

# **Quality Assurance Project Plan**

**for**

## **Pajaro Valley Water Management Agency Groundwater Monitoring Program**

December 2016

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***Pajaro Valley***  
***Water Management Agency***

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## 1. PROJECT/TASK ORGANIZATION

### 1.1 Involved Parties and Roles

The Pajaro Valley Water Management Agency (PVWMA) is a state-chartered water management district formed to efficiently and economically manage existing and supplemental water supplies in the Pajaro Valley in order to prevent further increase in, and to accomplish continuing reduction of, long-term overdraft. The PVWMA also works to provide and ensure sufficient water supplies for present and future anticipated needs within its boundaries, generally the greater coastal Pajaro Valley. To help achieve this mission, the PVWMA monitors a network of publicly and privately owned wells in order to obtain water quality and water level data. The collected data is used to track and understand basin responses to groundwater condition changes associated with factors such as recharge, extractions, and groundwater management activities. Collectively, the network of wells and data collected from them is known as the PVWMA Groundwater Monitoring Program (PVWMA GMP). To ensure the capture of high quality data, the PVWMA is responsible for maintaining the network, performing sample collection, performing field water quality measurements, conducting water level measurements, and housing collected data in databases.

PVWMA's General Manager/Hydrogeologist is responsible for providing oversight and guidance to the PVWMA GMP.

PVWMA's Associate Hydrologist is responsible for managing the PVWMA GMP, maintaining PVWMA databases, collecting samples, and ensuring compliance to this Quality Assurance Project Plan (QAPP).

PVWMA's Water Resources Technician is responsible for collecting samples, coordinating laboratory analytical services, measuring field water quality data, and measuring groundwater levels.

Laboratory analytical services for water samples collected as part of the PVWMA GMP are provided by Monterey Bay Analytical Services (MBAS). MBAS analyzes submitted samples in accordance with all method and quality assurance requirements specified in this QAPP and the two associated appendices.

Table 1 below provides a list of the PVWMA staff filling the roles above along with the lead personnel at MBAS.

**Table 1. Personnel**

| <b>Name</b>               | <b>Organizational Affiliation</b>   | <b>Title</b>                       | <b>Contact Information<br/>(Telephone number, fax<br/>number, email address.)</b> |
|---------------------------|-------------------------------------|------------------------------------|-----------------------------------------------------------------------------------|
| Brian Lockwood            | PVWMA                               | General Manager/<br>Hydrogeologist | T (831) 722-9292<br>F (831) 722-3139<br>Lockwood@pvwater.org                      |
| Casey Meusel              | PVWMA                               | Associate Hydrologist              | T (831) 722-9292<br>F (831) 722-3139<br>Meusel@pvwater.org                        |
| Marino Hernandez          | PVWMA                               | Water Resources<br>Technician      | T (831) 722-9292<br>F (831) 722-3139<br>Hernandez@pvwater.org                     |
| David Holland             | Monterey Bay Analytical<br>Services | Lab Director                       | T (831) 375-6227<br>F (831) 641-0734<br>DHolland@MBASinc.com                      |
| Mason Weidner-<br>Holland | Monterey Bay Analytical<br>Services | Administrative Support             | T (831) 375-6227<br>F (831) 641-0734<br>MWeidner@MBASinc.com                      |

### 1.2 Quality Assurance Officer Role

The Associate Hydrologist functions as the Quality Assurance Officer (QA Officer) and is responsible for developing the quality assurance and quality control procedures outlined in this QAPP. The QA Officer ensures the proper implementation of these procedures by PVWMA staff. The QA officer coordinates with the MBAS Lab

Director and Administrative Support person to ensure that all quality assurance and quality control measures of laboratory water quality analyses are followed.

### **1.3 Persons Responsible for QAPP Update and Maintenance**

The Associate Hydrologist administers all changes and updates to this QAPP after receiving approval from the General Manager/Hydrogeologist.

## **2. PROBLEM DEFINITION/BACKGROUND**

### **2.1 Problem Statement**

The Pajaro Valley Groundwater Sub-basin is in a state of long-term overdraft, a condition that has caused groundwater elevations to drop below sea level, leading to seawater intrusion. Seawater intrusion has caused chloride contamination of groundwater wells up to three miles inland. Seawater intrusion is an immediate and direct threat to the Pajaro Valley economy. Elevated chloride concentrations may make groundwater unusable for irrigating high value, salt-sensitive crops in the coastal region of the Pajaro Valley.

Historical and existing conditions of the basin have been modeled utilizing the Pajaro Valley Hydrologic Model (PVHM). Projects built and implemented by the PVWMA to date were confirmed to reduce, but not solve, both the seawater intrusion and the groundwater overdraft problems. The basin shortfall is estimated to be approximately 12,100 acre-feet/year.

The PVWMA GMP, and the monitoring programs operated by Santa Cruz County, Monterey County, and the California Department of Water Resources before it, provide the necessary information that PVWMA and stakeholders need to make informed management decisions. At present, the PVWMA GMP is composed of 255 wells distributed throughout the Pajaro Valley that provide water quality and water level data. Most of these wells are monitored directly by PVWMA staff and with a small subset of wells monitored by the neighboring agencies of Soquel Creek Water District, Central Water District, and the Monterey County Water Resources Agency.

### **2.2 Decisions or Outcomes**

Water quality data generated by the PVWMA GMP assists in tracking spatial and temporal trends in groundwater, the progression of seawater intrusion, and the impacts of water management projects and programs. Water level data obtained through the PVWMA GMP tracks changes in groundwater storage, impacts of water management projects, is used to comply with regulatory permit monitoring requirements, and is utilized in the development and refinement of the PVHM. In addition to the functions listed above, the data collected through the PVWMA GMP generates a catalogue of groundwater data for use in future investigations that have yet to be conceived.

### **2.3 Water Quality or Regulatory Criteria**

Maintaining beneficial uses of water is a primary objective of the PVWMA. To achieve it, the PVWMA completed a Salt and Nutrient Management Plan (SNMP). The SNMP was required by the State Water Resources Control Board as part of the Recycled Water Policy and requires the development of such plans to manage salts and nutrients in groundwater basins. As part of PVWMA's SNMP, assimilative capacity thresholds were established for three indicator constituents and included chloride, total dissolved solids, and nitrate as NO<sub>3</sub>. The assimilative capacity thresholds are 1,000 mg/L for total dissolved solids; 150 mg/L for chloride; and 45 mg/L for nitrate as NO<sub>3</sub>. These assimilative capacities define the amount of loading that the groundwater basin can receive from salts and nutrients without resulting in damage to aquatic life or humans who utilize and consume the water.

In addition to the water quality criteria established in the SNMP, PVWMA utilizes chloride concentrations in groundwater to track the progression of seawater intrusion. Chloride is an anion frequently occurring in nature as a salt, such as sodium chloride and is the most common salt in seawater. PVWMA uses a chloride threshold concentration of 100 mg/L to identify areas impacted by seawater intrusion.

### **3. PROJECT/TASK DESCRIPTION**

#### **3.1 Work Statement and Produced Products**

PVWMA obtains groundwater level and water quality data from over 255 wells, both publicly and privately owned, each year. Over the past decade more than 300 unique wells have been monitored, a majority of which are privately owned. The PVWMA has been working since the 1980s to install more publicly owned dedicated monitoring wells in strategic locations to increase both the availability and reliability of valuable data collection points.

The PVWMA's largest groundwater level and quality data collection effort occurs semi-annually, during which time PVWMA staff visit approximately 170 wells distributed throughout the basin. Some of the wells included in this network were monitored by the counties of Monterey and Santa Cruz prior to the formation of the agency in 1984, and have historical records that date back as far as the 1940s. Monitoring activities are conducted in the spring and the fall during times when groundwater surface elevations are anticipated to be at the highest and lowest levels respectively. During monitoring efforts, staff visit each well in the network up to three times in an attempt to obtain both 1) a static water level measurement and 2) a water sample for quality analysis when the well is in operation.

In an effort to track seasonal variations to groundwater levels throughout the valley, staff monitor a subset of the semi-annual wells on a monthly frequency. This "monthly monitoring network" consists of 48 wells and is composed of a combination of public and privately owned wells. This subset includes the "PV Wells" series, which are dedicated monitoring wells that were first constructed in 1988, proximate to the coast, to provide controlled sampling locations in order to investigate the extent seawater intrusion. Additional PV Wells have since been constructed at locations further inland to fill known data gaps. The PV Wells are instrumented with autonomous pressure transducers that record water level measurements on a specified frequency (often every 15 or 60 minutes), and low flow pumps that allow staff to efficiently collect water quality samples from targeted elevations within the aquifer. The groundwater level data derived from the monthly monitoring network provide staff with the resolution needed to observe groundwater level fluctuations in the basin that are not captured in semi-annual monitoring and help inform timing of semi-annual monitoring events each year.

In addition to semi-annual and monthly monitoring efforts described above, the Agency monitors 27 wells associated with the Harkins Slough Managed Aquifer Recharge & Recovery Facility. Of the wells proximate to the recharge basin, 16 are dedicated monitoring wells and 11 are recovery (production) wells. Nearly all of these wells are equipped with autonomous pressure transducers to track water levels and pumps to obtain samples for water quality analyses. Data collected from the 27 Harkins Slough wells serve to inform staff of changing groundwater conditions resulting from facility operations and enables more effective operation of the project.

Data collected from the PVWMA GMP are used for a variety of purposes that support and inform basin management activities. For example, groundwater surface elevation maps are produced annually using collected water level data. Water level data have also been used extensively in the development of the PVHM, from serving as calibration points, to checking the accuracy of predicted water levels. Maps and tables describing groundwater quality conditions are produced annually and as needed. The data are used to support other hydrologic studies, including those investigating groundwater – surface water interactions and the development of environmental impact reports. Products generated from the data are regularly presented during stakeholder, committee, and board meetings in an effort to inform the community of the conditions within their groundwater basin.

#### **3.2 Constituents to be Monitored and Measurement Techniques**

Provided below in Table 2 is a list of analytes routinely analyzed as part of the PVWMA GMP and the method of analysis used. Typically water quality samples submitted to MBAS are analyzed for the irrigation suitability panel which evaluates the salt and nutrient content of water along with other ions that have the potential to impact agricultural productivity. Additional parameters are added for wells based on the associated subset and/or spatial location. Kjeldahl nitrogen and total nitrogen are performed for all wells located in the delivered water zone and for active Harkin's Slough recovery wells. Chromium VI, iron, and total manganese are monitored for the PV20 series wells. Turbidity analysis is performed for the Harkins Slough recovery wells and the blend wells.

**Table 2. Groundwater Monitoring Constituents**

| Analyte                                         | Method                      | Unit     | Irrigation Suitability Panel |
|-------------------------------------------------|-----------------------------|----------|------------------------------|
| Alkalinity, Total (as CaCO <sub>3</sub> )       | SM2320B                     | mg/L     | X                            |
| Bicarbonate (as HCO <sub>3</sub> <sup>-</sup> ) | SM2320B                     | mg/L     | X                            |
| Boron                                           | EPA200.7                    | mg/L     | X                            |
| Bromide                                         | EPA300.0                    | mg/L     | X                            |
| Calcium                                         | EPA200.7                    | mg/L     | X                            |
| Carbonate as CaCO <sub>3</sub>                  | SM2320B                     | mg/L     | X                            |
| Chloride                                        | EPA300.0                    | mg/L     | X                            |
| Chromium VI                                     | EPA218.6                    | µg/L     |                              |
| Fluoride                                        | EPA300.0                    | mg/L     | X                            |
| Hardness (as CaCO <sub>3</sub> )                | SM2340B                     | mg/L     | X                            |
| Iron                                            | EPA200.7                    | µg/L     |                              |
| Kjeldahl Nitrogen                               | SM4500-NH <sub>3</sub> B,C. | mg/L     |                              |
| Langlier Index ( 15 deg. C)                     | SM2330B                     |          | X                            |
| Magnesium                                       | EPA200.7                    | mg/L     | X                            |
| Manganese, Total                                | EPA200.7                    | µg/L     |                              |
| Nitrate as NO <sub>3</sub>                      | EPA300.0                    | mg/L     | X                            |
| Nitrate as NO <sub>3</sub> -N                   | EPA300.0                    | mg/L     | X                            |
| Nitrate+Nitrite as N                            | EPA300.0                    | mg/L     | X                            |
| Nitrite as NO <sub>2</sub> -N                   | EPA300.0                    | mg/L     | X                            |
| o-Phosphate-P                                   | EPA300.0                    | mg/L     | X                            |
| pH (Laboratory)                                 | SM4500-H+B                  | pH       | X                            |
| Potassium                                       | EPA200.7                    | mg/L     | X                            |
| SAR (Sodium Adsorption Ratio)                   | Suarez, 1981                |          | X                            |
| SAR, Adjusted                                   | Suarez, 1981                |          | X                            |
| Sodium                                          | EPA200.7                    | mg/L     | X                            |
| Specific Conductance (E.C)                      | SM2510B                     | umhos/cm | X                            |
| Sulfate                                         | EPA300.0                    | mg/L     | X                            |
| Total Dissolved Solids                          | SM2540C                     | mg/L     | X                            |
| Total Nitrogen                                  | Calculation                 | mg/L     |                              |
| Turbidity                                       | EPA180.1                    | NTU      |                              |

### 3.3 Sampling Schedule

**Table 3. PVWMA GMP Monitoring Schedule**

| PVWMA GMP Component         | Data Type     | Sampling Frequency | Timing                           |
|-----------------------------|---------------|--------------------|----------------------------------|
| <b>Semi-Annual Wells</b>    | Water Level   | Semi-Annually      | Spring and Fall                  |
|                             | Water Quality | Semi-Annually      | Spring and Fall                  |
| <b>Monthly Wells</b>        | Water Level   | Monthly            | Monthly                          |
|                             | Water Quality | Semi-Annually      | Spring and Fall                  |
| <b>PV Wells</b>             | Water Quality | Quarterly          | March, June, September, December |
| <b>Harkins Slough Wells</b> | Water Level   | Quarterly          | January, April, July, October    |
|                             | Water Quality | Quarterly          | January, April, July, October    |

### 3.4 Geographical Setting

The hydrogeology of the Pajaro Valley Groundwater Sub-basin has been evaluated by many investigators. Most notable, is the work by the California State Water Resources Board in 1953 (Bulletin 5), by Ludroff and Scalomini (1987), by Dupre (1975), and by the USGS (Muir, Hanson). The Pajaro Valley Groundwater Sub-basin consists of a

thick sequence of sedimentary deposits filling a structural basin west of the San Andreas Fault. These sedimentary materials have traditionally been assigned based on their lithology and hydraulic responses into four major aquifer units. The shallowest deposits consist of the alluvial deposits flanking the river on the valley floor. Underlying the alluvium (Qal) and flanking the valley floor, are the Quaternary-aged Aromas Sands Formation (Qa) – an aeolian-fluvial sequence of sand and gravels. Past analyses of data from water well logs revealed an extensive regional fine-grained unit within this sequence subdividing the Aromas Sands into an upper (Qa<sub>up</sub>) and lower (Qa<sub>lo</sub>) aquifer. Underlying the Aromas Sands Formation is the Tertiary-aged Purisima Formation (Tp), which extends to significant depth below ground surface. Although not confirmed in many locations, it is inferred that the Purisima Formation overlies granitic basement.

Most groundwater in the Pajaro Valley Groundwater Sub-basin is extracted from wells completed in either the alluvial deposits or the Aromas Sands Formation, or some combination thereof. Although the Purisima Formation provides a significant portion of the supply to the Central and Soquel Creek Water Districts to the north, its use in the Pajaro Valley Groundwater Sub-basin is limited.

#### **4. SPECIAL TRAINING NEEDS/CERTIFICATION**

##### **4.1 Specialized Training or Certifications**

All PVWMA field staff undergo routine training upon hiring. PVWMA staff collecting water samples and water level data are familiar with appropriate sampling protocols and measurement methods. New staff are accompanied by an experienced staff person until such time that the individual can perform all requisite tasks consistently and correctly without guidance. No specialized certifications are required for staff to perform water quality sample collection or to measure water levels.

MBAS is a full service California State Certified Environmental Laboratory (ELAP # 2385) that has been providing laboratory testing and sampling since 1999. MBAS staff are trained to perform analytical testing and comply with quality assurance and quality control measures under the supervision of the Lab Director.

##### **4.2 Training Personnel**

The QA Officer or an individual appointed by the QA Officer is responsible for providing training to new PVWMA staff performing data collection activities. MBAS staff persons are trained under the direction of MBAS Lab Director David Holland.

#### **5. DOCUMENTS AND RECORDS**

PVWMA collects data records of sample collection, field analyses, and water level measurements. Samples sent to MBAS include a Chain of Custody form. MBAS generates data records for sample receipt and storage, analyses, and reporting.

PVWMA develops and maintains databases and spreadsheets for field measurements, water quality sample analysis, and water level measurements. The General Manager/Hydrogeologist, Associate Hydrologist, and Water Resources Technician work cooperatively to maintain the PVWMA databases and spreadsheets.

Records generated by PVWMA GMP data collection are stored at PVWMA's office in electronic format on agency owned server(s) or a subscribed cloud data service. Retention of hard copies of data records aren't necessary if redundancy measures to ensure record security are enacted and the capability to replicate hard copies exists. MBAS retains electronic copies of all analytical results indefinitely.

Copies of this QAPP are distributed to all PVWMA employees involved in the PVWMA GMP. Any future amended QAPPs will be distributed to the same recipients. All originals of this first and subsequent amended QAPPs will be held at the PVWMA office by the QA Officer. Copies of versions, other than the most current, shall be discarded by all other QAPP holders so as not to create confusion.

Data records for laboratory analysis and water level measurements are retained indefinitely. Field water quality data records are retained at minimum for ten years from date of collection. The General Manager/Hydrogeologist arbitrates any issues relative to records retention and approves any decisions to discard data records.

## **6. SAMPLING PROCESS DESIGN**

The majority of the wells in the network were inherited from existing groundwater monitoring networks established by the state of California, the County of Monterey, and the County of Santa Cruz. Almost all of the wells in the network provide water level data and a majority are capable of producing water quality samples for laboratory analysis. The PVWMA GMP network is an areally-extensive groundwater data collection network. The network allows monitoring of water level and water quality data across the basin and within the four primary aquifer units. The network has been developed over decades and the accumulated data represents an invaluable resource for understanding and managing the water resources of the basin. Routine evaluations of the network are performed to ensure that the network is able to produce sufficient data to meet the objectives of the PVWMA. At minimum, a thorough evaluation of the network and its efficacy will be performed every five years. Agency staff are currently performing a network review. The addition and/or removal of monitoring locations shall be based off of conclusions of network evaluations and approved by the General Manager/Hydrogeologist.

## **7. SAMPLING METHODS**

Static water level measurements are obtained prior to any sample collection at the same site. The date, time, depth to water measurement in feet, whether the measurement was questionable or not, and relevant notes are recorded for every water level measurement. Water quality samples are collected as grab samples from the most upstream sample port of each well. Prior to sample collection, the well is run long enough to purge all stagnant water in the pump casing, well, and/or pump tubing. Wells equipped with micropurge bladder pumps utilize the flow cell water quality sonde with stabilization criteria to determine when to collect the sample following the purging of stagnant water. Each sample bottle is labeled with the site name, date of sample, time of sample, and the desired analyses. Wearing a new pair of nitrile or latex gloves for each site, the staff person triple rinses the bottle and cap with the water being sampled. Routine samples are collected in a single HDPE plastic 1-liter bottle and capped. For specialized analyses, PVWMA staff follow the appropriate protocol as directed by MBAS. Although it is not necessary, it is good practice to minimize head space in the sample bottle. Hexavalent chromium sample bottles contain a preservative solution in the bottle and are not rinsed before the sample is collected. When collecting a hexavalent chromium sample, the bottle shall be filled to the neck of the bottle and then capped.

## **8. SAMPLE HANDLING AND CUSTODY**

Once samples are collected they are stored in a cooler with ice packs until the staff person returns to the PVWMA office. The samples remain in the Hydrology Unit refrigerator at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until being picked up by MBAS staff or a PVWMA staff person delivers them to MBAS for analysis. During transport to MBAS by PVWMA staff, the samples are once again placed in a cooler with ice packs. The only routine analysis that requires a preservative spike at the time of collection is hexavalent chromium. MBAS provides the hexavalent chromium samples bottles with the  $(\text{NH}_4)_2\text{SO}_4$  preservative solution already in the bottle. Water quality samples are picked up or delivered to MBAS in less than 48 hours after sample collection to meet the hold time requirements for the shortest hold time analytes, turbidity and nitrate. All other analytes routinely monitored by PVWMA have hold times greater than 48 hours except pH. pH has an instantaneous hold time and is always analyzed outside of the hold time by MBAS. MBAS administers additional preservatives to the samples once received if needed to ensure all desired analyses are performed within the mandated hold time. For specific detail of the handling protocols PVWMA and MBAS staff adhere to in handling laboratory water quality samples please refer to the Analyses Reference List on page 34 of Appendix A., MBAS Quality Assurance Manual Revision 11 – Effective October 2016.

PVWMA does not perform any in-house analysis of collected water samples.

No special handling or custody procedures beyond those outlined in the Analyses Reference List are needed. The chain of custody form is used as a shipping record.

MBAS disposes of the samples after analysis is completed and all analytical quality assurance/quality control measures are satisfied.

## 9. ANALYTICAL METHODS

Table 4 below outlines the field data measurement methods used as part of the PVWMA GMP.

**Table 4. Field Measurement Methods**

| Parameter            | Equipment to be Used | Measurement Unit   |
|----------------------|----------------------|--------------------|
| Depth to Water       | Sounder or Oil Tape  | Feet, Decimal Feet |
| pH                   | MP20 Flow Cell       | pH Units           |
| Dissolved Oxygen     | MP20 Flow Cell       | mg/L               |
| Specific Conductance | MP20 Flow Cell       | µg/L               |
| Temperature          | MP20 Flow Cell       | °C                 |

Please refer to Appendix B. of this QAPP, MBAS Analytical Standard Operating Procedures, for detail of the analytical methods used for laboratory analysis of water samples collected as part of the PVWMA GMP.

## 10. QUALITY CONTROL

### 10.1 MBAS Analytical Quality Control

MBAS performs quality control measures to maintain the analytical testing process within acceptable limits of accuracy and precision. Accuracy and reproducibility are the primary goals of MBAS's quality assurance and quality control plan. To ensure this, method blanks, laboratory control samples, second source samples, matrix spikes, duplicates, and replicates are analyzed as applicable to each analysis. Quality control requirements for each analytical technique are clearly outlined in Appendix B. MBAS Analytical Standard Operating Procedures of this QAPP. All MBAS analysts receive extensive training in these requirements.

