  
**Hexane Extractable Material and**  
**Silica-Gel Treated Hexane Extractable Material**

**METHOD SUMMARY:** A 1 liter water sample is extracted with hexane. The extract is dried and the residue weighed (HEM) or treated with silica gel to remove polar materials, dried and weighed (SGT-HEM). The 1664a procedure represents the EPA's response to the ban on Freon-113, the extraction solvent used for 413.1, 413.2 and 9070. 1664a is only applicable to the analysis of aqueous matrices.

**DETECTION LEVEL:** 5 mg/L in water

**SAMPLING:** For waters, a minimum of 2 liters should be collected in glass jars. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Samples should be taken directly into the sample container to minimize such losses.

**PRESERVATIVE:** Refrigerate at 4 °C, add H<sub>2</sub>SO<sub>4</sub> to pH < 2.

**HOLDING TIMES:** 28 days.

**COMMENTS:**

This method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70 °C (the concentration bath temperature). Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation. Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not readily soluble in hexane. Accordingly, recoveries of these materials will be low.

Although this method represents the replacement for the traditional Oil and Grease procedures, the numbers generated will not necessarily compare. The parameter "Oil and Grease" is defined by the solvent used (anything soluble in Freon-113 is "Oil & Grease" per the method), and the 1664a procedure uses hexane, a solvent with noticeably different solubilities. In spite of these differences, EPA and other regulatory agencies have not revised permit discharge limits when adopting this procedure.

Despite the exceptions noted in the previous paragraph, HEM is considered roughly equivalent to O&G, and the SGT-HEM is roughly equivalent to TPH.

**PREFERRED SAMPLING CONTAINER:** 2x1 Liter amber glass with Teflon lined cap.

**TRPH, EPA Method 418.1/SW-846 Method 9073**  
**Total Recoverable Petroleum Hydrocarbons**

**METHOD SUMMARY:** A 1 liter water sample or 30 g soil sample is acidified and serially extracted with fluorocarbon-113 (freon). Silica gel is added to the extract to remove polar materials leaving only the nonpolar petroleum hydrocarbons. The concentration of TRPH present is measured via infrared spectroscopy.

**DETECTION LEVEL:** 1 mg/L – water, 5 mg/Kg - soil

**SAMPLING:** A representative sample of water or soil should be collected in a glass bottle. Because losses will occur on sampling equipment, the collection of a composite sample is impractical.

**PRESERVATIVE:** Refrigerate at 4 °C, add H<sub>2</sub>SO<sub>4</sub> to pH < 2 for aqueous samples.  
Refrigerate at 4 °C for soils.

**HOLDING TIMES:** 28 days

**COMMENTS:**

As in the case of oil & grease, the parameter "petroleum hydrocarbons" is defined by the method based upon solubility in freon-113. The measurement may be subject to interferences and the results should be evaluated accordingly. Oil and grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Total Recoverable Petroleum Hydrocarbons is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.

This method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70 °C (the concentration bath temperature). Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation. Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

Due to increasing pressures to eliminate the uses of chlorofluorocarbons, the EPA has developed an alternative procedure (EPA Method 1664a - Silica Gel Treated Hexane Extractable Material). This procedure does yield different concentrations versus the freon based methods, and this variation can result in higher or lower results.

Additionally, many states have adopted GC-based TPH analyses such as the FL-PRO, GRO, and DRO to further eliminate the use of freon.

**PREFERRED SAMPLING CONTAINER:** 2x1liter amber glass jar with Teflon lined lid for liquid samples and 500 mL amber glass jar with Teflon lined lid for soil samples.

**TOC, EPA Method 415.1/SW-846 Method 9060/SM 5310 B**  
**Total Organic Carbon**

**METHOD SUMMARY:** Total Organic Carbon is measured by the high temperature combustion and conversion of organic matter into CO<sub>2</sub>. Inorganic carbon components, such as CO<sub>2</sub>, carbonates and bicarbonates are removed from the sample prior to analysis by acidification and sparging with an inert gas.

**DETECTION LEVEL:** 1 mg/L

**PRESERVATIVE:** Refrigerate at 4°C, H<sub>3</sub>PO<sub>4</sub> to pH <2.

**SAMPLING;** A minimum of 40 mL of sample is required for this analysis.

**HOLDING TIME:** 28 days.

**COMMENTS:** This method is applicable to the analysis of drinking waters, surface waters, groundwaters and industrial wastewaters. Care must be taken in the sample preparation steps to ensure all inorganic carbon forms have been removed.

This method does not permit the reliable analysis and quantitation of volatile materials such as tetrachloroethene or benzene due to their losses in the preparation procedure.