Summarized below are the quality control checks that are used by MBAS to monitor performance. The frequency and acceptance criteria for each are outlined in MBAS's individual standard operating procedure for each method and can be found in Appendix B.

**Method Blank:** a sample of reagent water that is subjected to the method and includes reagents that are normally in contact with samples during the analytical method; used to monitor background values and contamination; equivalent to a Laboratory Control Blank (LCB) or a Laboratory Reagent Blank (LRB).

**Field Reagent Blank:** lab reagent water that is supplied to samplers to be processed in the field in the same manner as samples including any field preservation or filtering; used to monitor contamination during sample collection and transportation. Field blanks are analyzed by the lab when requested and submitted by the client.

Initial Calibration Verification (ICV): a calibration standard that is used to verify that the instrument has been successfully calibrated to produce results that meet acceptance criteria for accuracy of known analyte concentrations.

Continuing Calibration Verification (CCV): calibration standards that are used to verify that there is no significant change in the instrument performance since calibration.

Laboratory Control Standard (LCS): a sample of reagent water to which a known amount of analyte has been added; used to evaluate accuracy of the analytical method. The LCS is submitted to all steps of the analytical process and is equivalent to a Laboratory Fortified Blank (LFB).

Sample Duplicate: a second aliquot of sample that is tested to determine reproducibility of the analytical method.

Matrix Spike (MS): a known amount of analyte that is added to a sample. Recovery is measured to determine if there are any matrix effects; equivalent to a Laboratory Fortified Matrix (LFM).

Matrix Spike Duplicate (MSD) is used to determine reproducibility of the analytical method.

Quality Control Sample (QCS): a mid-range solution that is made from a different source than the calibration standards; used to evaluate correctness of instrument calibration.

## **10.2 Field Analytical Quality Control**

Field water quality data is collected using the flow cell water quality sonde and is collected after stabilization criteria are achieved. After purging the stagnant water in the well, an operator engages a sampling sequence in the sonde. The sonde compares parameter measurement deviations at the 30 second mark, 60 second mark, 90 second mark, and 120 second mark. If the sonde's stabilization criteria is met, the sonde signals the operator that stabilization was achieved at which point the readings are recorded and a water quality sample is collected. If stabilization is not met within the first four measurements, the sonde continues sampling at regular intervals until the stabilization criteria are achieved.

## **10.3 Water Level Quality Control**

Electric sounders and oil tapes are routinely cleaned to ensure operational integrity. To ensure the accuracy of each sounder and tape unit, a quarterly quality control check of all active sounders and tapes are performed by staff. The quality control check consists of staff measuring the depth to water of a single well with all active sounders to verify that all active sounders are within +/- 0.05 feet of the median measurement. Oil tape measuring instruments are measured against a new measuring tape to verify measurement accuracy. Any sounders or oil tapes deemed to be inaccurate in the quality control test are repaired if possible or disposed.

# **11. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE**

All water level sounders and oil tapes are inspected for damage and tested for functionality before use. Accuracy of the sounders and tapes are verified on a quarterly basis as described in the previous section.

Prior to any use or calibration, all water quality monitoring equipment are inspected for damage and any visible buildup of solids is cleaned.

It is best practice that immediately before use in the field, the flow cell sonde or other water quality instrument being used is calibrated. If a calibration of the unit has been performed within the previous two months, a calibration should be performed but is not necessary unless the unit's parameters appear to be drifting. A calibration is required if it has been more than two months since the last calibration.

pH measurement devices are calibrated against standards of 4, 7, and 10. After calibration the unit is checked against the pH 7 standard to verify an accurate calibration.

Dissolved oxygen devices are calibrated by creating a 100% saturated environment as directed by the instrument manuals but may be calibrated to known standards.

Conductivity devices are calibrated to a known standard of either 1,000  $\mu\text{S}/\text{cm}$  or 1,413  $\mu\text{S}/\text{cm}$ . A standard of higher or lower conductance may be used if the water to be measured is of comparable concentration.

Temperature devices are not calibrated by PVWMA staff. PVWMA staff verify that the measured temperature values appear valid prior to use.

When any device cannot be calibrated or appears to be failing, it is retired and a replacement sensor or device installed. Staff keep track of the service life of all sensors and attempt to replace sensors prior to the end of the expected service life.

MBAS maintains calibration practices that follow the standard operating procedures for each analytical method and are outlined in Appendix B.

## **12. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES**

Supplies such as pH standards, conductivity standards, and new field devices are examined for damage upon receipt. Signed certificate of analysis from the supplier/manufacture should be included for all new devices and standards.

MBAS inspects all supplies and consumable materials upon arrival and verify the validity of the certificate of analysis.

## **13. NON-DIRECT MEASUREMENTS**

Non-direct field water quality, laboratory water quality, and water level measurements collected by individuals other than PVWMA staff are incorporated in the PVWMA databases and spreadsheets if comparable measures of precision and accuracy are used in obtaining the data. All non-direct data added to PVWMA databases and spreadsheets identify the supplying source in the notes section of each record. Non-direct data that are not collected with comparable accuracy and precision are included in PVWMA databases and spreadsheets but are retained in a supplementary location for future reference.

## **14. DATA MANAGEMENT**

Data are maintained as outlined in Section 5, Documents and Records, above. PVWMA maintains a digital archive of all fieldsheets and form data used in the collection of water quality and water level data for reference on PVWMA servers. PVWMA's databases and spreadsheets are located on the agency's servers which are backed up to tape on a nightly basis. Back up tapes are taken offsite daily and retained for a period of three weeks. The PVWMA databases and spreadsheets are only updated by the Water Resources Technician, Associate Hydrologist, or General Manager/Hydrogeologist. Access to the agency servers is limited to users with administrator authority only.

MBAS maintains record of all analysis results in electronic format indefinitely and can be accessed by PVWMA staff through the MBAS website customer login page.

## **15. ASSESSMENTS & RESPONSE ACTIONS**

Reviews of field water quality data collection, water level data collection, and samples for laboratory analysis are performed by the QA Officer. The QA Officer also conducts reviews of measurement and sampling procedures on an annual basis. Any observed deviations by PVWMA staff persons from the procedures outlined in this QAPP are

remedied immediately. Notation of any potential data record issues are noted in the applicable database records, fieldsheets, or monitoring forms.

MBAS executes performance and system audits on a regular basis. External audits include California State Environmental Laboratory Accreditation Program (ELAP) compliance audits every two years and routine proficiency testing studies. Internal audits include individual performance reviews held at least annually and quality assurance reports to be conducted quarterly. For further detail of MBAS audits please refer to page 24 of Appendix A., MBAS Quality Assurance Manual Revision 11 – Effective October 2016.

## **16. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS**

Data generated from PVWMA GMP monitoring activities that follow the procedures, quality assurance measures, and quality controls outlined in this QAPP are utilized by PVWMA for planning and reporting activities and are maintained in the agency databases. Data generated either internally by agency staff or from non-direct measurements that do not adhere to the standards outlined in this QAPP are retained by PVWMA staff in a supplementary location.

## **17. VERIFICATION AND VALIDATION METHODS**

All field water quality measurements and water level measurements are reviewed by the data collector prior to being included in the PVWMA databases. Analytical results provided by MBAS are visually scanned to identify any potential erroneous data. Analytical results from MBAS are also be evaluated by database import tools that flag anomalous data. For any anomalous data, a PVWMA staff person confirms the value or corrects it if it is an error. For accurate anomalous data, the staff person makes note of the occurrence in the notes field of the data record.

**APPENDIX A. MBAS QUALITY ASSURANCE MANUAL – REVISION 11, EFFECTIVE OCTOBER 2016**



# Quality Assurance Manual

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Revision 11 – Effective October 2016



# Quality Assurance Manual

For

Monterey Bay Analytical Services, Inc.

## Revision 11

This manual has been reviewed and is determined to be accurate and appropriate for the scope, volume, and range of testing activities in the laboratory. Furthermore, management at MBAS is committed to ensuring that the quality system defined in this Quality Assurance Manual is implemented and followed at all times.



David Holland, Lab Director

October 24, 2016

Date

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## Introduction and Scope

Monterey Bay Analytical Services (MBAS) was established in April 1999 to provide laboratory services to the residents of Monterey County and the surrounding areas. MBAS primarily focuses on water quality testing and offers a wide array of analyses for drinking water and wastewater as well as agricultural and surface waters.

MBAS offers analysis of the following fields:

- Microbiology
- Inorganic chemistry
- Physical properties

MBAS is a California State Certified Environmental Laboratory that provides water and wastewater analyses in support of the Safe Drinking Water Act and the National Pollution Discharge Elimination System. As such data quality is vitally important. A copy of the Lab Certification and Accreditation is included as Appendix A.

## Quality Policy Statement

MBAS is committed to providing results that are scientifically sound and legally defensible. MBAS continuously strives for precision, accuracy, and dependability in every aspect of the services we provide. It is the responsibility of the managers and the analysts to ensure that data produced is well documented and meets the expected level of standards.

## Quality Assurance Objectives

Quality assurance (QA) is the systematic program that outlines the measures required to meet the lab's defined standards of quality, or QA objectives. The QA program includes quality control, quality assessment, and quality improvement. Quality assurance involves all steps of the data collection processes including sample collection, receiving, and holding; equipment maintenance; and data reduction, validation, and reporting.

Quality assurance also requires a thorough understanding of the client's quality assurance and reporting requirements. Data Quality Objectives (DQOs) are the specific criteria for the quality of data to be collected and the decisions to be made based on that data. If a client communicates specific DQOs for a project, the lab will strive to meet or exceed those DQOs.

## Scope

This Quality Assurance Manual describes the policies and procedures followed at MBAS to achieve the quality goals stated in the quality policy. It covers sample collection, handling, and receipt; sample preparation; analysis; and reporting.

Each member of the laboratory staff has the responsibility to understand and comply with all statements in this manual and to follow all written standard operating procedures.

## Laboratory Organization and Responsibilities

An effective quality assurance (QA) program requires participation and diligence from all laboratory personnel. Each member of the team must understand his/her role in the QA plan to ensure that the laboratory runs smoothly and meets its quality standards and goals.

### Analyst Responsibilities

Analysts are required to know and understand the quality control (QC) requirements for each test they perform. These are outlined in the Standard Operating Procedure (SOP) for each method. Analysts must understand which QC solutions and calibration solutions are required, how to make the solutions, how often they must be analyzed, and the acceptability limits for accuracy and reproducibility.

Other analyst responsibilities include:

- Maintaining a working knowledge of the QA plan
- Understanding and following the written SOPs
- Writing, reviewing, and updating SOPs as necessary with approval of the Lab Directory
- Completely and accurately documenting all work on bench sheets
- Immediately notifying management of QC problems
- Meeting hold-times

### QA Manager Responsibilities

It is the QA manager's responsibility to ensure that the QA/QC plan as outlined in this QA manual is being followed at all times by all laboratory staff. This involves the following responsibilities.

- Developing, evaluating, and implementing laboratory methods
- Reviewing SOPs and assisting with SOP updates
- Overseeing QA/QC practices
- Reviewing QC results
- Monitoring and prescribing corrective actions as necessary in coordination with the lab director
- Conducting data quality and laboratory performance audits
- Recommending QC training for laboratory personnel as necessary
- Reviewing the QA manual at least annually and recommending QA policies to the lab director
- Maintaining physical and electronic records
- Monitoring overall laboratory performance and turnaround times

### Lab Director Responsibilities

Ultimately, the lab director is accountable for all data generated in the laboratory as well as all operational activities. Specific QA responsibilities include:

- Developing laboratory policies and procedures
- Having final authority on all procedures and approval of SOPs
- Auditing the QA plan periodically to ensure all objectives are being met
- Coordinating with QA manager with revising and implementing QA plan
- Coordinating with QA manager with determining and implementing corrective actions

- Reviewing laboratory data and reports for completeness, precision, and accuracy
- Conducting individual performance reviews and communicating quality and performance expectations

### Laboratory Organization

All analysts are to report any QA/QC issues to the QA manager and follow received instruction from the QA manager. The QA manager reports directly to the lab director. Figure 1 below displays a graphical representation of the basic chain of command.

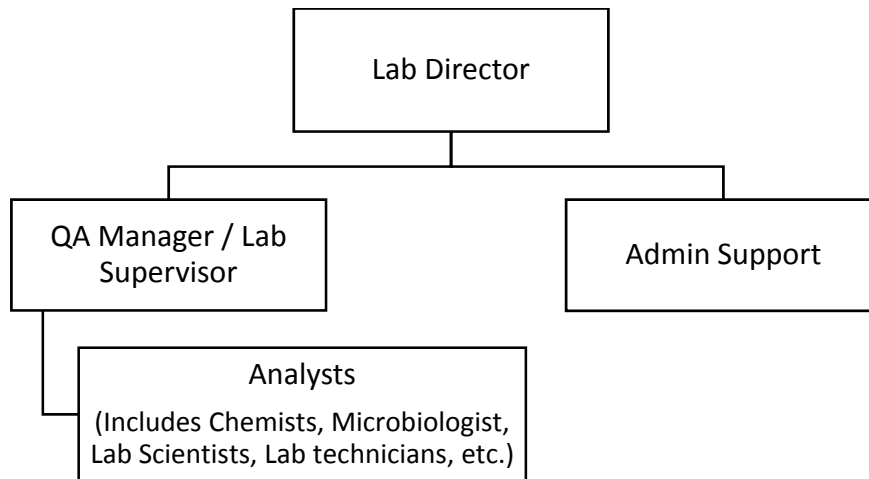


*Figure 1: Laboratory Organizational Chart*

Figure 2 below displays current breakdown of laboratory organization and analytical responsibilities.

|                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                          |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p style="text-align: center;"><b>David Holland</b><br/>Lab Director<br/>Chemical Hygiene and Safety Officer</p>                                                                                                                                           |                                                                                                                                                                                                                                          |
| <p><b>Sarah McGinnis</b><br/>Lab Supervisor   QA Manager</p> <ul style="list-style-type: none"> <li>• ICP MS and ICP OES</li> <li>• Special reporting, Geotracker</li> <li>• Lims Administrator</li> </ul>                                                 | <p><b>Mason Weidner-Holland</b><br/>Administrative Support   Accounts Specialist</p> <ul style="list-style-type: none"> <li>• Reporting and invoicing</li> <li>• Customer services</li> <li>• Sample Collection</li> </ul>               |
| <p><b>Mollie Wooden</b><br/>Laboratory Scientist   Microbiologist</p> <ul style="list-style-type: none"> <li>• Ion Chromatography and TOC</li> <li>• Microbiology</li> <li>• ICP OES</li> <li>• EDD reports-CEDEN, SWAMP</li> </ul>                        | <ul style="list-style-type: none"> <li>• <b>Ben Sanchez</b></li> <li>• Laboratory Scientist <ul style="list-style-type: none"> <li>• Sample Control</li> <li>• Colorimetric analyses</li> <li>• Sample collection</li> </ul> </li> </ul> |
| <p><b>Lilian Reyes Hernon</b><br/>Laboratory Scientist</p> <ul style="list-style-type: none"> <li>• Colorimetric analyses</li> <li>• Titrimetric analyses</li> </ul>                                                                                       |                                                                                                                                                                                                                                          |
| <p><b>Hayden Maccagno</b><br/>Laboratory Scientist</p> <ul style="list-style-type: none"> <li>• Gravimetric analyses</li> <li>• Colorimetric analyses</li> <li>• Sample collection</li> <li>• Ion Chromatography</li> <li>• Write On Submission</li> </ul> |                                                                                                                                                                                                                                          |
| <p><b>Michelle Plum</b><br/>Laboratory Scientist</p> <ul style="list-style-type: none"> <li>• Sample Control</li> <li>• Colorimetric analyses</li> <li>• Sample collection</li> </ul>                                                                      |                                                                                                                                                                                                                                          |

## Analyst Training and Performance Requirements

Analysts receive training for every analytical method that they are expected to perform. Training includes individual analyses but also extends to laboratory safety practices, data entry, generating QC reports, and QA/QC requirements.

Training is conducted by a qualified analyst who has shown proficiency in the analytical procedures and a clear understanding of the method as determined by management. Before an analysts is deemed trained in a particular analysis, the analyst must pass all parts of the Initial Demonstration of Capability. This includes demonstrating:

- Adequate knowledge of the method
- Knowledge and understanding of the written SOP
- Knowledge of and compliance with safety protocols for the method
- Knowledge of the QC requirements for the method
- Ability to perform and properly document all routine maintenance checks for the associated equipment
- Ability to correctly perform all steps of the SOP
- Proper preparation of standards and reagents used in the method
- At least 4 consecutive acceptable QC results demonstrating accuracy and precision or another demonstration of capability

After an analyst has been trained and has demonstrated capability, the analyst is expected to continue meeting QC requirements for accuracy and precision. Performance will periodically be reviewed by management and further or ongoing training prescribed as deemed appropriate.

Analysts should continue to strive for improvement in technique, knowledge, and application of the analytical methods in which they have been trained. All analysts are encouraged to obtain California Water Environment Association (CWEA) Lab Analyst certifications which require proof of continuing education credits.

## Sample Collection

Quality assurance includes proper collection and handling of all samples regardless of whether they are collected by laboratory personnel or the client. This includes collecting samples in the correct containers, proper labeling of sample containers, completing the chain of custody/analysis request form, holding samples at the correct temperatures, and meeting hold times. Information on hold times, containers, and storage conditions can be found in the Analysis Reference List (Appendix B).

Sample collection is a coordinated effort between the client and the laboratory. The laboratory will provide clients with appropriate sample containers and sample collection and preservation instructions. Clients are expected to fully comply with these instructions and to follow the proper sampling procedures.

Laboratory personnel conducting field collection are first required to complete training in field sample collection as well as training for all field tests they will be required to perform. Staffs must then be

approved by the laboratory director before they can collect samples in the field. Training records are maintained by the Director.

### Sample Labels

All samples submitted for testing should be appropriately labeled. Sample containers provided by our laboratory have a suitable label which should be filled out legibly with indelible ink at the time of sampling by the sample collector. The following information must be provided on all sample containers:

- Sample identification – submitter's identification of the sample (e.g., well number, system ID)
- Location – an address or brief description of where the sample was taken
- Time and date of sample collection
- Name of sample collector
- Any preservatives

### Chain of Custody

A Chain of Custody (COC) form is an analysis request form and a completed COC should accompany all samples (see Appendix C). The COC should be filled out legibly with indelible ink. The COC must include the following information:

- Submitter's name and address
- Contact phone number
- Sample identification
- Location of sample collection
- Time and date of sample collection
- Sample matrix (drinking water, wastewater, storm water, etc.)
- Analyses to be performed
- Signatures of persons involved in the collection and chain of possession, including dates of possession
- Any subsampling should be noted

Regulatory drinking water samples have additional requirements for reporting purposes:

- The system name should be included
- The system ID number and source number must be included
- Coliform samples must be identified as Other, Routine, Repeat, or Special

### General Sampling Guidelines

Proper sample collection and handling is important to obtaining accurate and reliable results as improper sample collection can have undesired influences on analytical results. The Analyses Reference List (Appendix B) contains information on sample container and hold time requirements.

While some sampling events may require special handling, there are several general guidelines that can be applied to most sample collecting:

- Clearly fill out the sample label so that samples are clearly identified – this will help avoid confusion later
- Avoid contaminating the bottle or sample in any way – this is particularly important for bacteria samples and organic carbon determinations but should be applied to all sampling
  - Do not touch the inside of the cap or bottle
  - Be careful not to drop the cap
  - Avoid contact with the water that is being collected
  - Replace the cap quickly after sampling
- Return samples to the laboratory as soon as possible
- If samples cannot be submitted to the lab within one hour of collection, keep samples cold
  - Refrigerate samples and transport them in a cooler with ice
- If containers are cracked or appear to be leaking, resample in a new container

Additional sampling instructions are available in the laboratory for samples requiring certain analyses such as coliform analysis or volatile organic chemicals determination. Refer to these instructions prior to sample collection.

## Laboratory Sample Receipt and Handling

Proper handling and storage of all samples is an important aspect of the QA plan and is vital to ensuring valid and reliable results. Guidelines on sample receipt and handling can be found below.

### Sample Receipt

When samples are received at the lab, the receiving staff member must ensure that the COC is completed, samples are labeled and in the proper containers, samples are properly preserved, and that holding times can reasonably be met by the analysts. If hold time, temperature, or sampling violations occur, the client must be informed and asked how to proceed. If the client wishes to continue with analysis, the violation must be noted on the COC and the client instructed on how to correct the issue for future sampling.

Before accepting a sample, review the COC with the client. Be sure to ask the following questions and make sure that the COC matches the client's answers.

1. Is the sample for regulatory compliance?
2. To which agency are the results to be submitted?
  - a. If the samples require Electronic Data Transfer (EDT), make sure that the source number and system numbers are recorded
3. What analytes are to be tested?

- a. If the sample is regulatory drinking water, make sure that the source number and system numbers are recorded and that coliforms are identified as Other, Routine, Repeat, or Special
  - b. If bacterial analyses are requested, make sure it is clear whether the client wants a Present/Absent (P/A) determination or a Most Probable Number (MPN or QT)
4. Do you want regular turnaround time?
  - a. Be sure to inform the client of additional charges for rush analyses if this is selected.
5. Are there any special requests or other special requirements?
6. When were the samples collected?

Make sure that the information on the sample labels match the information on the COC. If there is any discrepancy between the samples and the COC notify the client immediately and make note of the correction on the COC.

Next, use the infrared (IR) thermometer to measure the temperature of each sample. Samples submitted to the lab within two hours and samples submitted for just metals determination have no temperature requirements. Bacteria samples submitted after two hours of collection must be below 10 °C. Samples collected for chemical analyses must be below 6 °C. Note any temperature violations on the COC and inform the client.

Laboratory personnel receiving samples must sign and date the COC. Make sure that any special requests made by the client are recorded under the comments section of the form and that the client has also signed the COC.

### Sample Preservation and Handling

Proper sample preservation and handling is an essential part of the QA plan. If samples are not properly handled, it is possible for the biological and/or chemical composition of the sample to change prior to analysis. Sample preservation, including refrigeration, should be performed as quickly as possible after sample receipt to ensure the integrity of the sample.

After samples have been received, they must be preserved according to the analytical methods to be performed on the samples. Each analytical method has different preservation requirements. These are summarized in the Analysis Reference List (Appendix B). The staff member who received the samples is responsible for making sure that the sample is preserved. If samples have been preserved by the client or collected in pre-preserved containers, the receiving staff member should check that the sample have been properly preserved (generally by checking the pH of the sample) before storing them.

If a sample requires any preservation beyond refrigeration, this should be noted on the COC by the staff member who preserves the sample.

The best results are obtained by immediate analysis. However, if immediate analysis is not possible, all samples other than samples requiring only metals analysis should be stored in the refrigerator at 4°C ± 2°C when not in use. Many analytical methods require that the sample be tested at room temperature; in this case, the samples should be brought to room temperature before analysis and returned to the refrigerator after analysis.

### Sample Logging

Upon receipt all samples must be entered into the Laboratory Information Management System (LIMS) software which will assign each sample a lab ID # and maintain record of pending analyses. When logging samples into the software, be sure to include the proper client code, sample identification information, sampling date, sampling time, requested analyses and the name of the sampler. If the sample is a drinking water sample for regulatory purposes, include the system ID number and source number. Also include the coliform designation (Routine, Other, Repeat, or Special) as applicable.

Once the samples have been submitted to the LIMS software, it will assign each sample a lab ID # and print new sample labels that contain that ID#. Affix the new sample label to each sample container and record the lab ID # on the COC.

### Calibration and Measurement Procedures

Calibration is the process of comparing instrument readouts to known concentrations of an analyte of interest. This data, when plotted graphically, is referred to as a calibration curve. Correct calibration is crucially important to achieving accurate and reliable analytical results.

Calibration must be conducted under the same instrumental and chemical conditions as those that will exist during the measurement process for samples. Calibration accuracy is severely dependent on the reliability of the standards used for the required comparisons. Only the highest quality chemicals are used to provide necessary standard solutions and due care is exercised in their preparation.

Calibration procedures for each method are outlined in the SOPs as well as the working range for each analysis. For most inorganic chemistry analyses, general guidelines for calibration apply. A minimum of three dilutions of standard are to be used for calibration. The calibration should bracket the expected concentration values for the samples; the lowest calibration solution should be equal to the reporting limit and no values should be reported above the highest calibration solution. The calibration curve must achieve a correlation coefficient of 0.995 or greater.

Routine calibration for most analyses involves the process of direct comparison and can be used with many instruments to give a direct readout of the analyte concentration. With direct comparison, calibration standards are prepared at a range of concentrations using laboratory reagent water and the calibration standards are then analyzed to make a calibration curve. All other measurements are then compared to the calibration curve and analyte concentrations are extrapolated. Generally the instrument does this and displays the resulting analyte concentration.

Calibration by standard additions may be used as indicated by the method when a sample contains severe matrix interferences. In this case, small amounts of standard solution are added in increasing amounts to aliquots of the sample. A calibration graph can then be constructed. This method is often used with samples that have a complex matrix and where spike recoveries have been unacceptable low.

Some analyses, such as pH, electrical conductance, and dissolve oxygen (DO) have different guidelines for calibration. Always refer to the SOP for calibration instructions.

The proper calibration of pH meters requires the use of two buffer solutions. The pH meters are typically calibrated with a pH 4 buffer solution and a pH 7 buffer solution. A buffer solution of pH 10 is available when necessary. The calibration is then checked with a separate lot buffer. Refer to the SOP for pH determinations for more information.

Many analyses employ the use of calibration verification solutions and second source solutions to check the continued accuracy of the calibration curve. These checks are performed in accordance with the individual SOPs.

The frequency of calibration depends on the accuracy requirements of the method and the stability of the instrument used for the measurements. Some analyses require daily calibration while others require weekly, monthly, or other specified periods between calibrations. Some instruments only require calibration as necessary, reliant upon the accuracy and precision of continuing calibration and other QC checks. Refer to the individual method and its SOP for guidelines on calibration frequency.

## Analytical Procedures

MBAS employs methods approved by the California State Environmental Laboratory Accreditation Program (ELAP). A full list of analyses for which MBAS is California State ELAP certified can be found in the Lab Certification and Accreditation document (Appendix A). The method used for each procedure can be found in the Analysis Reference list (Appendix B).

Analysts are expected to follow the instructions outlined in the written SOP for each analytical procedure. Analysts are also expected to periodically review the written SOPs to ensure correctness and to update SOPs if necessary under the approval of the Lab Supervisor.

Each time an analytical procedure is performed quality controls are included. Duplicate samples, known additions, and known controls are routinely tested as outlined in the SOP to ensure accuracy and precision of the method.

## Subcontracted Analyses

MBAS subcontracts analyses only to labs that are fully certified for the intended analyses and that have the same level of commitment to quality as MBAS. The lab director is responsible for approving all laboratories used for subcontracted analyses.

When processing samples that are to be subcontracted to another laboratory, the analyst responsible for preparing the samples must ensure that all containers are appropriately labeled and a completed COC for that laboratory is included. This COC should include:

- MBAS lab ID number
- Original sample identification
- Sample matrix
- Sample date and time
- Required analyses

- System number and source number if applicable and sample requires EDT reporting
- Signature of approval from the lab director or appropriate management

Care must be taken to ensure that coolers are packed tightly and with enough ice to maintain the proper temperature of the sample throughout transit.

Subcontracted results are received with QC reports that are carefully reviewed before the data is released to our clients.

## Data Reduction, Validation, and Reporting

Proper recording, reduction, and reporting of data is an essential part of producing accurate and reliable results. Analysts must understand how to complete bench sheets, how to perform any necessary calculations or conversions, any applicable rounding rules for the analysis, and how to report the data with the appropriate number of significant figures or decimal places.

### Data Reduction

Data reduction is the mathematical process of converting raw numerical values into meaningful results with the proper significant figures and units.

Most of the instruments and equipment in the laboratory are programmed to display results in the appropriate units with any conversion factors or equations already calculated. Very few methods in the lab require the analyst to use equations to convert raw data into results. For these methods, the analyst must carefully follow the instructions set in the written SOPs and demonstrate the ability to properly perform the calculations.

For coliform counts, the analyst must refer to charts to determine the most probable number (MPN) based on the number of positive wells observed in the Quanti-Trays or positive tubes for multiple tube fermentation (MTF) technique. The Idexx MPN Generator software program may also be used to determine the MPN when using the Idexx Quanti-Trays.

When samples have been diluted, returned values must be multiplied by the dilution factor. This should be done before any rounding is performed.

Each analytical method has its own requirements for the number of significant figures or decimal places to which the data is reported. This is to be consistent with the method's limit of uncertainty. Reporting requirements are outlined in the standard operating procedures (SOPs). Some analyses such as turbidity and color have specific rounding requirements; these are also detailed in the SOPs.

### Detection Limits

Detection limits are determined for each analysis performed in the laboratory. It is imperative that all analysts understand the different detection limits.

**Instrument Detection Limit (IDL):** the lowest signal that the instrument can reliably detect above the background noise of that instrument.

**Method Detection Limit (MDL):** the lowest concentration of analyte that can be identified and measured with 99% confidence that the concentration is greater than zero.

**Minimum Level (ML):** the lowest concentration at which an acceptable calibration point can be achieved. Generally, the ML is equal to the lowest calibration point for a procedure.

**Practical Quantitation Limit (PQL):** the lowest level that can be reliably quantified during routine laboratory operation within the specified accuracy and precision limits. The PQL is determined by multiplying the minimum level (ML) by the dilution factor.

**Reporting Limit / Reporting Level (RL):** the level at which results are reported; this is equal to the PQL.

Values at or above the reporting limit (PQL) are reported to the appropriate number of significant figures or decimal places as described in the SOP. Values below the reporting limit are reported as Non Detect (ND) or < PQL. Reporting limits are detailed in the SOPs and are also included in the Analysis Reference List (Appendix B).

In special cases, when requested by the client, the numerical value for data that is above the MDL but below the PQL may be entered. This is then qualified with a **j** flag to indicate that it is an estimated value. See Appendix D for more information on data qualifiers.

#### Detection Limits

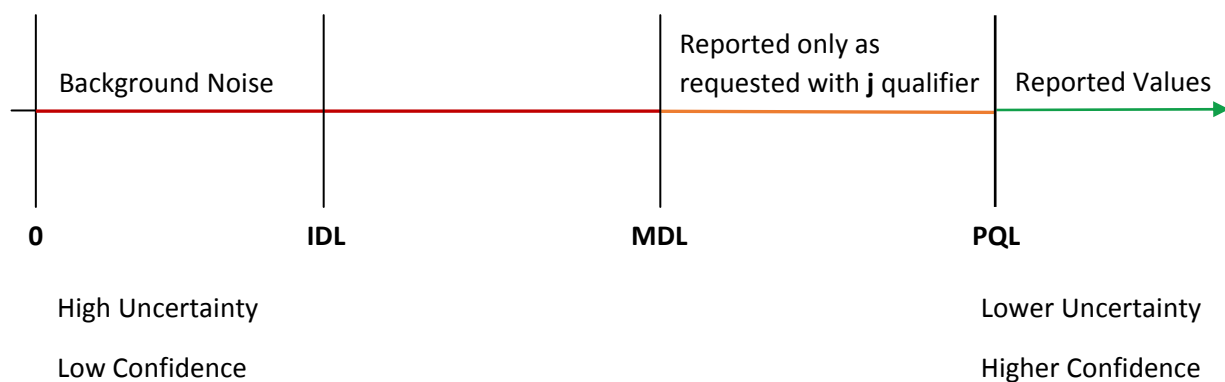


Figure 2: Graph of Detection Limits

#### Data Validation

Certain correlation checks are routinely performed to determine the correctness of analyses. The ratios of certain analytical determinations have expected theoretical ranges for natural waters. Some of these are outlined in Standard Methods section 1030 E.

One of these is the measured total dissolved solids to measured specific electrical conductance (TDS/SEC) ratio. This ratio is expected to fall within the range of 0.55 and 0.70.

Anion and cation sums should balance; ideally the ratio of the anion sum to the cation sum should be 1. The lab's set tolerance criteria is  $\pm 10\%$  for drinking waters and  $\pm 20\%$  for agricultural and unknown waters. Similarly, the anion and cation sums can be compared to the measured SEC as follows.

$$100 \times \frac{\text{anion or cation sum } (\frac{\text{meq}}{\text{L}})}{\text{SEC}} = 0.9 \text{ to } 1.1$$

These ratios will be calculated by the Laboratory Information Management System (LIMS) software when all of the data involved has been entered for a sample. For example, the TDS/SEC ratio will be calculated once the results for both TDS and SEC have been entered. See below for more information on data reporting.

If a correlation check falls outside of the expected ranges and one of the analyses is suspect, reanalyze. If the correlation check continues to fail, management should review the data to determine acceptability or request reanalysis. Additional correlation checks may be used in identifying the problem. One such example would be the ratio of the measured SEC to the calculated SEC. More information on these types of correlations checks can be found in Standard Methods 1030 E.

### Data Reporting

Data must be entered into the LIMS software before a report can be generated. Care must be taken to ensure that values are entered with the correct number of significant figures or decimal places and that values below the reporting limit is entered appropriately.

When entering results into the LIMS software, be sure that that date of analysis, analyst initials, and the appropriate dilution factor are also entered. By selecting Detailed Edit for a particular result, additional information such as data qualifiers or comments may also be added.

After all analytical data has been entered for a particular sample, a report can then be generated. This is done through the LIMS system.

All sample reports include:

- Sample identification including the lab ID number, system and source numbers if applicable, and the sample description as provided by the client
- Date and time of sample collection
- Name of the sampler
- Analyte name and method
- Date of analysis
- Result
- Units of concentration
- Reporting level
- Initials of the analyst
- Any data qualifiers if necessary

Reports should be reviewed for accuracy and completeness before being released to the client. Certain data packages require review by management before they can be released.

## Internal Quality Control

Quality control (QC) is defined as the routine procedures undertaken in the laboratory to maintain the analytical testing process within acceptable limits of accuracy and precision.

Accuracy and reproducibility are the primary goals of the QA/QC plan. To ensure this, method blanks, laboratory control samples, second source samples, matrix spikes, duplicates, and replicates are analyzed as applicable to each analysis. QC requirements for each analytical technique are clearly outlined in the SOPs and all analysts receive extensive training in these requirements.

### Chemistry QC Checks

The following QC checks are used in the lab to monitor performance. The frequency and acceptance criteria for each are outlined in the individual SOP for each method.

**Method Blank:** a sample of reagent water that is subjected to the method and includes reagents that are normally in contact with samples during the analytical method; used to monitor background values and contamination; equivalent to a Laboratory Control Blank (LCB) or a Laboratory Reagent Blank (LRB).

**Field Reagent Blank:** lab reagent water that is supplied to samplers to be processed in the field in the same manner as samples including any field preservation or filtering; used to monitor contamination during sample collection and transportation. Field blanks are analyzed by the lab when requested and submitted by the client.

**Initial Calibration Verification (ICV):** a calibration standard that is used to verify that the instrument has been successfully calibrated to produce results that meet acceptance criteria for accuracy of known analyte concentrations.

**Continuing Calibration Verification (CCV):** calibration standards that are used to verify that there is no significant change in the instrument performance since calibration.

**Laboratory Control Standard (LCS):** a sample of reagent water to which a known amount of analyte has been added; used to evaluate accuracy of the analytical method. The LCS is submitted to all steps of the analytical process and is equivalent to a Laboratory Fortified Blank (LFB).

**Sample Duplicate:** a second aliquot of sample that is tested to determine reproducibility of the analytical method.

**Matrix Spike (MS):** a known amount of analyte that is added to a sample. Recovery is measured to determine if there are any matrix effects; equivalent to a Laboratory Fortified Matrix (LFM).

Matrix Spike Duplicate (MSD) is used to determine reproducibility of the analytical method.

**Quality Control Sample (QCS):** a mid-range solution that is made from a different source than the calibration standards; used to evaluate correctness of instrument calibration.

Table 1 below summarizes many of the QC checks that MBAS uses. Further information for the type of QC used for each method can be found in the individual SOPs and in the chart provided in Appendix E.

| Acronym | Name                                      | Description                                    |
|---------|-------------------------------------------|------------------------------------------------|
| ICVB    | Initial Calibration Verification Blank    | Blank after calibration                        |
| CCVB    | Continuing Calibration Verification Blank | Blank after spikes/dups                        |
| ICV     | Instrument Calibration Verification       | Mid-range calibration standard                 |
| ICVL    | Instrument Calibration Verification Low   | Low-range calibration standard                 |
| ICVH    | Instrument Calibration Verification High  | High-range calibration standard                |
| QCS     | Quality Control Standard                  | Second source mid-range standard               |
| MS      | Matrix Spike                              | Mid-range calibration spike                    |
| MSD     | Matrix Spike Duplicate                    | Mid-range calibration spike                    |
| CCV     | Continuing Calibration Verification       | Mid-range standard                             |
| Dup     | Sample Duplicate                          | Client sample duplicate                        |
| GGA     | Glucose Glutamic Acid                     | BOD QC                                         |
| LCB     | Laboratory Control Blank                  | Digested/extracted/filtered blank              |
| LCCB    | Laboratory Control Continuing Blank       | Digested/extracted/filtered blank              |
| LCS     | Laboratory Control Standard               | Digested/extracted/filtered mid-range standard |
| LCSD    | Laboratory Control Standard Duplicate     | Digested/extracted/filtered mid-range standard |
| LCSL    | Laboratory Control Standard Low           | Digested/extracted/filtered low-range standard |

*Table 1: Summary of Typical Chemistry QC Check Types*

**Internal Standard:** a solution of compounds that analytically behave similarly to the analytes of interest. Internal standards are added to all blanks, standards, and samples prior to analysis to determine the response factors used in calculating analyte concentrations.

Internal standards are used in metals determination by ICP-MS and are also monitored as a continuing instrument performance check. If the recovery of the internal standards falls outside of the acceptance range of 60-125%, analysis is halted and corrective actions are performed.

**Method Detection Limit (MDL) study:** a study to determine the lowest concentration of analyte that can be identified and measured with 99% confidence that the concentration is greater than zero.

MDL studies are conducted by analyzing at least seven replicates of a low-level analyte solution over the course of at least three days. This low-level solution should be one to five times the estimated MDL and be subjected to all steps of the analytical process including digestion where applicable. Guidelines for the MDL study are as follows:

- Recovery for each replicate should be 50% - 150%
- Relative standard deviation (RSD) should be between 10%-20%

- MDL =  $t$  value x standard deviation ( $s$ );  $t = 3.14$  for 7 replicates
  - For 7 replicates, MDL =  $3.14 \times s$
- The calculated MDL should be greater than 10% of the analyte concentration and less the analyte concentration.

If the MDL study is unsuccessful, choose a new analyte concentration and perform the study again. MDL studies should be conducted with the frequency required by the SOP.

**Proficiency Testing (PT) study:** a set of blind samples that the laboratory analyzes under typical laboratory conditions; the results of the analyses are then compared to the published concentrations.

MBAS routinely participates in proficiency testing (PT) programs. These PT studies are an essential part of evaluating analytical methodology and is an important part of the QA program. MBAS participates in the following PT studies:

- Water Supply (WS) study for drinking water samples
- Water Pollution (WP) study for wastewaters and other polluted waters
- Microbiology study

### Microbiology QC Checks

In addition to the PT study samples, microbiology QC checks include the following:

**Sterility Controls:** Sterile media is placed in incubator for 48 hours and monitored for growth.

**Positive Culture Controls:** Media is inoculated with bacteria and watched for expected reaction

**Negative Culture Controls:** Media is inoculated with bacteria and watched for expected reaction

### Preventive Maintenance

As part of the QA plan, MBAS has a comprehensive preventive maintenance program. All of our instruments undergo routine maintenance and accuracy checks by a manufacturer's representative or by laboratory personnel as described below. Adequate spare parts are kept on hand to perform routine maintenance and minimize downtime. Manufacturer's instructions and service manuals are readily accessible.

All preventive maintenance performed in-house is documented on instrument maintenance logs. Maintenance logs include dates and results of all routine maintenance checks along with the initials of the analyst performing the checks. Maintenance procedures such as replacing parts or refilling internal solutions according to manufacturer instructions should also be noted in the maintenance logs along with the date and analyst initials.

Instruments that undergo routine professional maintenance have labels affixed to indicate the date of the last servicing. Equipment records documenting preventive maintenance and emergency servicing/repairs are kept for a minimum of three years.

## Thermometers

The accuracy of thermometers and temperature recording devices are checked annually against a certified National Institute of Standards and Technology (NIST) thermometer or one traceable to NIST and conforming to NIST specifications. All thermometers are labeled with the date of calibration and the correction factor. [Replace thermometers with > 0.5 degree error]

## Balances

Accuracy of the analytical balances is verified each month using four ASTM type 1 or 2 reference weights; the weights used for this are 0.1000 g, 1.0000 g, 10.0000 g, and 100.0000 g weights. Furthermore, prior to use for certain analytical procedures, the accuracy of the analytical balances are checked and noted on the bench sheets. Calibration is performed as necessary.

Accuracy of the top-loading balance is verified each month using 1.00 g, 10.00 g, and 100.00 g weights. Accuracy checks for all balances are documented in the balance maintenance log book. Additionally, all balances are serviced and certified annually through a maintenance contract.

## pH Meters and Other Probes

### pH Meters

Preventive maintenance for the pH probes includes cleaning and changing the internal solution. Be sure that there is always adequate internal solution prior to analysis. If the fill solution needs to be changed or refilled, be sure to allow the probe at least 30 minutes to stabilize prior to use. If organic buildup is noticed on the probe, particularly near the junction point, the probe requires cleaning; follow the manufacturer instructions for cleaning the probe. Always check to be sure that there is adequate storage solution.

pH meters are to be calibrated daily with two pH buffers, generally of pH 4 and pH 7. The slope of the calibration should be 100%. Poor slope, unacceptable recovery of the QC buffer solution, or slow response may indicate that the probe needs cleaning.

Calibration results and any preventive maintenance performed is to be recorded in the maintenance log book for the pH probes along with the date and analyst initials.

### Dissolved oxygen (DO) Probes

When the % Slope falls outside the range of 5.9-12.6 or the current falls out of the range of 8.0-17.0  $\mu$ A, the probe may need new fill solution or a new membrane. Record the type of maintenance performed, date, the lot number of the new solution or membrane, the slope value, the current, and the analyst initials in the maintenance log whenever either action is taken.

### Ammonia Probe (Selective Ion Probe)

When the slope falls outside the range of -59 mV/decade  $\pm$  4 mV/decade, change the fill solution and let the probe soak in the storage solution overnight. If the probe continues to calibrate outside the acceptable range, change the membrane and fill solution. Record the type of maintenance performed, date, the lot number of the new solution or membrane, and the analyst initials in the maintenance log

whenever either action is taken. If the probe will not be used for more than a week, then the probe is stored dry.

### Water Purification System

Conductivity of both the reverse osmosis (RO) and deionized (DI) water is checked monthly. A heterotrophic plate count on the DI water is also performed monthly. Filters are changed as indicated by the conductivity readings and the heterotrophic plate count. Records are maintained in the maintenance log book. Metals are checked annually.

### Refrigerators, Freezers, and Ovens

The temperatures of all refrigerators are recorded daily. Refrigerators are defrosted and cleaned as needed. Media and reagents are stored in a refrigerator that is separate from the samples.

The temperature of the freezers are recorded each day samples are stored. Freezers are cleaned semiannually and outdated materials discarded.

The temperature of the ovens and muffle furnace are recorded each day of use. Separate logs are maintained for each oven.

### Incubators and Water Baths

The temperature of the coliform incubator is checked and recorded twice daily, in the morning and the afternoon. It is cleaned as needed.

The temperature of all other incubators are recorded twice daily each day of use. The temperatures of the water baths are also recorded as used. These are cleaned as necessary.

### Autoclave

Each time the autoclave is used, it records information about the temperatures, times, and pressure obtained throughout the cycle. This information is recorded on printer tape which is installed on the front of the autoclave. Prior to use, make sure that there is adequate printer tape.

The autoclave is to be cleaned as necessary. Before each use, check to make sure that the water levels are appropriate. If growth is observed in the water tank, drain, rinse, and refill the tank.

### Fume Hoods

Flow rates of the fume hoods are checked annually using an anemometer. These readings are recorded in a preventive maintenance log.

### Other Instruments

Routine maintenance for larger analytical equipment are performed according to the manufacturer's instructions, method instructions, and SOPs by analysts that are trained on the instrument. Each of these instruments has a trained primary analyst who is responsible for performing routine maintenance, scheduling servicing, and recording all maintenance activities. Maintenance logs are kept for each instrument, generally in a PM binder for the particular instrument and include the date, the results of routine maintenance checks, any maintenance actions performed, and the initials of the analyst.

## Performance and System Audits

Performance and system audits are vitally important in determining the effectiveness of the QA plan and in identifying areas for improvement. Any deficiency found during one of these audits should trigger a corrective action.