This method has been adapted by many laboratories for the analysis of solids, however such modifications should be considered on a case-by-case basis to determine applicability and consistency. Common modifications involve the use of a leaching procedure, such as the Army Corps of Engineers method CE-81-1 to produce an aqueous extract that is then analyzed using standard techniques. Another alternative approach to determining TOC in soils is the measurement of "loss on ignition" to determine the amount of organic matter present. From this result, organic carbon is calculated based upon a table of factors dependent upon soil type, consistency, etc.

**PREFERRED SAMPLING CONTAINER:** 250 mL amber glass containers or amber vials are suitable for this analysis.

## **TOC, Walkley Black Total Organic Carbon**

**METHOD SUMMARY:** This method quantifies the amount of oxidizable organic matter in which organic carbon is oxidized with a known amount of dichromate in the presence of sulfuric acid. The remaining unreacted dichromate is determined by titration. The calculation of organic matter is based on organic matter containing 58% carbon. The method has a detection limit of approximately 0.01% and is generally reproducible within 8%.

**DETECTION LEVEL:** 500 mg/Kg

**PRESERVATIVE:** Refrigerate at 4°C

**SAMPLING;** A minimum of 100 grams of sample is required for this analysis.

**HOLDING TIME:** 28 days.

**COMMENTS:** This method is applicable to the analysis of soil samples.

**PREFERRED SAMPLING CONTAINER:** 4oz. glass containers

## Chlorophyll A SM 10200-H

**METHOD SUMMARY:** Chlorophyll a is extracted from aqueous samples by filtration. The concentrated chlorophyll a is resuspended in 90% acetone and macerated. The resulting slurry is clarified and optical density at multiple wavelengths is measured on the supernatant. The various optical density values are utilized to calculate the concentration of chlorophyll a.

**DETECTION LEVEL:** 0.5 mg/m<sup>3</sup>

**PRESERVATIVE:** Refrigerate at 4°C

**SAMPLING;** A minimum of 1L of sample is required for this analysis.

**HOLDING TIME:** 48 hours.

**COMMENTS:** This method is applicable to the analysis of aqueous samples.

**PREFERRED SAMPLING CONTAINER:** 1L Amber Container.

## Total Phenols, EPA Method 420.1/SW-846 Method 9065

**METHOD SUMMARY:** The sample is treated with copper sulfate and preserved to a pH of < 2.0. The sample is then steam distilled to remove most interferences. The distillate is then complexed with 4-aminoantipyrine at a pH of 7.9 +/- 0.1 and then complexed with potassium ferric cyanide to form a yellow/orange/red dye. The intensity of the color is measured on a spectrophotometer at 510 nm.

**DETECTION LEVEL:** 0.05 mg/L or 0.25 mg/Kg

**PRESERVATIVE:** Refrigerate at 4°C, add H<sub>2</sub>SO<sub>4</sub> to a pH < 2.0

**SAMPLING:** A minimum of 500 mL or 50 grams is required for the analysis.

**HOLDING TIME:** 28 days.

### COMMENTS:

This method is applicable to domestic and industrial wastewaters, as well as natural and potable water supplies. Bacteria, oxidizing and reducing substances and alkaline pH values are dealt with by acidification. Chlorine, sulfur compounds, oils and tars may also cause interference.

**PREFERRED SAMPLING CONTAINER:** 1 Liter amber glass for liquid samples and 500 mL amber glass container for soils.

**MBAS, EPA Method 425.1/SM 5540-C**  
**Methylene Blue Active Substances or Surfactants**

**METHOD SUMMARY:** Methylene blue dye in aqueous solution reacts with anionic surfactants such as LAS, other sulfonates and sulfate esters as well as other strongly amphiphilic anions, natural or man made, to form a blue colored salt. These materials are designated as MBAS. The salt is extracted with chloroform and the intensity of color is proportional to the concentration of MBAS. This color intensity is measured on a spectrophotometer at 652 nm. This methylene blue method is used successfully in analyzing drinking water, however many materials present in wastewater and sludge can interfere with the results.

**DETECTION LEVEL:** 10 ug/L

**PRESERVATIVE:** Refrigerate at 4°C.

**SAMPLING;** A minimum of 1 L of sample is required for this analysis.

**HOLDING TIME:** 48 hours.

**COMMENTS:** If a direct determination of LAS or of any other LAS species is sought, all other MBAS interfere. Substances such as organic sulfonates, sulfates, carboxylates, phenols, cyanates, chlorides, nitrates and thiocyanates that form ion pairs with methylene blue are among positive interferences. Cationic surfactants and other cationic materials such as amines will give negative interference by competing with the cationic methylene blue. Sulfides, often present in wastewater, may react with methylene blue to form a colorless reduction product, making the analysis impossible. Eliminate this interference by prior oxidation with hydrogen peroxide. The interference from chlorides and nitrates can be eliminated by a backwash step.