### External Audits

#### **California State Environmental Laboratory Accreditation Program (ELAP) compliance audit**

External audits are conducted every two years by an auditor from ELAP to determine if the laboratory is in compliance with regulations and to highlight areas of improvement. During this audit, an auditor will visit the laboratory and review SOPs along with the analysts' knowledge of the procedures. The auditor may also review training logs, bench sheets, QC reports, maintenance logs, etc.

Throughout the site visit the auditor will note deficiencies and areas for improvement. The auditor then issues a corrective action report that the laboratory must respond to showing that all items in the report have been addressed. The lab director is responsible for making sure that all items on the correction action report is addressed and the QA manager is responsible for ensuring that any resulting corrective actions are implemented.

#### **Proficiency Testing (PT) studies**

The lab director is responsible for enrolling the laboratory in ELAP approved proficiency testing programs and assuring that proficiency testing is performed for all regulated tests. PT samples are treated in the same manner as routine samples; they are analyzed using routine methods during normal sample analyses by the analysts who typically conduct the analyses. The laboratory results must fall within the set acceptance range for the PT samples.

If a PT analysis fails, the cause for the problem needs to be identified and corrected immediately; document any corrective actions. Subsequent QC results should be closely monitored to be sure that any corrective actions have been successful. The lab director must order a new PT sample for that method and they must be analyzed between 30 and 90 days from the receipt of the evaluation and the results resubmitted.

### Internal Audits

#### **Individual performance reviews**

The lab director is responsible for conducting individual performance reviews that should be held at least annually. This involves reviewing the employee's training file and competence. Areas for review may include but are not limited to:

- QC reports and QC performance
- Adherence to laboratory safety practices and the QA manual

- Workload and ability to manage responsibilities
- Progress toward CWEA certification or maintenance of current certifications
- Employee and customer interactions

The lab director should clearly communicate any areas for improvement and make suggestions for continued training.

### **QA Reports**

Internal QA audits are to be conducted quarterly by the QA manager to ensure that the laboratory is adhering to the policies and procedures outlined in the QA manual.

## **Corrective Action**

Corrective action will be required if QC results fall out of acceptable range and begins with the analyst. When a QC check fails, the analyst is responsible for troubleshooting the problem according to instructions in the written SOP or manuals and reanalyzing. The general guideline is as follows:

1. Identify the problem (e.g., QC result too high, QC result too low, etc.)
2. Determine the cause (e.g., pipetting error, poor calibration, etc.)
3. Take corrective action (e.g., retest and/or remake the QC solution, re-calibrate, etc.)
4. Verify effectiveness of the corrective action
5. Document the problem and corrective action - this may be done on the bench sheet

If the problem has been corrected through the above process and is random, no further action is required. If the analyst cannot correct the problem or it recurs persistently, the QA manager must then assist with determining how to proceed.

The QA manager should monitor QC data for any trends in the corrective actions required. If an analyst is unable to correct a problem or a trend exists, the following corrective actions may be required:

- Further training or retraining of the analyst
- Specialized maintenance or tuning of an instrument
- Reevaluation of the analytical method and SOP

If a deficiency is detected during an internal or external audit or a proficiency test fails, the QA manager and lab director are then responsible for initiating and documenting any corrective action necessary.

## References

APHA, AWWA, WEF. (1992). *Standard Methods for the Examination of Water and Wastewater, 18th Ed.*

USEPA. (1979). *Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019*. Cincinnati, Ohio.

USEPA. (1983). *Methods for Chemical Analysis of Water and Wastes, EPA/600/4-79/020*.

USEPA. (1997). *Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures Quality Assurance, 5th Ed., EPA 815-R-05-004*. Cincinnati, Ohio.

Quality Assurance Manual for MBAS written by David Holland

Date: April 1999

- Revision 1: January 2, 2002
- Revision 2: July 21, 2003
- Revision 3: July 21, 2005
- Revision 4: July 21, 2007
- Revision 5: July 24 2009
- Revision 8: March, 2011
- Revision 9: May 21, 2013
- Revision 10: November 3, 2014
- Revision 11: May 21, 2016

## Appendix A

### Lab Certification and Accreditation

## State Water Resources Control Board

December 18, 2015

David Holland  
Monterey Bay Analytical Services  
4 Justin Court, Suite D  
Monterey, CA 93940

Dear David Holland:

Certificate No. 2385

This is to advise you that the laboratory named above has been granted an interim certificate pursuant to California Health and Safety Code (HSC), Division 101, Part 1, Chapter 4, Section 100850(d).

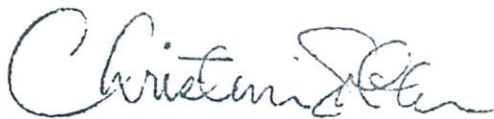
The Fields of Testing for which this laboratory has been granted interim certification is shown in the enclosed "Fields of Testing". The Interim certificate shall remain in effect until **October 31, 2016** or until a certificate pursuant to HSC 100825(a) is issued.

Your laboratory is required to participate in the appropriate performance evaluation studies and to perform acceptably in such studies as stated in HSC 100870 and Title 22 of the California Code of Regulations Section 64809. Continued compliance with the Environmental Laboratory Accreditation Program statutes and regulations is required for maintaining the interim certification status.

Any changes in laboratory location or structural alterations, which may adversely affect the quality of analysis in the fields of testing for which the laboratory has been granted certification, require prior notification. Notification is also required for changes in ownership or laboratory director within 30 days after the change (HSC 100845(b) and (d)).

For general inquiries please contact our office via the phone number or email address listed below. For specific concerns regarding your certification, please contact me at (916) 341-5175 or [Christine.Sotelo@waterboards.ca.gov](mailto:Christine.Sotelo@waterboards.ca.gov).

Sincerely,



Christine Sotelo, Chief  
Environmental Laboratory Accreditation Program

Enclosure



**CALIFORNIA STATE  
ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM  
Accredited Fields of Testing**



**Monterey Bay Analytical Services**

4 Justin Court, Suite D  
Monterey, CA 93940  
Phone: (831) 375-6227

Certificate No. 2385  
Expiration Date 10/31/2016  
INTERIM

**Field of Testing: 101 - Microbiology of Drinking Water**

|         |     |                              |            |
|---------|-----|------------------------------|------------|
| 101.010 | 001 | Heterotrophic Bacteria       | SM9215B    |
| 101.011 | 001 | Heterotrophic Bacteria       | SimPlate   |
| 101.060 | 002 | Total Coliform               | SM9223     |
| 101.060 | 003 | E. coli                      | SM9223     |
| 101.115 | 001 | Total Coliform               | Colitag    |
| 101.115 | 002 | E. coli                      | Colitag    |
| 101.160 | 001 | Total Coliform (Enumeration) | SM9223     |
| 101.200 | 001 | E. coli (Enumeration)        | SM9223B    |
| 101.300 | 001 | E. coli                      | SM9223B    |
| 101.310 | 001 | Enterococci                  | Enterolert |

**Field of Testing: 102 - Inorganic Chemistry of Drinking Water**

|         |     |                                 |                         |
|---------|-----|---------------------------------|-------------------------|
| 102.030 | 001 | Bromide                         | EPA 300.0               |
| 102.030 | 003 | Chloride                        | EPA 300.0               |
| 102.030 | 005 | Fluoride                        | EPA 300.0               |
| 102.030 | 006 | Nitrate                         | EPA 300.0               |
| 102.030 | 007 | Nitrite                         | EPA 300.0               |
| 102.030 | 008 | Phosphate, Ortho                | EPA 300.0               |
| 102.030 | 010 | Sulfate                         | EPA 300.0               |
| 102.100 | 001 | Alkalinity                      | SM2320B                 |
| 102.130 | 001 | Conductivity                    | SM2510B                 |
| 102.140 | 001 | Total Dissolved Solids          | SM2540C                 |
| 102.270 | 001 | Surfactants                     | SM5540C                 |
| 102.280 | 001 | UV254                           | SM5910B                 |
| 102.520 | 001 | Calcium                         | EPA 200.7               |
| 102.520 | 002 | Magnesium                       | EPA 200.7               |
| 102.520 | 003 | Potassium                       | EPA 200.7               |
| 102.520 | 004 | Silica                          | EPA 200.7               |
| 102.520 | 005 | Sodium                          | EPA 200.7               |
| 102.520 | 006 | Hardness (calculation)          | EPA 200.7               |
| 102.551 | 002 | Chlorine, Free, Combined, Total | SM4500-Cl G             |
| 102.564 | 001 | Cyanide                         | Quickchem 10-204-00-1-X |

**Field of Testing: 103 - Toxic Chemical Elements of Drinking Water**

|         |     |           |           |
|---------|-----|-----------|-----------|
| 103.130 | 008 | Copper    | EPA 200.7 |
| 103.130 | 009 | Iron      | EPA 200.7 |
| 103.130 | 011 | Manganese | EPA 200.7 |
| 103.130 | 017 | Zinc      | EPA 200.7 |
| 103.130 | 018 | Boron     | EPA 200.7 |

As of 12/18/2015, this list supersedes all previous lists for this certificate number.  
Customers: Please verify the current accreditation standing with the State.

|         |     |           |           |
|---------|-----|-----------|-----------|
| 103.140 | 001 | Aluminum  | EPA 200.8 |
| 103.140 | 002 | Antimony  | EPA 200.8 |
| 103.140 | 003 | Arsenic   | EPA 200.8 |
| 103.140 | 004 | Barium    | EPA 200.8 |
| 103.140 | 005 | Beryllium | EPA 200.8 |
| 103.140 | 006 | Cadmium   | EPA 200.8 |
| 103.140 | 007 | Chromium  | EPA 200.8 |
| 103.140 | 008 | Copper    | EPA 200.8 |
| 103.140 | 009 | Lead      | EPA 200.8 |
| 103.140 | 010 | Manganese | EPA 200.8 |
| 103.140 | 011 | Mercury   | EPA 200.8 |
| 103.140 | 012 | Nickel    | EPA 200.8 |
| 103.140 | 013 | Selenium  | EPA 200.8 |
| 103.140 | 014 | Silver    | EPA 200.8 |
| 103.140 | 015 | Thallium  | EPA 200.8 |
| 103.140 | 016 | Zinc      | EPA 200.8 |
| 103.140 | 018 | Vanadium  | EPA 200.8 |

**Field of Testing: 107 - Microbiology of Wastewater**

|         |     |                        |                    |
|---------|-----|------------------------|--------------------|
| 107.010 | 001 | Heterotrophic Bacteria | SM9215B            |
| 107.020 | 002 | Total Coliform         | SM9221B-2006       |
| 107.040 | 002 | Fecal Coliform         | SM9221C,E-2006     |
| 107.242 | 001 | Enterococci            | Enterolert         |
| 107.245 | 002 | E. coli                | SM9223B (Colisure) |

**Field of Testing: 108 - Inorganic Chemistry of Wastewater**

|         |     |                        |                 |
|---------|-----|------------------------|-----------------|
| 108.090 | 001 | Residue, Volatile      | EPA 160.4       |
| 108.110 | 001 | Turbidity              | EPA 180.1       |
| 108.112 | 001 | Boron                  | EPA 200.7       |
| 108.112 | 002 | Calcium                | EPA 200.7       |
| 108.112 | 003 | Hardness (calculation) | EPA 200.7       |
| 108.112 | 004 | Magnesium              | EPA 200.7       |
| 108.112 | 005 | Potassium              | EPA 200.7       |
| 108.112 | 006 | Silica                 | EPA 200.7       |
| 108.112 | 007 | Sodium                 | EPA 200.7       |
| 108.120 | 001 | Bromide                | EPA 300.0       |
| 108.120 | 002 | Chloride               | EPA 300.0       |
| 108.120 | 003 | Fluoride               | EPA 300.0       |
| 108.120 | 004 | Nitrate                | EPA 300.0       |
| 108.120 | 005 | Nitrite                | EPA 300.0       |
| 108.120 | 006 | Nitrate-nitrite        | EPA 300.0       |
| 108.120 | 007 | Phosphate, Ortho       | EPA 300.0       |
| 108.120 | 008 | Sulfate                | EPA 300.0       |
| 108.381 | 002 | Oil & Grease Total     | EPA 1664 Rev. B |
| 108.385 | 001 | Color                  | SM2120B-2001    |
| 108.410 | 001 | Alkalinity             | SM2320B         |
| 108.430 | 001 | Conductivity           | SM2510B         |
| 108.440 | 001 | Residue, Total         | SM2540B         |

|         |     |                             |                               |
|---------|-----|-----------------------------|-------------------------------|
| 108.441 | 001 | Residue, Filterable TDS     | SM2540C                       |
| 108.442 | 001 | Residue, Non-filterable TSS | SM2540D                       |
| 108.443 | 001 | Residue, Settleable         | SM2540F                       |
| 108.444 | 001 | Temperature                 | SM2550B-2000                  |
| 108.465 | 001 | Chlorine, Total             | SM4500-Cl G-2000              |
| 108.490 | 001 | Hydrogen Ion (pH)           | SM4500-H+ B                   |
| 108.492 | 001 | Ammonia                     | SM4500-NH3 C (19th/20th)      |
| 108.492 | 002 | Kjeldahl Nitrogen           | SM4500-NH3 C (19th/20th)      |
| 108.493 | 001 | Ammonia                     | SM4500-NH3 D or E (19th/20th) |
| 108.493 | 002 | Kjeldahl Nitrogen           | SM4500-NH3 D or E (19th/20th) |
| 108.531 | 001 | Dissolved Oxygen            | SM4500-O G                    |
| 108.590 | 001 | Biochemical Oxygen Demand   | SM5210B                       |
| 108.591 | 001 | Carbonaceous BOD            | SM5210B                       |
| 108.597 | 001 | Organic Carbon-Total (TOC)  | SM5310C-2000                  |
| 108.602 | 001 | Chemical Oxygen Demand      | SM5220D                       |
| 108.675 | 001 | Phosphorus, Total           | HACH8190                      |
| 108.926 | 001 | Cyanide                     | Quickchem 10-204-00-1-X       |

**Field of Testing: 109 - Toxic Chemical Elements of Wastewater**

|         |     |            |           |
|---------|-----|------------|-----------|
| 109.010 | 011 | Copper     | EPA 200.7 |
| 109.010 | 012 | Iron       | EPA 200.7 |
| 109.010 | 015 | Manganese  | EPA 200.7 |
| 109.010 | 027 | Zinc       | EPA 200.7 |
| 109.020 | 001 | Aluminum   | EPA 200.8 |
| 109.020 | 002 | Antimony   | EPA 200.8 |
| 109.020 | 003 | Arsenic    | EPA 200.8 |
| 109.020 | 004 | Barium     | EPA 200.8 |
| 109.020 | 005 | Beryllium  | EPA 200.8 |
| 109.020 | 006 | Cadmium    | EPA 200.8 |
| 109.020 | 007 | Chromium   | EPA 200.8 |
| 109.020 | 008 | Cobalt     | EPA 200.8 |
| 109.020 | 009 | Copper     | EPA 200.8 |
| 109.020 | 010 | Lead       | EPA 200.8 |
| 109.020 | 011 | Manganese  | EPA 200.8 |
| 109.020 | 012 | Molybdenum | EPA 200.8 |
| 109.020 | 013 | Nickel     | EPA 200.8 |
| 109.020 | 014 | Selenium   | EPA 200.8 |
| 109.020 | 015 | Silver     | EPA 200.8 |
| 109.020 | 016 | Thallium   | EPA 200.8 |
| 109.020 | 017 | Vanadium   | EPA 200.8 |
| 109.020 | 018 | Zinc       | EPA 200.8 |
| 109.020 | 021 | Iron       | EPA 200.8 |



STATE WATER RESOURCES CONTROL BOARD  
REGIONAL WATER QUALITY CONTROL BOARDS

Interim



CALIFORNIA STATE

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

## CERTIFICATE OF ENVIRONMENTAL ACCREDITATION

Is hereby granted to

**Monterey Bay Analytical Services**

4 Justin Court, Suite D

Monterey, CA 93940

Scope of the certificate is limited to the  
"Fields of Testing"  
which accompany this Certificate.

Continued accredited status depends on successful completion of on-site inspection,  
proficiency testing studies, and payment of applicable fees.

This Certificate is granted in accordance with provisions of  
Section 100825, et seq. of the Health and Safety Code.

Certificate No.: **2385**

Expiration Date: **10/31/2016**

Effective Date: **11/1/2015**

A handwritten signature in black ink, reading "Christine Sotelo".

Sacramento, California  
subject to forfeiture or revocation

Christine Sotelo, Chief  
Environmental Laboratory Accreditation Program

## Appendix B

### Analysis Reference List



# MBAS

## Monterey Bay Analytical Services

• 4 Justin Court, Suite D, Monterey 93940 • (831)375-MBAS(6227) • (831)641-0734(Fax)  
• MontereyBayAnalytical@USA.net • www.MBASinc.com

### Analyses Reference List

| Analyses                                                                                     | Method                           | Hold Time | Container(s)             | Preservative(s)                               | Storage   | MDL         | RL (PQL)    | Units                     |
|----------------------------------------------------------------------------------------------|----------------------------------|-----------|--------------------------|-----------------------------------------------|-----------|-------------|-------------|---------------------------|
| Acrolein & Acrylonitrile**                                                                   | EPA 624                          | 3 Days    | 40ml VOA                 | None                                          | 4°C ± 2°C | **          | **          | µg/L                      |
| Alkalinity                                                                                   | SM 2320B                         | 14 Days   | 250ml Plastic            | None                                          | 4°C ± 2°C | 1           | 2           | mg/L<br>CaCO <sub>3</sub> |
| Aluminum – Al                                                                                | EPA 200.8                        | 6 Months  | 125ml Plastic            | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 2.5         | 10          | µg/L                      |
| Ammonia – NH <sub>3</sub> (Dist/ISE)                                                         | SM 4500-NH3B,C/D                 | 28 Days   | 250ml Plastic            | H <sub>2</sub> SO <sub>4</sub> pH<2           | 4°C ± 2°C | 0.3<br>0.05 | 0.5<br>0.05 | mg/L                      |
| Anions - {Cl, F, Br, NO <sub>3</sub> , NO <sub>2</sub> , SO <sub>4</sub> , PO <sub>4</sub> } | EPA 300.0                        | 48 Hours  | 250ml Plastic            | None                                          | 4°C ± 2°C | See         | Analyte     | mg/L                      |
| Arsenic – As                                                                                 | EPA 200.8                        | 6 Months  | 125ml Plastic            | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.2         | 1           | µg/L                      |
| Arsenic, Speciation (III/V) **                                                               | IC-ICPMS                         | 28 days   | 250 Plastic              | EDTA, Acetic Acid                             | 4°C ± 2°C | **          | **          | µg/L                      |
| Asbestos**                                                                                   | EPA 600/R-94/134<br>100.2 Method | 48 Hours  | 1L Plastic               | None                                          | 4°C ± 2°C | **          | **          |                           |
| Barium – Ba                                                                                  | EPA 200.8                        | 6 Months  | 125ml Plastic            | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.1         | 10          | µg/L                      |
| Bacteria – Coliform DW                                                                       | Colitag/<br>SM 9223              | 30 Hours  | 100ml Sterile<br>Plastic | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | 1           | 1           | MPN/<br>100mL             |
| Bacteria – Coliform WW                                                                       | Colilert/<br>SM 9223             | 6 Hours   | 100ml Sterile<br>Plastic | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | 1           | 1           | MPN/<br>100mL             |
| Bacteria – HTPC                                                                              | SimPlate                         | 24 Hours  | 100ml Sterile<br>Plastic | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | 2           | 2           | MPN/<br>mL                |
| BioAssay<br>Requires Advanced Notification                                                   | EPA -821-R-<br>02-012            | 36 Hours  | cubitainer               | None                                          | 4°C ± 2°C | **          | **          | TU                        |
| Biochemical Oxygen Demand – BOD                                                              | SM 5210B                         | 48 Hours  | 1L Plastic               | None                                          | 4°C ± 2°C | 2           | 2           | mg/L                      |
| Boron – B                                                                                    | EPA 200.7                        | 6 Months  | 125ml Plastic            | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.05        | 0.05        | µg/L                      |
| Bromate - BRO <sub>3</sub> **                                                                | EPA 317.0                        | 28 Days   | 250ml Amber Glass        | EDA Preserv.                                  | 4°C ± 2°C |             | 0.001       | mg/L                      |
| Bromide – Br                                                                                 | EPA 300.0                        | 28 Days   | 250ml Plastic            | None                                          | 4°C ± 2°C | 0.01        | 0.1         | mg/L                      |

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| Analyses                                                                                      | Method                 | Hold Time  | Container(s)                   | Preservative(s)                                                | Storage                    | MDL       | RL (PQL) | Units       |
|-----------------------------------------------------------------------------------------------|------------------------|------------|--------------------------------|----------------------------------------------------------------|----------------------------|-----------|----------|-------------|
| <b>BTEX / TPH – Gas**</b> (Collect w/o Air Bubbles)                                           | GC/MS                  | 14 Days    | (3) 40ml VOA                   | HCl pH<2                                                       | 4°C ± 2°C                  | **        | **       |             |
| <b>Cadmium – Cd</b>                                                                           | EPA 200.8              | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | 0.1       | 0.5      | µg/L        |
| <b>Calcium – Ca</b>                                                                           | EPA 200.7              | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | 0.1       | 0.5      | mg/L        |
| <b>Cam 16 Metals**</b><br>(Sb, As, Ba, Be, Ca, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Th, V, Zr)     | EPA 200.8              | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | **        | **       | µg/L        |
| <b>Cam 17 Metals**</b><br>(Hg, Sb, As, Ba, Be, Ca, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Th, V, Zn) | EPA 200.8              | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | **        | **       | µg/L        |
| <b>Cations</b> - (B, Ca, Cu, Fe, Mn, Mg, K, Si, Na, Zr)                                       | EPA 200.7              | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | See       | Analyte  | mg/L        |
| <b>Carbamates**</b>                                                                           | EPA 531.1              | 28 Days    | 40ml VOA                       | MCAA Buffer<br>+ Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C                  | **        | **       | µg/L        |
| <b>Carbonaceous Biological Oxygen Demand</b> - CBOD                                           | SM 5210B               | 48 Hours   | 1L Plastic                     | None                                                           | 4°C ± 2°C                  | 2         | 2        | mg/L        |
| <b>Corrosivity - Langlier Index</b><br>(Includes Ca, Alk, pH, & TDS)                          | SM 2330B               | 15 minutes | 500ml Plastic<br>125ml Plastic | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | See       | Analyte  |             |
| <b>Chemical Oxygen Demand</b> - COD                                                           | SM5220D                | 28 Days    | 500ml Plastic                  | H <sub>2</sub> SO <sub>4</sub>                                 | 4°C ± 2°C                  | 5         | 5        | mg/L        |
| <b>Chloramines</b>                                                                            | SM 4500-Cl G           | 24 Hours   | 250ml Plastic                  | None                                                           | 4°C ± 2°C                  | 0.05      | 0.05     | mg/L        |
| <b>Chloride – Cl</b>                                                                          | EPA 300.0              | 28 Days    | 250ml Plastic                  | None                                                           | 4°C ± 2°C                  | 0.25      | 1        | mg/L        |
| <b>Chlorinated Herbicides**</b>                                                               | EPA 515.1              | 14 Days    | 250ml Amber Glass              | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>                  | 4°C ± 2°C                  | **        | **       | µg/L        |
| <b>Chlorine Residual (Free or Total)</b>                                                      | SM 4500-Cl G           | 15 Minutes | 250ml Plastic                  | None                                                           | 4°C ± 2°C                  | 0.05      | 0.05     | mg/L        |
| <b>Chlorophyll</b>                                                                            | SM 10200H              |            | 1L Amber Glass<br>or filter    | None                                                           | 4°C ± 2°C<br>Freeze Filter | 5         | 5        | µg/L        |
| <b>Chromium (total) – Cr</b>                                                                  | EPA 200.8              | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | 0.7       | 1        | µg/L        |
| <b>Chromium VI - Cr6 **</b>                                                                   | EPA 218.7              | 5 days     | 250ml Plastic                  | Buffer                                                         | 4°C ± 2°C                  | **        | 0.2      | µg/L        |
| <b>Color</b>                                                                                  | SM 2120B               | 48 Hours   | 250ml Amber Glass              | None                                                           | 4°C ± 2°C                  | 3         | 3        | Color Units |
| <b>Conductivity – SEC</b>                                                                     | SM 2510B               | 28 Days    | 250ml Plastic                  | None                                                           | 4°C ± 2°C                  | 1         | 1        | Umhos/cm    |
| <b>Copper – Cu</b>                                                                            | EPA 200.7<br>EPA 200.8 | 6 Months   | 125ml Plastic                  | HNO <sub>3</sub> pH>2                                          | 4°C ± 2°C                  | 10<br>0.2 | 10<br>4  | µg/L        |
| <b>Cyanide – CN</b>                                                                           | QuickChem<br>10-204    | 14 Days    | 250ml Plastic                  | NaOH pH>12                                                     | 4°C ± 2°C                  | 5         | 5        | µg/L        |
| <b>Dioxin 2,3,7,8 TCDD**</b>                                                                  | EPA 1613               | 28 Days    | 2 X 1L Amber Glass             | None                                                           | 4°C ± 2°C                  | **        | **       | pg/L        |
| <b>Dioxin plus TCDD equivalents Cl4-Cl8**</b>                                                 | EPA 1613               | 28 Days    | 2 X 1 L Amber Glass            | None                                                           | 4°C ± 2°C                  | **        | **       | pg/L        |
| <b>Dissolved Oxygen - DO</b>                                                                  | SM 4500-O G            | 15 Minutes | 500ml Plastic                  | None                                                           | None                       | 0.5       | 0.5      | mg/L        |
| <b>Diquat/Paraquat**</b>                                                                      | EPA 549                | 7 Days     | 1L Brown Plastic               | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>                  | 4°C ± 2°C                  | **        | **       | µg/L        |
| <b>Diuron**</b>                                                                               | EPA632                 | 7 Days     | (2) 1L Amber Glass             | None                                                           | 4°C ± 2°C                  | **        | **       | µg/L        |

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| Analyses                                                                              | Method                 | Hold Time | Container(s)          | Preservative(s)                               | Storage   | MDL      | RL (PQL) | Units |
|---------------------------------------------------------------------------------------|------------------------|-----------|-----------------------|-----------------------------------------------|-----------|----------|----------|-------|
| <b>EDB, DBCP**</b>                                                                    | EPA 504.1              | 14 Days   | (3) 40ml VOA          | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | **       | **       | µg/L  |
| <b>Endothall**</b>                                                                    | EPA 548                | 7 Days    | 250ml Amber Glass     | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | **       | **       | µg/L  |
| <b>Formaldehyde**</b>                                                                 | SW8315A                | 3 days    | 1 L Amber Glass       | None                                          | 4°C ± 2°C | **       | 5.0      | µg/L  |
| <b>Fluoride – F</b>                                                                   | EPA 300.0              | 28 Days   | 250ml Plastic         | None                                          | 4°C ± 2°C | 0.02     | 0.1      | mg/L  |
| <b>Glyphosate**</b>                                                                   | EPA 547                | 14 Days   | 40ml VOA              | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | **       | **       | µg/L  |
| <b>Gross Alpha**</b>                                                                  | EPA 900.0              | 6 months  | 1L Plastic            | None                                          | 4°C ± 2°C | **       | **       | pCi/L |
| <b>Haloacetic Acids – HAA-5**</b>                                                     | EPA 552.3              | 14 Days   | 250ml Amber Glass     | NH <sub>4</sub> Cl                            | 4°C ± 2°C | **       | 2.0      | µg/L  |
| <b>Hardness -</b> (Includes Ca & Mg)                                                  | SM 2340B               | 6 Months  | 125ml Plastic         | HNO <sub>3</sub>                              | 4°C ± 2°C | 10       | 10       | mg/L  |
| <b>Iodide**</b>                                                                       | EPA 9056A              | 14 days   | 250 ml Plastic        | None                                          | 4°C ± 2°C | **       | 10       | µg/L  |
| <b>Iron – Fe</b>                                                                      | EPA 200.7<br>EPA 200.8 | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 5<br>10  | 10<br>10 | µg/L  |
| <b>Iron Related Bacteria</b>                                                          | BART Test              | 24 Hours  | 100ml Sterile Plastic | None                                          | 4°C ± 2°C |          |          |       |
| <b>Lead – Pb</b>                                                                      | EPA 200.8              | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.2      | 5        | µg/L  |
| <b>Lead &amp; Copper Rule -</b> (Includes Pb, Cu & Turbidity)                         | EPA 200.8              | 6 Months  | 1L Plastic            | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C |          |          | µg/L  |
| <b>Lithium – Li</b>                                                                   | EPA 200.8              | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 1        | 1        | µg/L  |
| <b>Manganese – Mn</b>                                                                 | EPA 200.7<br>EPA 200.8 | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.2<br>1 | 10<br>10 | µg/L  |
| <b>Magnesium – Mg</b>                                                                 | EPA 200.7              | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.05     | 0.5      | mg/L  |
| <b>MBAS (Detergents/Surfactants)</b>                                                  | SM 5540C               | 48 Hours  | 250ml Plastic         | None                                          | 4°C ± 2°C | 0.05     | 0.05     | mg/L  |
| <b>Mercury – Hg</b>                                                                   | EPA 200.8              | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.04     | 0.5      | µg/L  |
| <b>Mercury by Cold Vapor **</b><br>Wastewater                                         | EPA 245.1              | 28 days   | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | **       | 0.05     | µg/L  |
| <b>Metals</b><br>(As, Cd, Cu, Fe, Mn, Pb, Zn, Al, Cr, Ni, Ag, Ba, Be, Hg, Se, Sb, Ti) | EPA 200.8              | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | See      | Analyte  | µg/L  |
| <b>Methane** - CH<sub>4</sub></b>                                                     | RSK175                 | 14 Days   | 3X40 ml VOA           | HCL                                           | 4°C ± 2°C | **       | 0.1      | µg/L  |
| <b>Methanol **</b> (Includes VOCs)                                                    | EPA 624                | 14 Days   | 3X40 ml VOA           | HCL                                           | 4°C ± 2°C | **       | 500      | µg/L  |
| <b>Nickel – Ni</b>                                                                    | EPA 200.8              | 6 Months  | 125ml Plastic         | HNO <sub>3</sub> pH>2                         | 4°C ± 2°C | 0.2      | 10       | µg/L  |
| <b>Nitrite – NO<sub>2</sub></b>                                                       | EPA 300.0              | 48 Hours  | 250ml Plastic         | None                                          | 4°C ± 2°C | 0.01     | 0.1      | mg/L  |
| <b>Odor</b>                                                                           | SM 2150B               | 48 Hours  | 250ml Amber Glass     | None                                          | 4°C ± 2°C |          | 1        | TON   |
| <b>Oil &amp; Grease – O&amp;G Polar &amp; Non Polar</b>                               | EPA 1664B              | 28 Days   | 1L Amber Glass        | HCl                                           | 4°C ± 2°C | 3        | 5        | mg/L  |
| <b>Organochlorine Pesticides &amp; PCBS ** DW</b>                                     | EPA 505                | 7 Days    | (3) 40ml VOA          | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C | **       | **       | µg/L  |
| <b>Organochlorine Pesticides &amp; PCBs ** WW</b>                                     | EPA 608                | 7 days    | 1L Amber Glass        | None                                          | 4°C ± 2°C | **       | **       | µg/L  |

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| Analyses                                                                    | Method               | Hold Time         | Container(s)                                | Preservative(s)                                                       | Storage   | MDL  | RL (PQL)              | Units            |
|-----------------------------------------------------------------------------|----------------------|-------------------|---------------------------------------------|-----------------------------------------------------------------------|-----------|------|-----------------------|------------------|
| <b>Organophosphorus Pesticides**</b>                                        | EPA 8141             |                   |                                             | None                                                                  | 4°C ± 2°C | **   | **                    | µg/L             |
| <b>Perchlorate**</b>                                                        | EPA 314.0            | 28 Days           | 250ml Plastic                               | None                                                                  | 4°C ± 2°C | **   | 2                     | µg/L             |
| <b>pH</b>                                                                   | SM 4500-H B          | <b>15 Minutes</b> | 250ml Plastic                               | None                                                                  | 4°C ± 2°C |      |                       | pH Units         |
| <b>Phosphate (ortho) – PO<sub>4</sub></b>                                   | EPA 300.0            | <b>48 Hours</b>   | 250ml Plastic                               | None                                                                  | 4°C ± 2°C | 0.02 | 0.1                   | mg/L             |
| <b>Phosphorus, Total</b>                                                    | Hach 8190            | 28 Days           | 250ml Plastic                               | H <sub>2</sub> SO <sub>4</sub> pH<2                                   | 4°C ± 2°C | 0.03 | 0.03                  | mg/L             |
| <b>Potassium – K</b>                                                        | EPA 200.7            | 6 Months          | 125ml Plastic                               | HNO <sub>3</sub> pH>2                                                 | 4°C ± 2°C | 0.3  | 0.5                   | mg/L             |
| <b>Radium 226**</b>                                                         | EPA 903.0            | 6 Months          | 2L Plastic                                  | None                                                                  | 4°C ± 2°C | **   | **                    | pCi/L            |
| <b>Radium 228**</b>                                                         | Ra - 05              | 6 Months          | 2L Plastic                                  | None                                                                  | 4°C ± 2°C | **   | **                    | pCi/L            |
| <b>Selenium –Se</b>                                                         | EPA 200.8            | 6 Months          | 2L Plastic                                  | None                                                                  | 4°C ± 2°C | 0.8  | 2                     | µg/L             |
| <b>Silica</b>                                                               | EPA 200.7            | 6 Months          | 125ml Plastic                               | HNO <sub>3</sub> pH>2                                                 | 4°C ± 2°C | 0.5  | 0.5                   | mg/L             |
| <b>Silver – Ag</b>                                                          | EPA 200.8            | 6 Months          | 125ml Plastic                               | HNO <sub>3</sub> pH>2                                                 | 4°C ± 2°C | 1    | 10                    | µg/L             |
| <b>Sodium – Na</b>                                                          | EPA 200.7            | 6 Months          | 125ml Plastic                               | HNO <sub>3</sub> pH>2                                                 | 4°C ± 2°C | 0.03 | 0.5                   | mg/L             |
| <b>Sulfate – SO<sub>4</sub></b>                                             | EPA 300.0            | 28 Days           | 250ml Plastic                               |                                                                       | 4°C ± 2°C | 0.25 | 1                     | mg/L             |
| <b>Semi-Volatile Organic Compounds** DW</b>                                 | EPA 525              | 14 Days           | (2) 1L Amber Glass                          | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>                         | 4°C ± 2°C | **   | **                    | µg/L             |
| <b>Semi-Volatile Organic Compounds** WW</b>                                 | EPA 625              | 7 Days            | (2) 1L Amber Glass                          | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub><br>(If Chlorinated)     | 4°C ± 2°C | **   | **                    | µg/L             |
| <b>Settleable Solids – SS</b>                                               | SM 2540F             | <b>48 Hours</b>   | 1L Plastic                                  | None                                                                  | 4°C ± 2°C |      | 0.1                   | ml/L             |
| <b>Total Dissolved Solids – TDS</b>                                         | SM 2540C             | 7 Days            | 500ml Plastic                               | None                                                                  | 4°C ± 2°C | 10   | 10                    | mg/L             |
| <b>Total Suspended Solids – TSS</b>                                         | SM 2540D             | 7 Days            | 500ml Plastic                               | None                                                                  | 4°C ± 2°C | 2    | 2                     | mg/L             |
| <b>Total Kjeldahl Nitrogen – TKN</b>                                        | SM 4500-NH3B,C,E     | 28 Days           | 500ml Plastic                               | H <sub>2</sub> SO <sub>4</sub> pH<2                                   | 4°C ± 2°C | 0.5  | 0.5                   | mg/L             |
| <b>Total Nitrogen</b><br>(Includes NO <sub>3</sub> , NO <sub>2</sub> , TKN) | 300.0<br>SM 4500-NH3 | <b>48 Hours</b>   | 500 ml Plastic                              | Preserved Upon Arrival (H <sub>2</sub> SO <sub>4</sub> pH<2)          | 4°C ± 2°C | See  | Analyte               | mg/L             |
| <b>Total Organic Carbon – TOC</b>                                           | SM 5310C             | 28 Days           | (3) 40ml VOA                                | H <sub>3</sub> PO <sub>3</sub>                                        | 4°C ± 2°C | 0.03 | 0.2                   | mg/L             |
| <b>Total Sulfide – S<sup>2-</sup></b>                                       | SM 4500-S2D          | <b>48 Hours</b>   | 500ml Plastic                               | ZnAc <sub>2</sub>                                                     | 4°C ± 2°C | 2    | 2                     | µg/L             |
| <b>Total Trihalomethanes – TTHMs**</b><br>(Collect w/o Air Bubbles)         | EPA 524.2            | 14 Days           | (3) 40ml VOA                                | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>                         | 4°C ± 2°C | **   | 0.5                   | µg/L             |
| <b>TPH Extractable**</b> (Diesel & Oil Range Organics)                      | EPA 8015B            | 7 Days            | 1 liter Amber Glass<br>(100 grams for soil) | (Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub><br>If Chlorinated) HCL | 4°C ± 2°C | **   | Oil 0.5<br>Diesel 0.1 | mg/L             |
| <b>TPH Extractable**</b> (Gasoline Range Organics )                         | EPA 8015B            | 14 Days           | 3X40ml VOA                                  | HCL                                                                   | 4°C ± 2°C | **   | 0.1                   | mg/L             |
| <b>Turbidity</b>                                                            | EPA 180.1            | <b>48 Hours</b>   | 250ml Plastic                               | None                                                                  | 4°C ± 2°C | 0.03 | 0.05                  | NTU              |
| <b>Uranium</b>                                                              | EPA 200.8            | 6 Months          | 125ml Plastic                               | HNO <sub>3</sub> pH>2                                                 | 4°C ± 2°C | 0.3  | 1                     | µg/L or<br>pCi/L |

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| Analyses                        | Method                 | Hold Time | Container(s)                       | Preservative(s)       | Storage   | MDL       | RL (PQL) | Units     |
|---------------------------------|------------------------|-----------|------------------------------------|-----------------------|-----------|-----------|----------|-----------|
| Urea                            | Mulvanna, Savidge      | 28 Days   | 125ml Plastic                      | None                  | Frozen    | 8         | 10       | µg/L      |
| UV <sub>254</sub>               | SM 5910B               | 24 Hours  | 250ml Amber Glass                  | None                  | 4°C ± 2°C |           | 0.001    | Abs/Trans |
| Volatile Org. Compounds ** DW   | EPA 524.2              | 14 Days   | (3) 40ml VOA                       | HCl pH<2              | 4°C ± 2°C | **        | **       | µg/L      |
| Volatile Org. Compounds** WW    | EPA 624                | 7 Days    | (3) 40ml VOA                       | HCl pH<2              | 4°C ± 2°C | **        | **       | µg/L      |
| Volatile Suspended Solids - VSS | SM 2540G               | 7 Days    | 500ml Plastic                      | None                  | 4°C ± 2°C | 5         | 5        | mg/L      |
| WET TEST** for STLC values      |                        |           | 1 liter liquid<br>100 grams sludge | None                  | 4°C ± 2°C | **        | **       |           |
| Zinc – Zn                       | EPA 200.7<br>EPA 200.8 | 6 Months  | 125ml Plastic                      | HNO <sub>3</sub> pH>2 | 4°C ± 2°C | 10<br>4.8 | 10<br>10 | µg/L      |

## Chemistry Panels

| Panel                                                                   | Hold Time       | Container(s)                                                            | Preservative(s)                                                                                                                                                                                         | Storage   |
|-------------------------------------------------------------------------|-----------------|-------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <b>Title – 22</b><br>(Primary & Secondary)                              | <b>24 Hours</b> | 250ml Glass<br>1L Plastic<br>250ml Plastic<br>125ml Plastic             | NaOH pH>12<br>HNO <sub>3</sub>                                                                                                                                                                          | 4°C ± 2°C |
| <b>SOC's</b><br>(Monterey County)                                       | 7 Days          | (2) 1L Amber Glass<br>250ml Amber Glass<br>40ml VOA<br>1L Brown Plastic | Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub><br>Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub><br>MCAA + Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub><br>Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 4°C ± 2°C |
| <b>General Water Quality Panel</b><br><b>Domestic Suitability Panel</b> | <b>24 Hours</b> | 1L Plastic<br>125ml Plastic                                             | HNO <sub>3</sub>                                                                                                                                                                                        | 4°C ± 2°C |
| <b>General Physical</b> (Color, Odor, Turbidity, pH)                    | <b>24 Hours</b> | 250ml Amber Glass                                                       |                                                                                                                                                                                                         | 4°C ± 2°C |
| <b>Lead &amp; Copper Rule</b> (Pb&Cu)                                   | 6 Months        | 1L Plastic                                                              |                                                                                                                                                                                                         | 4°C ± 2°C |
| <b>Irrigation Suitability Panel</b>                                     | <b>24 Hours</b> | 1L Plastic<br>125ml Plastic                                             | HNO <sub>3</sub>                                                                                                                                                                                        | 4°C ± 2°C |
| <b>Storm Drain Panel</b>                                                | <b>48 Hours</b> | 1L Plastic<br>1L Amber Glass                                            | HCl                                                                                                                                                                                                     | 4°C ± 2°C |
| <b>R.O. / Softener Functionality Panel</b>                              | <b>24 Hours</b> | 500ml Plastic<br>125ml Plastic                                          | HNO <sub>3</sub>                                                                                                                                                                                        | 4°C ± 2°C |

- µg/L = Micrograms per Liter = ppb
- mg/L = Milligrams per Liter = ppm
- MDL = Minimum Detection Limit
- RL = Reporting Limit = PQL = Practical Quantitation Limit
- \*\*=Analysis Performed by External Laboratory

## Appendix C

### Chain of Custody

# Monterey Bay Analytical Services Chain Of Custody / Analysis Request

4 Justin Ct. Suite D • Monterey, Ca 93940 • (831) 375-MBAS (6227) • (831) 641-0734 (Fax)



|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|---------------------------|-------------|------------------------|---------------------|-------------------------------------------------------------------|--|-------------|----------------|------------------------------------------|--|--|--|--|--|--|--|
| <b>Client/Company Name:</b><br><b>Billing Address:</b>                                                                                                                                                                                                              |                                    | <b>Attention:</b>                                                                                                                                                                                                 |  | <b>Analysis Requested</b> |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| <b>Project/System Information:</b>                                                                                                                                                                                                                                  |                                    | <b>E-Mail Address(es):</b>                                                                                                                                                                                        |  | <b>Contract/P.O. #:</b>   |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| For Regulatory Compliance?    YES <input type="checkbox"/> NO <input type="checkbox"/><br>For State or Local Health Department reporting:<br>Electronic Data Transfer (EDT)?    YES <input type="checkbox"/> NO <input type="checkbox"/><br>System ID Number: _____ |                                    | Turn Around Time:<br>STD (7-14 Days) <input type="checkbox"/> 48-Hour <input type="checkbox"/><br>5-Day <input type="checkbox"/> 24-Hour <input type="checkbox"/>                                                 |  | Phone #<br>Fax #          |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    | Drinking water <input type="checkbox"/> Wastewater <input type="checkbox"/> Monitoring Well <input type="checkbox"/> Soil <input type="checkbox"/> Sludge <input type="checkbox"/> Other <input type="checkbox"/> |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| <b>MBAS Lab #</b>                                                                                                                                                                                                                                                   | <b>Project ID or Source Code #</b> | <b>Sample Site / Description</b><br>(Well Name, APN#, Address, Stormdrain #)                                                                                                                                      |  | <b>Sampling Date</b>      | <b>Time</b> | <b>Receiving Temp.</b> | <b>CL3 Residual</b> | <b>Coliform Analysis</b><br>Routine    Other    Repeat    Special |  |             | <b># Conf.</b> | <b>Container</b><br>Type    Size         |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                     |                                    | <b>Printed Name</b>                                                                                                                                                                                               |  | <b>Signature</b>          |             |                        |                     | <b>Date</b>                                                       |  | <b>Time</b> |                | <b>Comments or Special Instructions:</b> |  |  |  |  |  |  |  |
| Sampled by:                                                                                                                                                                                                                                                         |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| Relinquished by:                                                                                                                                                                                                                                                    |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| Received by:                                                                                                                                                                                                                                                        |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| Relinquished by:                                                                                                                                                                                                                                                    |                                    |                                                                                                                                                                                                                   |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |
| Received by:                                                                                                                                                                                                                                                        |                                    | Monterey Bay Analytical Services                                                                                                                                                                                  |  |                           |             |                        |                     |                                                                   |  |             |                |                                          |  |  |  |  |  |  |  |

|                                           |         |         |           |       |
|-------------------------------------------|---------|---------|-----------|-------|
| <input type="checkbox"/> Payment received | Check # | Amount: | Receipt # | Date: |
|-------------------------------------------|---------|---------|-----------|-------|