**PREFERRED SAMPLING CONTAINER:** Plastic or glass containers are suitable for this analysis.

**TOX, EPA Method 450.1/SW-846 Method 9020**  
**Total Organic Halogens**

**METHOD SUMMARY:**Organic halogens are separated from inorganic halogens by running the sample through an activated charcoal bed, which binds any organics present. This charcoal is then subjected to pyrolysis in a furnace at approximately 900°C, from which the exhaust gases are swept into a microcoulometric cell (a cell in which conductivity is measured). Any halogens present in the sample are converted into their base ions (chloride, fluoride, iodide, and bromide) in the furnace, and then result in changes in conductivity in the cell.

**DETECTION LEVEL:** 10 ug/L

**PRESERVATIVE:** Refrigerate at 4°C, H<sub>2</sub>SO<sub>4</sub> to pH <2.

**SAMPLING;** A minimum of 250 mL of sample is required for this analysis.

**HOLDING TIME:** 14 days.

**COMMENTS:**This method is applicable to the analysis of drinking waters, surface waters, and industrial wastewaters. Care must be taken in the sample preparation steps to ensure all inorganic halides have been removed. In addition, care must be taken in sample preparation to ensure that the charcoal bed is not overloaded with the organics present.

This method does not permit the reliable analysis and quantitation of volatile halogenated materials such as tetrachloroethene or methylene chloride, due to their losses in the preparation procedure.

This method has been adapted by many laboratories for the analysis of solids, however such modifications should be considered on a case-by-case basis to determine applicability and consistency.

**PREFERRED SAMPLING CONTAINER:** 250 mL amber glass containers are suitable for this analysis.

## **Total and Fecal Coliforms, SM 9222-B, SM 9222-D**

### **Membrane Filtration**

**METHOD SUMMARY:** Known volumes of sample are passed through sterile filters, capturing coliform bacteria. The filters are placed in petri dishes and depending upon the analysis (total or fecal) different media are added, allowing for the selective growth of the bacteria. The plates are incubated for twenty-four hours at either 44.5°C (fecal) or 35.5 °C (total). Upon completion of incubation, the coliform colonies are counted. Ten percent of all colonies are confirmed by the use of fermentation tubes.

**DETECTION LEVEL:** 1 cfu/100mL

**PRESERVATIVE:** Refrigerate at 4°C, use Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to neutralize any residual chlorine present.

**SAMPLING;** A minimum of 100mL of sample is required for this analysis.

**HOLDING TIME:** 6hrs for environmental matrices (drinking water samples are 24 hrs.).

**COMMENTS:** This method is applicable to the analysis of drinking waters, surface waters, and industrial wastewaters. Care must be taken in the sample collection steps to avoid contamination.

The laboratory runs many quality control checks to ensure against cross-contamination or other method errors. Such QC measures involve the use of positive and negative controls, as well as preparation blanks at the beginning and end of each batch.

Sterile containers must be used to ensure consistent results.

**PREFERRED SAMPLING CONTAINER:** 1 or 2 sterile 120 mL cups.

**HPC, STD METHODS 9215B**  
**Heterotrophic Plate Count (Pour Plate Technique)**

**METHOD SUMMARY:** Known volumes of sample are mixed volumetrically with media, and then poured into sterile petri dishes. R2A or plate count agar are the two most commonly used media, allowing for the growth of heterotrophic bacteria. The plates are incubated for five to seven days at 20°C, or 35°C for 48 hours in a humid environment. Upon completion of incubation, the colonies are counted.

HPC has also been referred to as Standard Plate Count.

This procedure estimates the number of live heterotrophic bacteria in water and measures the changes in water quality during treatment and distribution. It has also been used to monitor swimming pools.

**DETECTION LEVEL:** 1 cfu/mL

**PRESERVATIVE:** Refrigerate at 4°C, use Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to neutralize any residual chlorine present.

**SAMPLING;** A minimum of 5mL of sample is required for this analysis.

**HOLDING TIME:** 24hrs from sampling if refrigerated upon collection, otherwise 8 hrs.

**COMMENTS:** This method is applicable to the analysis of drinking waters, surface waters, and industrial wastewaters. Care must be taken in the sample collection steps to avoid contamination.

The laboratory runs preparation blanks at the beginning of each batch to ensure against contamination.

Sterile containers must be used to ensure consistent results.

The lower incubation temperature coupled with a longer incubation period typically yields higher, more accurate counts.

**PREFERRED SAMPLING CONTAINER:** 1 sterile 120 mL cups.