## Sample Condition Upon Receipt

COC Info

|                                                                                         |     |    |    |       |                                |     |    |    |
|-----------------------------------------------------------------------------------------|-----|----|----|-------|--------------------------------|-----|----|----|
| Was temp acceptable? Chemistry $\leq 6^{\circ}\text{C}$ Micro $\leq 10^{\circ}\text{C}$ | YES | NO | NA | <2 Hr | Is there evidence of chilling? | YES | NO | NA |
| Did bottles arrive intact?                                                              | YES | NO | NA |       |                                |     |    |    |
| Did bottle labels agree with COC?                                                       | YES | NO | NA |       |                                |     |    |    |

### Discrepancy Documentation:

Person Contacted: \_\_\_\_\_ Method: In Person/Phone/Email \_\_\_\_\_

Problem \_\_\_\_\_

Resolution \_\_\_\_\_

Person Contacted: \_\_\_\_\_ Method: In Person/Phone/Email \_\_\_\_\_

Problem \_\_\_\_\_

Resolution \_\_\_\_\_

Sample Split/Filtration

| Lab ID | Cont. Size | Pres | Date/Initials |
|--------|------------|------|---------------|
|        |            |      |               |
|        |            |      |               |
|        |            |      |               |
|        |            |      |               |
|        |            |      |               |
|        |            |      |               |

| Lab ID | Cont. Size | Pres | Date/Initials |
|--------|------------|------|---------------|
|        |            |      |               |
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|        |            |      |               |
|        |            |      |               |
|        |            |      |               |

Comments

## Appendix D

### Data Qualifiers

Data qualifiers are codes used to describe sampling conditions, testing conditions, or QC results. They are also referred to as flags.

| Data Qualifier / Flag | Description                                                             |
|-----------------------|-------------------------------------------------------------------------|
| H                     | Hold-time violation – Sample was received or analyzed out of hold time  |
| J                     | Reported value is below the reporting limit (PQL) – greater uncertainty |

## Appendix E

### Type of QC Performed for Each Analysis

| Analysis name                          | Method reference | ICVB | CCVB | LCB | LCCB | LCS | LCSD | LCSL | ICV | ICVL | ICVH | QCS | MS | MSD | CCV | DUP | GGA |
|----------------------------------------|------------------|------|------|-----|------|-----|------|------|-----|------|------|-----|----|-----|-----|-----|-----|
| Oil & Grease Nonpolar                  | EPA1664          |      |      |     |      | X   |      |      |     |      |      |     |    |     |     |     |     |
| Oil & Grease Polar                     | EPA1664          |      |      |     |      |     |      |      |     |      |      |     |    |     |     |     |     |
| Oil & Grease (HEM)                     | EPA1664 rev.B    |      |      | X   |      | X   |      |      |     |      |      |     | X  | X   |     |     |     |
| Turbidity                              | EPA180.1         | X    | X    |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Turbidity, 1.5 um Filter               | EPA180.1         | X    | X    |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Turbidity, 5 um Filter                 | EPA180.1         | X    | X    |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Boron                                  | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Calcium                                | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Calcium, Dissolved                     | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Copper                                 | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Iron                                   | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Iron, Dissolved                        | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Potassium                              | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Potassium, Dissolved                   | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Magnesium                              | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Magnesium, Dissolved                   | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Manganese, Total                       | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Manganese, Dissolved                   | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Sodium                                 | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Sodium, Dissolved                      | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Silica as SiO <sub>2</sub> , Total     | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Silica as SiO <sub>2</sub> , Dissolved | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Zinc                                   | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |

| Analysis name        | Method reference | ICVB | CCVB | LCB | LCCB | LCS | LCSD | LCSL | ICV | ICVL | ICVH | QCS | MS | MSD | CCV | DUP | GGA |
|----------------------|------------------|------|------|-----|------|-----|------|------|-----|------|------|-----|----|-----|-----|-----|-----|
| Zinc, Dissolved      | EPA200.7         | X    | X    | X   |      | X   | X    |      | X   |      |      | X   | X  | X   | X   |     |     |
| Silver, Total        | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Aluminum, Total      | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Arsenic, Total       | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Barium, Total        | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Barium, Dissolved    | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Beryllium, Total     | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Cadmium, Total       | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Cobalt, Total        | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Chromium, Total      | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Copper, Total        | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Copper, Dissolved    | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Iron, Total          | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Iron, Dissolved      | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Mercury, Total       | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Lithium              | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Manganese, Total     | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Manganese, Dissolved | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Molybdenum, Total    | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Nickel, Total        | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Lead, Total          | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Antimony, Total      | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Selenium, Total      | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Tin, Total           | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Strontium, Total     | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Strontium, Dissolved | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Thallium, Total      | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |

| Analysis name                            | Method reference | ICVB | CCVB | LCB | LCCB | LCS | LCSD | LCSL | ICV | ICVL | ICVH | QCS | MS | MSD | CCV | DUP | GGA |
|------------------------------------------|------------------|------|------|-----|------|-----|------|------|-----|------|------|-----|----|-----|-----|-----|-----|
| Uranium by ICP/MS                        | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Uranium                                  | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Vanadium, Total                          | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Zinc, Total                              | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Zinc, Dissolved                          | EPA200.8         | X    | X    | X   |      | X   | X    |      | X   | X    |      | X   | X  | X   | X   |     |     |
| Bromide                                  | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Bromide, Dissolved                       | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Chloride                                 | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Chloride, Dissolved                      | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Fluoride                                 | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Fluoride, Dissolved                      | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Nitrite as NO <sub>2</sub> -N            | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Nitrite as NO <sub>2</sub> -N, Dissolved | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Nitrate as NO <sub>3</sub>               | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Nitrate as NO <sub>3</sub> -N            | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Nitrate+Nitrite as N                     | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| o-Phosphate-P                            | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Orthophosphate as PO <sub>4</sub>        | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Sulfate                                  | EPA300.0         | X    | X    |     |      |     |      |      | X   | X    |      |     | X  | X   | X   |     |     |
| Chemical Oxygen Demand                   | Hach 8000        |      |      | X   |      | X   | X    |      |     |      |      |     | X  | X   |     |     |     |
| Chemical Oxygen Demand, Soluble          | Hach 8000        |      |      | X   |      | X   | X    |      |     |      |      |     | X  | X   |     |     |     |
| Phosphorus, Total                        | Hach 8190        |      |      | X   |      | X   | X    |      |     |      |      |     | X  | X   |     |     |     |
| Phosphorus, Dissolved                    | Hach 8190        |      |      | X   |      | X   | X    |      |     |      |      |     | X  | X   |     |     |     |
| o-Phosphate-P                            | Hach 8190        |      |      | X   |      | X   | X    |      |     |      |      |     | X  | X   |     |     |     |
| o-Phosphate-P, Dissolved                 | Hach 8190        |      |      | X   |      | X   | X    |      |     |      |      |     | X  | X   |     |     |     |
| Urea-N                                   | Mulvenna&Savidge |      |      | X   |      | X   | X    |      |     | X    | X    | X   | X  | X   |     |     |     |

| Analysis name                             | Method reference             | ICVB | CCVB | LCB | LCCB | LCS | LCSD | LCSL | ICV | ICVL | ICVH | QCS | MS | MSD | CCV | DUP | GGA |
|-------------------------------------------|------------------------------|------|------|-----|------|-----|------|------|-----|------|------|-----|----|-----|-----|-----|-----|
| Cyanide                                   | QuikChem 10-204              |      |      | X   | X    | X   | X    | X    |     |      |      | X   | X  | X   |     |     |     |
| Chlorophyll-a                             | SM10200H; 19th               |      |      | X   |      |     |      |      |     |      |      | X   |    |     |     | X   |     |
| Color, Apparent                           | SM2120B                      | X    | X    |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Alkalinity, Total (as CaCO <sub>3</sub> ) | SM2320B                      |      |      |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Specific Conductance (E.C)                | SM2510B                      |      |      |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Specific Conductance (E.C)                | EPA120.1                     |      |      |     |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Salinity                                  | SM2520B                      |      |      |     |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Total Solids                              | SM2540B                      |      |      | X   |      | X   |      | X    |     |      |      |     |    |     |     | X   |     |
| Total Dissolved Solids                    | SM2540C                      |      |      | X   |      | X   |      | X    |     |      |      |     |    |     |     | X   |     |
| Total Suspended Solids                    | SM2540D                      |      |      | X   |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Fixed Dissolved Solids                    | SM2540E                      |      |      | X   |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Total Volatile Solids                     | SM2540E                      |      |      | X   |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Volatile Dissolved Solids                 | SM2540E                      |      |      | X   |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Settleable Solids                         | SM2540F                      |      |      |     |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Volatile Solids                           | SM2540G                      |      |      | X   |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Volatile Suspended Solids                 | SM2540G                      |      |      | X   |      |     |      |      |     |      |      |     |    |     |     | X   |     |
| Chlorine Residual, Free                   | SM4500-Cl G                  | X    | X    |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| Chlorine Residual, Total                  | SM4500-Cl G                  | X    | X    |     |      |     |      |      | X   |      |      |     |    |     | X   | X   |     |
| pH                                        | SM4500-H+B                   |      |      |     |      |     |      |      | X   |      |      |     |    |     |     | X   |     |
| Ammonia-N                                 | SM4500NH <sub>3</sub> B, C   |      |      | X   |      | X   |      |      |     |      |      |     | X  | X   |     |     |     |
| Kjeldahl Nitrogen                         | SM4500-NH <sub>3</sub> B,C,E |      |      | X   |      | X   |      |      |     |      |      |     | X  | X   |     |     |     |
| Kjeldahl Nitrogen,<br>Dissolved           | SM4500-NH <sub>3</sub> B,C,E |      |      | X   |      | X   |      |      |     |      |      |     | X  | X   |     |     |     |
| Ammonia-N                                 | SM4500NH <sub>3</sub> D      | X    |      |     |      |     |      |      | X   | X    |      |     | X  | X   |     |     |     |
| Ammonia-N, Dissolved                      | SM4500NH <sub>3</sub> D      | X    |      |     |      |     |      |      | X   | X    |      |     | X  | X   |     |     |     |
| Sulfide, Total                            | SM4500-S <sub>2</sub> - D    |      |      | X   |      | X   |      |      |     |      |      |     |    |     |     | X   |     |

| Analysis name                     | Method reference | ICVB | CCVB | LCB | LCCB | LCS | LCSD | LCSL | ICV | ICVL | ICVH | QCS | MS | MSD | CCV | DUP | GGA |
|-----------------------------------|------------------|------|------|-----|------|-----|------|------|-----|------|------|-----|----|-----|-----|-----|-----|
| Sulfides, Dissolved               | SM4500-S2- D     |      |      | X   |      | X   |      |      |     |      |      |     |    |     |     | X   |     |
| Biological Oxygen Demand          | SM5210B          |      |      | X   |      |     |      |      |     |      |      |     |    |     |     |     | X   |
| Biological Oxygen Demand, Soluble | SM5210B          |      |      | X   |      |     |      |      |     |      |      |     |    |     |     |     | X   |
| Carbonaceous BOD                  | SM5210B          |      |      | X   |      |     |      |      |     |      |      |     |    |     |     |     | X   |
| Soluble Carbonaceous BOD          | SM5210B          |      |      | X   |      |     |      |      |     |      |      |     |    |     |     |     | X   |
| DOC                               | SM5310C          | X    | X    |     |      |     |      |      | X   | X    | X    | X   | X  | X   | X   |     |     |
| TOC                               | SM5310C          | X    | X    |     |      |     |      |      | X   | X    | X    | X   | X  | X   | X   |     |     |
| MBAS (Surfactants)                | SM5540C          |      |      | X   |      | X   |      | X    |     |      |      |     | X  | X   |     |     |     |
| UV absorbance @ 254 nm            | SM5910B          |      |      | X   | X    | X   | X    |      |     |      |      |     |    |     |     | X   |     |
| UV Transmittance @ 254, Soluble   | SM5910B          |      |      | X   | X    | X   | X    |      |     |      |      |     |    |     |     | X   |     |

## Appendix F

### List of Standard Operating Procedures

| <b>Method (ELAP Cert)</b>        | <b>Analyte</b>                                                                  |
|----------------------------------|---------------------------------------------------------------------------------|
| SM5210B                          | Biochemical Oxygen Demand                                                       |
| SM5220D                          | Chemical Oxygen Demand                                                          |
| SM4500-Cl G                      | Chlorine, Free, Combined, Total                                                 |
| Hach                             | Chlorophyll A                                                                   |
| SM5220D                          | Chemical Oxygen Demand                                                          |
| Quickchem 10-204-00-1-X          | Cyanide                                                                         |
| EPA 200.7                        | Metals by ICP-OES*                                                              |
| EPA 300.0                        | Anions by IC*                                                                   |
| SM5540C                          | Surfactants                                                                     |
| EPA 1664 Rev. B                  | Oil & Grease Total                                                              |
| SM2120B-2001                     | Color                                                                           |
| EPA 180.1                        | Turbidity                                                                       |
| SM2320B                          | Alkalinity                                                                      |
| SM2510B                          | Conductivity                                                                    |
| SM2540C                          | Total Dissolved Solids; Residue, Filterable TDS                                 |
| SM2540D                          | Residue, Non-filterable TSS                                                     |
| SM2540F                          | Residue, Settleable                                                             |
| SM2550B-2000                     | Temperature                                                                     |
| SM4500-H+ B                      | Hydrogen Ion (pH)                                                               |
| SM4500-NH3 C (19th/20th)         | Ammonia                                                                         |
| SM4500-NH3 C (19th/20th)         | Kjeldahl Nitrogen                                                               |
| SM4500-NH3 D or E<br>(19th/20th) | Ammonia                                                                         |
| SM5310C-2000                     | Organic Carbon- Total (TOC)                                                     |
| HACH8190                         | Phosphorus, Total                                                               |
| SM2540B                          | Residue, Total                                                                  |
| Mulvenna & Savidge (not cert)    | Urea Nitrogen                                                                   |
| SM5910B                          | UV254                                                                           |
| Colitag                          | Total Coliform, E. Coli                                                         |
| Enterolert                       | Enterococci                                                                     |
| SM9215B                          | Heterotrophic Bacteria                                                          |
| SM9221B,E-2006                   | Total Coliform, Fecal Coliform                                                  |
|                                  | Total Coliform, Total Coliform (Enumeration), E. Coli, E. Coli<br>(Enumeration) |
| SM9223                           |                                                                                 |
| SimPlate                         | Heterotrophic Bacteria                                                          |



|            |                   |
|------------|-------------------|
| EPA 200.8  | Metals by ICP-MS* |
| EPA 160.4  | Residue, Total    |
| SM4500-O G | Dissolved Oxygen  |
| SM5210B    | Carbonaceous BOD  |

## Appendix G

### List of Lab Equipment

- Dionex 3000 ion chromatograph with AS40 automatic sampler
- Shimadzu TOC-V<sub>wp</sub> TOC analyzer with Shimadzu ASI-V automatic sampler
- Shimadzu UV-1800 UV/Vis spectrophotometer
- Hach \_\_\_\_ spectrophotometer
- Metro Ohm Titrino Plus 877 auto-titrator
- Orion 950 auto-titrator
- Orion 940 ion analyzer
- YSI 3100 conductivity probe
- Hach 2100N nephelometer
- HF Scientific DRT-15CE nephelometer
- Mettler Toledo AB204 analytical balance
- Mettler Toledo PB3002 analytical balance
- Ohaus DV214C top loading balance
- Buchi K437 TKN digestion block
- Buchi B-414 distillation unit
- Varian 715ES Radial ICP-OES
- Perkin Elmer ELANN 6100 ICP-MS

## Appendix H

### Definitions and Abbreviations

**Accuracy:** a measure of the agreement between an experimental determination and the true value.

**Calibration:** the process of comparing instrument readouts to known concentrations of an analyte of interest.

**Calibration Curve:** a graphical plot of values comparing instrument readouts to known concentrations of an analyte of interest.

**Calibration Range:** the range of concentrations used in a calibration curve from the lowest concentration to the highest. The calibration range should bracket the expected analyte concentration of the samples.

**California Water Environment Association (CWEA):** a professional association for workers in the wastewater fields that offers certifications and training.

**Continuing Calibration Verification (CCV):** calibration standards that are used to verify that there is no significant change in the instrument performance since calibration.

**Correlation Coefficient:** a measure of calibration linearity.

**Data Qualifiers:** codes used to describe sampling conditions, testing conditions, or QC results. They are also referred to as flags.

**Data Quality Objectives (DQOs):** specific criteria for the quality of data to be collected and the decisions to be made based on that data.

**Data Reduction:** the mathematical process of converting raw numerical values into meaningful results with the proper significant figures and units.

**Environmental Laboratory Accreditation Program (ELAP):** a program that oversees accreditation and external audits of environmental labs. ELAP is operated by the California State Water Resources Control Board.

**Field Reagent Blank:** lab reagent water that is supplied to samplers to be processed in the field in the same manner as samples including any field preservation or filtering; used to monitor contamination during sample collection and transportation. Field blanks are analyzed by the lab when requested and submitted by the client.

**Holding Time:** the allowed time from sample collection to analysis.

**ICP-MS:** Inductively Coupled Plasma – Mass Spectrometry

**ICP-OES:** Inductively Coupled Plasma – Optical Emission Spectrometry

**Initial Calibration Verification (ICV):** a calibration standard that is used to verify that the instrument has been successfully calibrated to produce results that meet acceptance criteria for accuracy of known analyte concentrations.

**Initial Demonstration of Capability (IDC):** the set of qualifications that an analyst must pass prior to being deemed trained for a particular analysis; this includes demonstrating proficient and working knowledge of the method and acceptable performance on specific quality control checks.

**Internal Standard:** a solution of compounds that analytically behave similarly to the analytes of interest. Internal standards are added to all blanks, standards, and samples prior to analysis to determine the response factors used in calculating analyte concentrations.

**Instrument Detection Limit (IDL):** the lowest signal that the instrument can reliably detect above the background noise of that instrument.

**Laboratory Control Standard (LCS):** a sample of reagent water to which a known amount of analyte has been added; used to evaluate accuracy of the analytical method. The LCS is submitted to all steps of the analytical process and is equivalent to a Laboratory Fortified Blank (LFB).

**Matrix Spike (MS):** a known amount of analyte that is added to a sample. Recovery is measured to determine if there are any matrix effects; equivalent to a Laboratory Fortified Matrix (LFM).

Matrix Spike Duplicate (MSD) is used to determine reproducibility of the analytical method.

**Method Blank:** a sample of reagent water that is subjected to the method and includes reagents that are normally in contact with samples during the analytical method; used to monitor background values and contamination; equivalent to a Laboratory Control Blank (LCB) or a Laboratory Reagent Blank (LRB).

**Method Detection Limit (MDL):** the lowest concentration of analyte that can be identified and measured with 99% confidence that the concentration is greater than zero.

**Minimum Level (ML):** the lowest concentration at which an acceptable calibration point can be achieved. Generally, the ML is equal to the lowest calibration point for a procedure.

**Practical Quantitation Limit (PQL):** the lowest level that can be reliably quantified during routine laboratory operation within the specified accuracy and precision limits. The PQL is determined by multiplying the minimum level (ML) by the dilution factor.

**Proficiency Testing (PT) study:** a set of blind samples that the laboratory analyzes under typical laboratory conditions; the results of the analyses are then compared to the published concentrations.

**Reporting Limit / Reporting Level (RL):** the level at which results are reported; this is equal to the PQL.

**Precision:** the degree of reproducibility of a particular analytical procedure.

**Quality Assurance (QA):** the systematic program that outlines the measures required to meet the lab's defined standards of quality.

**Quality Control (QC):** the routine procedures undertaken in the laboratory to maintain the analytical testing process within acceptable limits of accuracy and precision.

**Quality Control Sample (QCS):** a mid-range solution that is made from a different source than the calibration standards; used to evaluate correctness of instrument calibration.

**Sample Duplicate:** a second aliquot of sample that is tested to determine reproducibility of the analytical method.

**Standard Operating Procedure (SOP):** a written document that describes the lab's process for completing a certain analysis or task.



## **APPENDIX B. MBAS ANALYTICAL STANDARD OPERATING PROCEDURES**

## Enterolert enterococcus test

### Defined CHROMOGENIC SUBSTRATE TEST (SM 9230E)

Enterolert is used for the simultaneous detection, specific identification, and confirmation of enterococcus bacteria in drinking water and recreational water.

#### PRINCIPLE:

Enterolert is a specially designed reagent formulation of salts, nitrogen, and carbon sources that are specific to *Enterococcus faecium* and *Enterococcus faecalis*. It provides specific indicator nutrients: (4-Methylumbeliferyl-B-d-glucuronide) for the target microbes. As this nutrient is metabolized, fluorescence (from MUG) is produced.

#### STORAGE AND SHELF LIFE:

The lab assistant in the section will be responsible for ordering the following supplies:

Enterolert: Store at 2-30°C, away from light in a cool, dry environment. Do not use beyond outdate.

Comparator: Store at 4-30°C, away from light. Do not use beyond outdate.

#### QUALITY CONTROL PROCEDURES:

- 1) Sterility - Check sterility of one bottle from each new lot sample collection containers. Record the results on the Quality Control card kept next to the gray water incubator.
- 2) Performance check - Test each new lot of Enterolert with one positive and two negative controls for MMO and MUG reactions as follows:
  - a) Aseptically empty contents of a tube of Enterolert into four sterile vessels containing 100 mL sterile, distilled water. Mix thoroughly to aid dissolution.
  - b) Inoculate and label vessel 2 with *Enterococcus faecium*, vessel 3 with *Aerococcus viridians* and vessel 4 with *Serratia marcescens*, leaving the vessel 1 as a sterile water control.
  - c) Incubate the four vessels at  $41.0 \pm 0.5^{\circ}\text{C}$  for 24 hours.
  - d) After 24 hours of incubation, the following results should be observed:

|                                        |                 |
|----------------------------------------|-----------------|
| Sterile water control                  | No fluorescence |
| <i>Enterococcus faecium</i> ATCC 35667 | Fluorescence    |
| <i>Aerococcus viridians</i> ATCC 10400 | No fluorescence |
| <i>Serratia marcescens</i> ATCC 43862  | No fluorescence |

- e) If the results listed above are not obtained, repeat the test on additional reagents

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from the same lot. If again the proper results are not obtained, notify the chemist or laboratory director.

**SAMPLE CRITERIA:**

1. Fresh or marine water samples should be collected in presterilized 125 ml capacity bottles containing sodium thiosulfate to dechlorinate the sample. Note:  $\text{Na}_2\text{S}_2\text{O}_3$  in IDEXX sample containers is sufficient to neutralize 15mg/L residual chlorine.
2. A 100 ml sample volume is required for testing. If the volume of water is less than 95 ml, the sample can be diluted. Note dilution factor on worksheet as this will affect detection limit.
3. When sample dilution is required for quantitative testing (ie. recreational water) use sterile water. Do not dilute sample in buffered water; Enterolert is already buffered and additional buffer compounds can adversely affect the growth of the target microbes and test performance. Marine waters must be diluted at least tenfold.
4. Samples which cannot be delivered to the laboratory within 1 hour should be transported in an ice cooler at 4°C. A temperature blank should be included in the cooler and the temperature recorded on the requisition form. Samples should be refrigerated upon arrival and processed as soon as possible.

**PROCEDURAL NOTES:**

1. Avoid prolonged exposure of the inoculated Enterolert to direct sunlight.
2. Enterolert is a primary water test. Enterolert performance characteristics do not apply to samples altered by any form of pre-enrichment or concentration.

**QUANTITRAY (MPN) ENUMERATION PROCEDURE**

- 1) Samples are set-up on the day they arrive.
  - a) Recreational water samples should be diluted 10 fold in sterile dH<sub>2</sub>O (ie add 10 ml sample to 90 ml dH<sub>2</sub>O).
  - b) Non recreational water samples require dilution only if the sample volume is less than 97.5 ml or high numbers are expected. If the specimen bottle is overfilled, aseptically remove the excess water. If the bottle is underfilled by more

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than 2.5 ml, prepare a 1:10 dilution in sterile dH<sub>2</sub>O.

- 2) Aseptically open a tube of Enterolert reagent and add the contents to the 100 mL water sample.
- 3) Mix gently to dissolve the reagent. Once the reagent is dissolved, pour this sample directly into the Quantitray avoiding contact with the foil tab. Then seal according to Quantitray instructions. **Record date/time of inoculation and sample dilution of quantitray.**
- 4) Incubate reagent/sample mixtures for 24 hours at  $41^{\circ} \pm 0.5^{\circ} \text{C}$ .
- 5) Read the tray at 24 hours. Compare each result against the comparator dispensed into an identical vessel.
  - a) Examine all wells for fluorescence by placing the tray three-five inches from the U.V. lamp (use Woods' Lamp-365nm) in a dark environment. Wells which fluoresce are positive for enterococcus, count the number of small and large wells which are positive and record on the quanti-tray worksheet.
  - b) Use the Quanti-tray MPN table to convert the number of positive wells to the number of enterococcus per 100 ml. Record date/time of inoculation, date/time of reading, sample dilution and MPN on worksheet.
  - c) If a quanti-tray is inadvertently incubated over 24 hours, the following guidelines apply: A fluorescence after 28 hours is not valid and should be repeated or verified. Positives before 24 hours and negatives after 28 hours are valid.

REFERENCES

1. Standard Methods for the Examination of Water and Wastewater. SM 9230E. APHA, AWWA, WPCF, Denver, Colorado (2007).
2. Idexx laboratories \*Enterolert, Defined Substrate Technology

Date: January 2009

Written by: David Holland  
Revised April, 2014



Laboratory Director



## Cyanide (CN<sup>-</sup>)

### **Scope and Applications:**

This method applies to drinking water, ground water, reagent water, and wastewater.

### **Principle:**

This method involves direct colorimetric determination of cyanide using chloramine T trihydrate and pyridine-barbituric acid. Distilled cyanide is converted to CNCl by addition of acidic MgCl releasing agent and reaction with chloramine T trihydrate. Pyridine-barbituric acid is added to form a red-blue CNCl complex. Absorbance at 578 nm is proportional to the concentration of cyanide.

### **Detection Limits:**

The method detection limit and the reporting limit for cyanide is 5 µg/L CN<sup>-</sup>.

### **Acceptance Criteria:**

Laboratory Control Standard Low (LCSL) of 5 µg/L standard: 50-150%

Laboratory Control Standard (LCS) 100 µg/L : 90-110%

Second-source solution (QCS) 100 µg/L: 85-115%

Matrix spike recovery: 75-125%

Duplicates: ≤ 10% RSD

### **Working range:**

5µg/L to 250 µg/L CN<sup>-</sup>

Samples >250µg/L CN<sup>-</sup> should be diluted.

### **Interferences:**

- Chlorine : neutralize with sodium sulfite(avoiding an excess of 0.002gNa<sub>2</sub>S<sub>2</sub>O<sub>3</sub>/ L)
- Sulfide ion (S<sup>2-</sup>): Before increasing the pH of the sample check for the presence of S<sup>2-</sup> using lead acetate paper moistened with acetate buffer. If present, treat with lead carbonate. Mix about 25 ml of sample with lead carbonate , then centrifuge and filter through a 0.45 µm filter. **Note:** If Sulfide is present the sample have to be analyzed during 24 hrs.
- Make sure the cuvette is clean and free from smudges. Clean with DI when necessary.

### **Preservation and Holding Times:**

Samples are to be preserved with NaOH to a pH between 12to 12.5 and can then be stored at 4 °C for up to 14 days. Samples must be analyzed within this holding time. Check the pH of the samples prior to analysis.

### **Safety Precautions:**

- a) CAUTION: HCN is a toxic gas; avoid inhalation when distilling by working under the hood. Do not wear contact lenses.
- b) The cyanide anion (CN<sup>-</sup>) is highly toxic. Avoid contact and inhalation.
- c) Pyridine-barbituric acid is an acute upper respiratory tract irritant. Use under the fume hood and avoid inhalation of fumes.

d) Pyridine-barbituric acid is flammable and corrosive. Avoid contact.

**Reagents:**

Chloramine T trihydrate:

Weigh out 1.5 g chloramine T trihydrate and add to 100 mL DI H<sub>2</sub>O.

Phosphate buffer (1 M NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O):

Add 200-300 mL of DI H<sub>2</sub>O to a 500 mL volumetric flask. Weigh out 69 g NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, add to the volumetric, and fill to 500 mL.

Magnesium chloride releasing agent:

Place container in an ice bath. Add to this container 63 mL of 51% MgCl solution and 61.3 mL DI H<sub>2</sub>O. Slowly add 75.7 mL concentrated H<sub>2</sub>SO<sub>4</sub>. CAUTION: reaction is exothermic.

**Instrumentation/ Equipment:**

UV-1800 spectrophotometer purchased from Shimadzu (Serial no. A11455150458)

Digestion Block purchased from Lachat

Distillation Tubes purchased from Lachat (A17157)

**Calibration Standards:**

Prepare a 10 mg/L CN<sup>-</sup> solution from the 1000 µg/mL Simple Cyanide stock solution (*Absolute Grade Standard, Catalog no. 59017*). Fill a clean 100 mL volumetric flask with 50-60 mL DI H<sub>2</sub>O. Add 1 mL of 1 M NaOH as preservative and 1 mL of the 1000 µg/mL Simple Cyanide stock solution. Bring the volume up to 100 mL. This 10 mg/L CN<sup>-</sup> solution is used to make the calibration standards and can be kept in an airtight bottle stored at 4 °C for up to three months.

| Concentration (µg/L) | Volume (mL) of 10 mg/L CN <sup>-</sup> | Volume (mL) of 1 N NaOH | Final Volume (mL) |
|----------------------|----------------------------------------|-------------------------|-------------------|
| 5                    | 0.050                                  | 0.5                     | 100               |
| 10                   | 0.100                                  | 0.5                     | 100               |
| 100                  | 1.00                                   | 0.5                     | 100               |
| 250                  | 2.50                                   | 0.5                     | 100               |

**Quality Control:**

Laboratory Control Blank (LCB):

A blank solution of laboratory dilution water is to be analyzed at the beginning and end of each run to check if the instrument is drifting.

Laboratory Control Standard Low (LCSL):

Measure the concentration of the low calibration solution to check that the calibration is valid.

Laboratory Control Standard (LCS):

Measure the concentration of the mid calibration at the beginning and at the end of each batch.

Second-source solution (QCS):

Prepare a second source 10 mg/L complex  $\text{CN}^-$  solution from the 1000  $\mu\text{g/mL}$  Complex Cyanide stock solution (*Absolute Grade Standard, Catalog no. 54150*). This solution can be kept in an airtight bottle stored at 4 °C for up to three months. The QCS is a 100  $\mu\text{g/mL}$  complex  $\text{CN}^-$  solution made by diluting 1 mL of the 10 mg/L complex  $\text{CN}^-$  solution and 0.500 mL of 1 M NaOH to a final volume of 100 mL.

**Matrix spikes:**

Add 1 mL of the 10 mg/L simple  $\text{CN}^-$  solution to a 100 mL aliquot of a chosen sample. Add 6 mL of this matrix spike solution into two sample tubes for digestion. Matrix spikes should be analyzed every ten samples or at least once per batch.

**Continuing Calibration Verification (CCV)**

Measure the concentration of the 100  $\mu\text{g/L}$  calibration solution to check that the calibration is still valid. This should be measured every ten samples or at least once per batch.

**Set Up Procedure:**

1. Verify presence of interferences
2. Preheat Lachat digestion block (*Lachat Instrument, Serial no. A2000-625*) at 120 °C for at least 40 minutes.
3. Add 1.59 mL of 0.95 N NaOH to each Lachat collector tube.
4. Top each collector tube with a membrane and cap.
5. Add 6 mL of blank, calibration standards, QC solutions, and samples into separate, labeled sample tubes.
6. Add 0.75 mL MgCl releasing agent to the blank sample tube and immediately place the collector tube on top and use the capper to seal. Then place into digestion block.
7. Repeat for all sample tubes.
8. After the last sample is added to the digestion block, digest for 30 minutes.
9. Remove the blank digestion tube from the digestion block and immediately remove the sample tube by twisting downward. CAUTION: samples are hot.
10. Repeat for all digestion tubes.
11. Allow to cool to room temperature.
12. Invert each digestion tube collecting all of the receiving solution and condensation in the bottom of the collector tube labeled M. Break apart the digestions tubes and retain the collector tube containing the analyte solution.
13. Add 1.8 mL phosphate buffer to each collector tube.
14. Add 0.24 mL chloramines T trihydrate to each tube, swirl, and allow reaction for two minutes from the addition to the first tube.
15. Add 0.60 mL pyridine-barbituric acid to the first tube, bring the volume up to the 10 mL mark with DI  $\text{H}_2\text{O}$ , vortex, and allow reaction for 8 minutes. Do this for each tube.
16. Measure absorbance at 578 nm using a UV/VIS spectrophotometer as indicated below.

Note: Verify the temperature of the digestion block at the beginning and at the end of the digestion, to verify that there is any variation on temperature.

**Instrument Set Up Procedure (Hach DR 4000):**

1. Turn on Hach DR/4000U Spectrophotometer; allow it to warm up for at least 20 minutes.
2. Under user programs select user program 20
3. Rinse a clean 1 cm cuvette with a small portion of the blank, then add the blank to the cuvette and zero the instrument. Pour this blank solution back into the tube to use again.
4. Measure and record the absorbance of each calibration standard.
5. Exit to the main menu and under user programs select edit user program 20 Cyanide
6. Enter the calibration and obtain a linear r-value. The intercept should be set to zero and the r-value must be greater than 0.995.
7. Save the calibration and exit back to the main menu.
8. Under user programs select user program 20 Cyanide.
9. Rinse the cuvette with a small portion of blank and re-zero.

**Instrument Set Up (Procedure (UV-1800)):**

1. Turn on UV-1800 Spectrophotometer (*Shimadzu, Serial no. A11455150458USL*).
2. Select PC control, open the UV probe software in the computer.
3. Open the cyanide method: File/Open/Data/Cyanide.pmd
4. Fill the standard table with your calibration standards name and concentrations, including the blank. Right click on the graph, select properties and mark the option of correlation coefficient square.
5. Fill the sample table with your samples IDs
6. To start with the instrument calibration, make active the standard table by clicking anywhere on the table.
7. Rinse a clean cuvette (10 x 20 mm) with a small portion of the blank, then add the blank to the cuvette and blank the instrument by marking the cell blank option.
8. Measure the absorbance of each calibration standard.
9. The linear r-value must be greater than 0.995.
10. If is greater than 0.995, save the calibration and proceed with the sample and control measures.

**Reporting:**

1. Report results as µg/L cyanide, report up to three significant figures.
  2. Report only values that fall between lowest and highest standard. Dilute and reanalyze samples as necessary. Samples below the lowest standard are report as none detect.
- Note: Data needs Lead Chemist approval before entering into the system.*

**Calculations:**

1. QCS, LCS and LCSL %Recovery:  $(\text{Measured Value}/\text{Theoretical Value}) \times 100\%$
2. MS %Recovery:  $[(\text{Spiked Sample Measured Value} - \text{Sample Measured Value}) / \text{Theoretical Value}] \times 100\%$
3. MS %Difference:  $[|\text{MS} - \text{MSD}| / \text{Average (MS \& MSD)}] \times 100\%$

**References:**

APHA; AWWA; WEF. (1998). 4500-CN- CYANIDE. In *Standard Methods for the Examination of Water & Wastewater* (20th ed.).

Stieg, S. (1999). *MICRO DIST Operation and Applications Manual*. Lachat Instruments.

USEPA. (1980). *EPA Method 335.2: Cyanide, Total (Titrimetric, Spectrophotometric)*.

Written By: \_\_\_\_\_ Title: \_\_\_\_\_ Date: \_\_\_\_\_

Approved By: \_\_\_\_\_ Title: \_\_\_\_\_ Date: \_\_\_\_\_

## ***Chlorine Residual, Free & Total***

### DPD Colorimetric Method

#### **1. Scope and Application**

For testing free chlorine residual (hypochlorous acid and hypochlorite ion) and total chlorine residual (residual chlorine and chloramines) in water, treated waters, estuary and seawater.

#### **2. Detection Limits**

The method detection limit is 0.05 mg/L for free chlorine residual and for total chlorine residual.

#### **3. Precision and Bias**

Repeated analysis of a 0.05 mg/L standard resulted in an average of 0.057 mg/L and a standard deviation of 0.008 mg/L for the free chlorine residual analysis. Using the same standard in the total chlorine residual analysis resulted in an average of 0.054 mg/L and a standard deviation of 0.005 mg/L.

#### **4. Working Range**

0.05 to 2.00 mg/L, (Increase range with dilution using DI water)

#### **5. Summary of Method**

Chlorine can be present in the water as free chlorine and as combined chlorine. Both forms can exist in the same water and be determined together as total chlorine. Free chlorine is present as hypochlorous acid or hypochlorite ion. Free chlorine in the sample immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color which is proportional to the chlorine concentration. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride, and other chloro derivatives. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine and free chlorine reacts with DPD (N,N-diethyl-p-phenylenediamine) along with the free chlorine to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run a free chlorine test and a total chlorine test. Subtract the result of the free chlorine test from the total chlorine test to obtain the combined chlorine concentration.

#### **6. Sample Collection, Preservation and Holding Times**

Chlorine in aqueous solution is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly. Exposure to sunlight or other strong light or agitation will accelerate the reduction of chlorine. Therefore, start chlorine determinations immediately after sampling, avoiding excessive light and agitation. DO not store samples to be analyzed for chlorine.

#### **7. Comments**

##### **7.1 Interferences**

- a) Sample color and turbidity may interfere. Compensate for color and turbidity by using sample to zero spectrophotometer.
- b) Acidity greater than 150 mg/L  $\text{CaCO}_3$  may interfere. Color may not develop full or may fade instantly. Neutralize to pH 6-7 with 1 N NaOH.
- c) Alkalinity greater than 250 mg/L may interfere. Color may not develop fully or color may fade instantly. Neutralize with 1 N  $\text{H}_2\text{SO}_4$ .
- d) Bromine, iodine, ozone and chlorine dioxide interferes at all levels.
- e) Hardness interferes at greater than 1,000 mg/L as  $\text{CaCO}_3$ .
- f) Oxidized manganese ( $\text{Mn}^{4+}$ ,  $\text{Mn}^{7+}$ ) interferences are removed with the following procedure:
  - 1) Adjust pH to 6-7.
  - 2) Add 3 drops of KI (30 g/L) to a 25 mL sample.
  - 3) Mix and wait one minute.
  - 4) Add 3 drops sodium arsenite (5 g/L) and mix.
  - 5) Analyze 10 mL of the treated sample as described in this procedure.
  - 6) Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
- g) Monochloramines cause a gradual drift to higher free chlorine residual readings.
- h) Peroxides may interfere.
- g) Extreme sample pH and highly buffered samples have to be adjusted to pH 6-7.

## 7.2 Helpful Hints

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

## 8. Safety Issues

Standard safety habits and laboratory techniques apply.

## 9. Instrumentation/Equipment

Hach Pocket Colorimeter  
10 ml sample cell

## 10. Reagents and Standards

- a) DPD Free Chlorine Reagent Powder Pillows (HACH Cat. 21055-69)
- b) DPD Total Chlorine Reagent Powder Pillows (HACH Cat. 21056-69)
- c) Chlorine Standard Solution, 20-30 mg/L (HACH Cat. 26300-20)

## 11. Procedure

### 11.1 Sample Preparation

see section 7.1 Interferences

### 11.2 Instrument Operating Conditions

see Pocket Colorimeter Manual

### 11.3 Calibration

Colorimeters have a stable default calibration. The instrument calibration can be reestablished if the instrument fails QC. Refer to manual for instruction.

### 11.4 Analysis

- c) Fill a sample cell with 10 mL of sample (the blank). Place it into the cell holder and close the light shield.
- d) Press the soft key under <ZERO>. The display will show "0.00 mg/L Cl<sub>2</sub>".
- e) Add the content of one DPD Free Chlorine Powder Pillow or one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Shake for 30 seconds.
- f) Place the prepared sample into the cell holder. Close the light shield. Read results in mg/L chlorine after 30 seconds of reagent addition for free chlorine and 3 minutes for total chlorine.

## 12. Q.A./Q.C. Requirements

### 12.1 QC Analysis

Analyze a QC standard solution with each set.

**0.50 mg/L CL STD** –Dilute 1 ml 891 mg/L KMNO<sub>4</sub> to 100 ml. Dilute 5 ml of this soln to 100ml. or Hach Chlorine standard solution.

If results are not within acceptable range, perform corrective action and document.

### 12.2 Acceptance Criteria

Percent recoveries for the QC standard solution should be between 90 to 110 %.

## 13. Calculations

Correct for volume adjustments or manganese interference adjustments.

mg/L Cl<sub>2</sub>, combined = (mg/L Cl<sub>2</sub>, total) - (mg/L Cl<sub>2</sub>, free)

#### **14. Reporting**

##### **14.1 Reporting Units**

mg/L Cl<sub>2</sub>, free or mg/L Cl<sub>2</sub>, total.

##### **14.2 Reporting Limits**

0.05 to 2 mg/L. Samples with a chlorine residual of greater than 2 mg/L have to be diluted and reanalyzed.

##### **14.3 Significant Figures and Reporting Values Below Detection Limit**

Report results to the second decimal place if values are less than 1 mg/L Report values between 1 to 2 mg/L to two significant figures. Values below 0.05 are reported as "ND" (not detected).

#### **15. Reference/Method Source**

Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> Edition, 1992, pages 4-45 to 4-46.

Hach Pocket Colormeter Manual, HACH Company

DR/4000 Spectrophotometer Handbook, HACH Company 1997, pages 137 to 156.

Written by: Sigrid Weidner-Holland 2004  
Revised by David Holland 2016

Approved by:   
Laboratory Director

## **Chemical Oxygen Demand**

Closed Reflux, Colorimetric Method

### **1. Scope and Application**

The closed reflux, colorimetric COD method is applicable to wastewater analysis. The colorimetric reaction vessels are capped culture tubes. Oxygen consumed is measured against standards at 350 nm or 600 nm with a spectrophotometer.

### **2. Reporting Limit**

The method reporting limit for the low range COD (0-150 mg/L) is 5 mg/l.

The method reporting limit for the high range COD (0-1500 mg/L) is 50 mg/l.

### **3. Precision and Bias**

For the low range COD, repeated analysis of a 5 mg/L standard resulted in an average of 4.62 mg/L with a standard deviation of 0.92 mg/L.

For the high range COD, repeated analyses of a 5 mg/L standard resulted in an average of 5.129, with a standard deviation of 2.63 mg/L.

### **4. Working Range**

The working range is 0 to 150 mg/L for the low range COD and 0 to 1,000 mg/L for the high range COD.

### **5. Summary of Method**

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The mg/L COD results are defined as the mg of O<sub>2</sub> consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for 2 hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) to green chromic ion (Cr<sup>3+</sup>). When the 0-150 mg/L colorimetric method is used, the amount of Cr<sup>6+</sup> remaining is determined. When the 0-1,500 mg/L colorimetric method is used, the amount of Cr<sup>3+</sup> produced is determined.

The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.

### **6. Sample Collection, Preservation and Holding Times**

Preferably collect samples in glass bottles. Test unstable samples without delay. If delay before analysis is unavoidable, preserve samples by acidifying to pH <2 using concentrated sulfuric acid. Preferable acidify any sample that cannot be analyzed the same day it is collected.

### **7. Comments**

#### **7.1 Interferences**

Volatile straight-chain aliphatic compounds are not oxidized to any appreciable content. This failure occurs partly because volatile organics are present in the vapor space and do not come into contact with the oxidizing liquid. Straight chain aliphatic compounds are oxidized more effectively when silver sulfate (AgSO<sub>4</sub>) is added as a catalyst. However AgSO<sub>4</sub> reacts with chloride, bromide and iodide to produce precipitates that are oxidized only partially. The difficulties caused by the presence of halides can be overcome largely, though not completely, by complexing with mercuric sulfate (HgSO<sub>4</sub>) before the refluxing procedure.

Nitrite (NO<sub>2</sub><sup>-</sup>) exerts a COD of 1.1 mg O<sub>2</sub>/mg NO<sub>2</sub><sup>-</sup>-N. Because concentrations of NO<sub>2</sub><sup>-</sup> in waters rarely exceed 1 or 2 mg NO<sub>2</sub><sup>-</sup>-N/L, the interference is considered insignificant. To eliminate a significant interference due to NO<sub>2</sub><sup>-</sup>, add 10 mg sulfamic acid for each mg NO<sub>2</sub><sup>-</sup>-N present in the sample volume used; add the same amount of sulfamic acid to the reflux vessel containing the distilled water blank.

Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively under the test conditions. For significant levels of these species, stoichiometric oxidation can be assumed from known initial concentrations of the interfering species and corrections can be made to the COD value obtained.

## 7.2 Helpful Hints

Store the COD Digestion Reagent Vials in the dark in the refrigerator.

## 8. Safety Issues

The digestion solution for COD may be fatal if swallowed, causes severe burns and is harmful if inhaled or absorbed through the skin. The digestion solution is also a carcinogen and contains material which affects the kidneys and central nervous system.

## 9. Instrumentation/Equipment

Shamadzu Spectrometer  
COD Reactor

## 10. Reagents and Standards

COD Digestion Vials:

Note: Store COD Digestion Vials in the dark.

- 1) 0 to 150 mg/L COD (Chemetrics Cat.K7356)
- 2) 0 to 1,000 mg/L COD (Chemetrics K7356).
- COD Standard Solution, 1000 mg/L (Fisher Scientific)

## 11. Procedure

### 11.1 Sample Preparation

- 1) Homogenize the sample either by shaking or stirring.
- 2) Turn on the COD Reactor. Preheat to 150 °C.
- 3) Remove the cap of a COD Digestion Reagent Vial for the appropriate range.
- 4) Hold the vial at a 45-degree angle. Pipet 2.00 mL of sample into the vial.
- 5) Replace the vial cap tightly.
- 6) Invert gently several times to mix. Place the vial in the preheated COD Reactor.
- 7) Prepare a blank by repeating steps 3 to 6, substituting 2.00 mL DI water for the sample. Place the blank in the COD reactor.
- 8) Heat the vials for 2 hours.
- 9) Turn the reactor off. Wait about 20 minutes for the vials to cool to 120 °C or less.
- 10) Invert each vial several times while still warm. Place the vials into a rack. Wait until the vials have cooled to room temperature

### 11.2 Analysis

#### Instrument Set Up (Procedure (UV-1800):

1. Turn on UV-1800 Spectrophotometer (*Shimadzu, Serial no. A11455150458USL*).
2. Select PC control, open the UV probe software in the computer.
3. Open the cyanide method: File/Open/Data/Cyanide.pmd
4. Fill the standard table with your calibration standards name and concentrations, including the blank. Right click on the graph, select properties and mark the option of correlation coefficient square.
5. Fill the sample table with your samples IDs
6. To start with the instrument calibration, make active the standard table by clicking anywhere on the table.
7. Rinse a clean cuvette (10 x 10 mm) with a small portion of the blank, then add the blank to the cuvette and blank the instrument by marking the cell blank option.
8. Measure the absorbance of each calibration standard.
9. The linear r-value must be greater than 0.995.
10. If is greater than 0.995, save the calibration and proceed with the sample and control measures.

## 12. Q.A./Q.C. Requirements

### 12.1 QC Analysis

Run a blank and analyze a QC Standard Solution with each set.

Analyze each 20<sup>th</sup> sample as matrix spike and matrix spike duplicate with QC Standard Solution.

Each quarter an external reference sample must be analyzed. If results are not within acceptable range, perform corrective action and document.

### 12.2 Acceptance Criteria

Results are acceptable if the recoveries of the QC and the spikes are between 80 to 120 %.

Duplicates are acceptable if recoveries are within 10 %.

## 13. Calculations

1. QCS, LCS and LCSL %Recovery:  $(\text{Measured Value}/\text{Theoretical Value}) \times 100\%$
2. MS %Recovery:  $[(\text{Spiked Sample Measured Value} - \text{Sample Measured Value})/\text{Theoretical Value}] \times 100\%$
3. MS %Difference:  $[|\text{MS} - \text{MSD}|/\text{Average (MS \& MSD)}] \times 100\%$

Results have to be adjusted for any applied dilution factors.

## 14. Reporting

### 14.1 Reporting Units

mg/L COD

### 14.2 Reporting Limits

50 to 1,000 mg/L for high range COD.

5 to 100 mg/L for low range COD.

### 14.3 Significant Figures and Reporting Values Below Detection Limit

Results are rounded to the nearest whole number, up to three significant figures. Results below 5.0 mg/L are reported as "ND" (not detected).

## 15. Reference/Method Source

Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition, 1998

-UV-1800 Spectrophotometer from Shimadzu (Serial no. A11455150458)

Written by: David Holland

Approved by: \_\_\_\_\_

David Holland  
Laboratory Director

## ***Biochemical Oxygen Demand (BOD)***

### Dilution Method

#### **1. Scope and Application**

Measurement of BOD is the means for determining the degree of water pollution. It is useful as a measure of nutrient removal efficiency of a sewage treatment plant.

#### **2. Detection Limits**

A lower detection limit of 2 mg/L is established by the requirement for a minimum DO depletion of 2 mg/L.

#### **3. Precision and Bias**

The BOD test measures only the oxygen taken up by wastewater during the biological oxidation of organic matter present. Therefore, a BOD test is a highly unreliable means of determining the amount of organic matter present in water. The test measures only the approximate amount of oxygen that will be required by polluted water when it is exposed to air or oxygen for an extended period of time.

There is no measurement for establishing bias on the BOD procedure. The glucose-glutamic acid check is intended to be a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique. Single laboratory tests using a 300 mg/L mixed glucose-glutamic acid solution provided an average monthly recovery of 204 mg/L and an average monthly standard deviation of 10.4 mg/L. In a series of interlaboratory studies, the average was 198 mg/L with a standard deviation of 30.5 mg/L.

#### **4. Working Range**

The working range is equal to the difference between the maximum initial DO (7 to 9 mg/L) and minimum DO residual of 1 mg/L multiplied by the dilution factor.

#### **5. Summary of Method**

Biochemical Oxygen Demand (BOD) is the amount of oxygen, expressed in mg/L, that bacteria take from water when they oxidize organic matter. To determine BOD, the amount of oxygen the bacteria use is calculated by comparing the amount left at the end of 5 days with the amount known to be present at the beginning. During the 5-day period of a BOD test, the bacteria oxidize mainly the soluble organic matter present in the water. Very little oxidation of the solid (insoluble) matter occurs in that short time.

The dilution method is conducted by placing various incremental portions of the sample into bottles and filling the bottles with dilution water. The dilution water contains a known amount of dissolved oxygen. The dilution water contains a portion of inorganic nutrients and a pH buffer. The bottles are completely filled, freed of air bubbles, sealed and allowed to stand for 5 days at a controlled temperature of 20 °C (68 °F) in the dark. During this period, bacteria utilize the organic matter using the dissolved oxygen present in the water. At the end of the 5-day period, the remaining dissolved oxygen is measured. The relationship of oxygen that was consumed during the 5 days and the volume of the sample increment are then used to calculate the BOD.

#### **6. Sample Collection, Preservation and Holding Times**

Samples for BOD analysis may degrade significantly during storage. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20 °C before analysis

a) Grab samples: If analysis is started within 2 hours, cold storage is unnecessary. If analysis is not started within 2 hours of sample collection, keep sample at or below 4 °C. Begin analysis within 6 hours of collection if possible. In no case start analysis more than 48 hours after grab sample collection.

b) Composite samples: Keep samples at or below 4 °C during compositing. Limit composite period to 24 hours. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and condition as part of the results.

## 7. Comments

### 7.1 Interferences

Bacteria in the water oxidize organic matter. The growth of bacteria is highly temperamental and erratic and is affected by numerous factors, many of which are unknown or difficult to control. Also, the bacteria grow somewhat slowly, so that in a 5-day period, at 20°C, the biological oxidation is never complete. It is approximately 60 percent complete in five days, but is not 100 percent complete even after 20 days.

Many other factors also affect the tests. Toxic substances in the sample inhibit or even prevent bacterial growth and, therefore, oxidation of the organic matter.

### 7.2 Helpful Hints

The dilution water should not be prepared more than 8 hours before use, because biological growth will develop. Monitor temperature of samples, warm to approximately 20 degrees before analyses.

**Important! The DO uptake of seed should be between 0.6 and 1.0 mg/L**

## 8. Safety Issues

Treat samples as biological hazards. Wash hands after handling samples, wear gloves and eyewear.

## 9. Instrumentation/Equipment

- a) VWR Scientific Low Temperature Incubator (Model 2005 or 2020)
- b) 300 ml BOD bottles
- c) YSI Dissolved Oxygen Meter (Model 5100) with self-stirring BOD Probe (Model 5010)
- d) Keep one membrane kit from YSI on hand for consumable parts (i.e. membrane and fill solution)

## 10. Reagents and Standards

- 1) Dilution Water
  - a) Add one BOD Nutrient Buffer Pillow (HACH 2436466) to each jug containing 4 L of RO water at 20 °C.
  - b) Cap the jug and shake vigorously for 1 minute.
- 2) Polyseed BOD Seed Inoculum (WWTP influent or Pond may be used for seed)
  - a) Place contents of ½ a B.O.D. Seed (Bio-Systems) capsule into 200 ml of Dilution Water
  - b) Aerate the solution for 20 minutes using a small aquarium pump with a dispersion tube.
  - c) Use the seed solution within 2 hours of rehydration.
- 3) BOD Standard Solution (HACH 14865-10) 198 +/- 30.5 mg/L
- 4) Sodium Sulfite, ACS
- 5) Nitrification Inhibitor (HACH 2533-35)

## 11. Procedure

### 11.1 Sample Preparation

#### Dechlorination

- 1) Prepare 0.811g Sodium Sulfite in 100 mL Deionized water, make fresh daily.
- 2) Measure total chlorine residual using the HACH Total DPD powder reagent and colorimeter.
- 3) Add 1 mL Sodium Sulfite solution per 1 mg/L Total chlorine per liter of sample.
- 4) Re-measure total chlorine residual to ensure total chlorine was removed.

#### pH Adjustment

Check pH of sample with pH paper and if necessary neutralize samples to pH 6.5 to 7.5 with sulfuric acid or sodium hydroxide.

#### DO Supersaturated Samples

Reduce DO to saturation at 20 °C by shaking the sample in a partially filled bottle.

#### Temperature Adjustment

Bring samples with low BOD to 20°C ±1°C before making dilutions. The DO meter will compensate for temperature fluctuations.

#### **Nitrification Inhibitor**

If nitrification inhibition is desired (= Carbonaceous BOD) add 0.16 g of Nitrification Inhibitor (HACH 2533-35) to BOD bottle.

#### **Soluble BOD**

If soluble BOD is requested filter the sample volume with a 47mm filter before adding seed.

### **11.2 Instrument Operating Conditions**

see YSI 5000/5100 Operations Manual

see YSI 5905/5010 BOD Probe Instruction Manual

### **11.3 Calibration (performed before every analysis)**

- a) From the Main mode, press the [CALIBRATE] soft-key.
- b) Place the probe in air at 100% relative humidity. To achieve this, the probe is placed in a BOD bottle containing 1" of water. No stirring is required with the membrane **completely** dry.
- c) Allow the probe to polarize and the temperature to stabilize (15-20 min).
- d) Press [AUTO CAL]. The message "D.O. CALIBRATION SAVED" will be displayed for a few seconds.
- e) Press [MODE] to return to the main menu. Press [DIAGNOSIS] then [SENSOR] and check the slope (5.9-12.6%) and the current (8.0-17.0uA). If these are within the parameters, preferably 7.3% and 13.7uA, the instrument is now calibrated and ready to measure dissolved oxygen and temperature. If not then recalibrate and check the slope and current again.

### **11.4 Analysis**

- 1) Bring samples to 20°C ±1°C.
- 2) Set up one Blank: 300 ml dilution water
- 3) Set up Seed Control: 1 to 15 ml of B.O.D. Seed solution with dilution water (300 ml total volume)
- 4) Set up QC: 2, 3, and 4 ml of BOD Standard solution with 1 ml of Polyseed solution (or 0.5 to 2 ml of interference-free influent sample or up to 4 ml effluent pond sample) and dilution water (300 ml total volume).
- 5) Dechlorinate, adjust pH, add nitrification inhibitor or filter samples if necessary and then set up samples with a minimum of 3 dilutions to obtain DO uptake in the BOD range.
- 6) Make sure water level in bottles are mid-neck and take DO readings of each setup then stopper, water-seal, and cap.
- 7) Incubate at 20 °C for 5 days.

## **12. Q.A./Q.C. Requirements**

### **12.1 QC Analysis**

Run blank and seed controls with each set (An influent sample can be substituted for a seed control.). With each set run 2, 3 and 4 ml of the BOD Standard Solution (HACH 14865-10)

### **12.2 Acceptance Criteria**

The 5-day BOD value of the standard should be in the range of 198 +/- 30.5 mg/L.

The DO uptake of the blank should not be more than 0.2 mg/L (<0.1 mg/L preferred)

The residual DO in samples should be at least 1 mg/L and a DO depletion of at least 2 mg/L is required. A residual DO of less than 1 mg/L and a DO depletion of less than 2 mg/L is acceptable if the overall R<sup>2</sup> of the linear regression is at least 0.95.

## **13. Calculations**

$$\text{BOD}_5 = [(\text{mg/L DO uptake}_{\text{sample}}) - (\text{mg/L DO uptake}_{2 \text{ ml seed}})] / 300$$
$$\text{BOD}_5 = (\text{slope} \times 300) - (\text{Y-Intercept}) + (\text{DO of sample})$$

## 14. Reporting

### 14.1 Reporting Units

Values are reported as mg/L BOD<sub>5</sub> or mg/L cBOD<sub>5</sub>.

### 14.2 Reporting Limits

For results to be valid the residual DO must be greater than 1.0 mg/L and the depletion must be greater than 2.0 mg/L; if the conventional BOD method is used. For the slope BOD method, the R<sup>2</sup> value has to be at least 0.95. If slope calculation used, flag with sample comment on report. The oxygen depletion of the dilution water blank should be less than 0.2 mg/L after 5 days. No compensation is allowed for a DO difference of greater than 0.2 mg/L when using the conventional BOD method. However the slope BOD determination can still be used.

### 14.3 Significant Figures and Reporting Values Below Detection Limit

Values greater than 100 are reported as 3 significant figures. Values less than 100 are reported to 2 significant numbers. BOD values below 2 mg/L are reported as "ND" (not detectable).

## 15. Reference/Method Source

Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> Edition, 1995, pages 5-2 to 5-6.

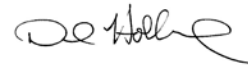
Introduction to Biochemical Oxygen Demand, Booklet No.7, HACH, 1992

YSI Model 5000/5100 Operation Manual, YSI Incorporated.

YSI 5905/5010 BOD Probe Instruction Manual, YSI Incorporated

Written by: Sarah McGinnis

Approved by:



David Holland

Reviewed September 7, 2016 DH

|                            | Media              | Incubaton Temperature | Incubation Time | Preparation                                                                                                                                       |
|----------------------------|--------------------|-----------------------|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| Total Coliform             | <b>Colitag</b>     | 35.0°C (+/- 0.5°C)    | 22-48 hours     | Add Media.<br>Gently shake to dissolve.                                                                                                           |
| Total Coliform 18 hour     | <b>Colitag</b>     | 35.0°C (+/- 0.5°C)    | 16-22 hours     | Add Media.<br>Gently shake to dissolve. Warm<br>in 44.5°C for 7-10 min.                                                                           |
| Total Coliform MPN         | <b>Colilert</b>    | 35.0°C (+/- 0.5°C)    | 24-28 hours     | Add Media.<br>Gently shake to dissolve.<br>Pour in tray, seal in QT Sealer                                                                        |
| Total Coliform MPN 18 hour | <b>Colilert-18</b> | 35.0°C (+/- 0.5°C)    | 18-22 hours     | Add Media.<br>Gently shake to dissolve.<br>Pour in tray, seal in QT Sealer                                                                        |
| Fecal Coliform             | <b>Colilert-18</b> | 44.5°C (+/- 0.2°C)    | 18-22 hours     | Add Media.<br>Gently shake to dissolve.<br>Pour in tray, seal in QT Sealer                                                                        |
| Enterococcus               | <b>Enterolert</b>  | 41.0°C (+/- 0.5°C)    | 24-28 hours     | Add Media.<br>Gently shake to dissolve.<br>Pour in tray, seal in QT Sealer                                                                        |
| Heterotrophic Pate Count   | <b>Simplate</b>    | 35.0°C (+/- 0.5°C)    | 45-72 hours     | Dilute 1mL sample into 9 mL<br>sterile DI in Simplate tube.<br>Include blank and dup each day.<br>Pour into plate and flick to<br>remove bubbles. |

Drinking water Total Coliform hold time: 30 hours

Surface Water Total Coliform hold time: 8 hours

Heterotrophic Plate Count hold time: 8 hours

## UV254 Absorption & Transmittance

### **Scope and Applications:**

Some organics compound found in water and waste water strongly absorb Ultraviolet (UV) radiation, UV absorption is a useful method to analyze the concentration of UV absorbing organic compounds in fresh water, salt waters, and wastewater.

### **Principle:**

The UV light absorption of a sample provides a proportion of the concentration of all UV-absorbing organic compounds that are present in the sample. More commonly found UV-absorbing organic compounds in water and wastewater include lignin, tannin, humic substances and various aromatics. UV absorption traditionally has been measured at 253.7 nm, if a sample is known to have interferences that absorbs light at this wavelength, the wavelength can be adjust. UV<sub>254</sub> absorption may also correlate to trihalomethanes (THM) precursors and other disinfection by-products (DBPs) as well as to organic carbon content and color. To control any variation in the UV absorption the sample should be filter before being analyze. The sample pH should be adjusted before filtering, filtering at lower pH may induce the lost of certain organic constituents. The sample pH of should be between 4 and 10, because UV absorption may vary when pH is lower than four or greater than ten.

### **Precison and bias**

A total of five KHP samples (pH=7) of a concentration of 0.54 mg/L as C, were measured in five different laboratories, for projected UV 254 absorption of 0.009 cm<sup>-1</sup>. The obtained results were a mean of 0.0086 cm<sup>-1</sup>, a standard deviation of 0.0011 and a relative standard deviation of 12.8 %.

### **Working Range**

The working range is between 0.000 cm<sup>-1</sup>-to 0.900 cm<sup>-1</sup>

### **Minimum Reporting Limits:**

For this test is not a method detection limit. The detection level for reporting is 0.001 cm<sup>-1</sup> UV<sub>254</sub>.

### **Acceptance Criteria:**

- Recovery of 0.009 cm<sup>-1</sup> standard: 88-112%, if is greater than this means that the instrument require maintenance.
- For UV values >0.045 cm<sup>-1</sup> the RPD % limit is ≤ 10 %
- For UV values <0.045 cm<sup>-1</sup> the RPD limit is ≤ 20 %

### **Interferences:**

- Colloidal particles, can be remove by filtering sample through a rinsed 0.45 µm filter
- Condensation and Smudges on the cuvette, can be remove by cleaning the cuvette with DI water
- UV<sub>254</sub>-absorbing inorganic: iron, nitrate, nitrite, and bromide

- Certain oxidants and reducing agents (e.g., ozone, chlorate, chlorite, chloramines, and thiosulfate) also absorb UV at 254 nm.

**Note:** Many natural and treated drinking water and treated drinking water have been shown to be free of these interferences.

### **Preservation and Holding Times:**

- Collect samples on amber glass bottles.
- Samples requiring shipping, should be transported on ice
- Store samples <6 ° C
- If needed, adjust Samples pH(4-10) before filtration.
- Analyze sample within 48 hours of collection

### **Instrumentation/Equipment:**

- UV-1800 Spectrophotometer* from Shimadzu (Serial no. A11455150458)
- Quartz 1 cm cuvette
- Filter 0.45  $\mu\text{m}$*  from Thermo Scientific (*Cat no. F2500-1*)

### **Reagents and Standards:**

- UV 254 Absorbance* 1,000  $\mu\text{g/mL}$  standard by Absolute Standards Inc. (Cat no. 54166).
- UV 254 0.009  $\text{cm}^{-1}$ : Dilute 500  $\mu\text{L}$  of stock solution (1,000  $\mu\text{g/mL}$ ) with 100 mL of DI water in a volumetric flask.

### **Quality Control:**

- Replicates Measurements:** Used at least two portions of the filtered sample.
- Duplicates analyses:** Analyzed every tenth samples a duplicate (i.e. repeating the entire procedure) or at least one per batch.
- Initial Calibration Verification Blank (ICVB):** A DI water is to be analyze at the beginning of each batch, every ten samples and at the end of each batch. A none zero absorbance of the blank means that the cell needs to be clean or there is variation in the spectrophotometer response.
- ICVB Filter:**  
A filter blank is to be analyzed at the beginning, every ten samples and end of each batch. A nonezero absorbance of the blank means that the filter is contributing to absorbance measurements..
- Instrument Calibration Verification (ICV):**  
A 0.009  $\text{cm}^{-1}$  standard is to be analyzed at the beginning of each batch, every 20 samples and at the end of each batch. This is to verify if there any variation in the instrument. The ICV should not be more than 25 % of difference of the first ICV measurement.

**-Filtered ICV:**

A portion of the  $0.009 \text{ cm}^{-1}$  standard is to be filtered through the rinsed  $0.45 \text{ }\mu\text{m}$  filter and analyzed at the beginning of each batch, every 20 samples and at the end of each batch. This is to determine if the filter results in gain or loss of absorbance.

**Instrument Setup Procedure:**

1. Turn on the spectrophotometer. Do not open the cover while it initializes.
2. Press Enter when prompted for a password.
3. Open the UV Probe software on the computer.
4. Select PC Control on the instrument (F4). Now all operations are controlled from the UV Probe Software.
5. Select Connect at the bottom of the screen.
6. To open the method, go to File, select open, and then change the file type at the bottom to Methods (\*.pmd). Select the UV254.pmd file and open.
7. Allow the instrument to warm-up.
8. If the absorbance with nothing inside the cover is not reading at 0.000, press auto zero.

**Analysis Procedure:**

1. Bring samples to room temperature prior to analysis.
2. Test and record the pH of each sample to ensure the pH is between 4 and 10. Adjust if necessary with either 0.1 N HCl or 0.1 N NaOH or include the pH in the report.
3. Rinse a clean 1 cm quartz cuvette with deionized  $\text{H}_2\text{O}$ . Fill the cuvette with DI  $\text{H}_2\text{O}$  and zero the instrument by selecting Cell Blank. A window will pop up displaying what the cell blank will be set to; select OK. The blank should measure  $0.000 \text{ cm}^{-1} \text{ UV}_{254}$ .
4. Rinse a  $0.45 \text{ }\mu\text{m}$  filter with at least 200 mL DI  $\text{H}_2\text{O}$  and draw up 12 mL of sample.
5. Discard at least 2 mL of sample and then filter into the cuvette.
6. Insert the cuvette into the holder and record the absorbance by selecting read.

**Note:** To make sure that there is not any variation of the instrument, analyze a ICV and Continuing Calibration Verification Blank (**CCVB**) at the end of each batch of samples or every 20 samples.

**Calculations**

$\text{UV}\lambda^{\text{pH}} = [A/b]D$ , pH superscript the pH used if it is other than 7

b= cell length path, cm

A= mean absorbance measured

D= dilution factor resulting from pH adjustment

**Reporting:**

1. Before entering data make sure that is approved by the lead chemist
2. Report the mean UV absorption of the replicate readings.
3. Reporting Units:
  - a. UV is reported as  $\text{cm}^{-1}$
4. Reporting Limits:  
The PQL for this test is  $0.001 \text{ cm}^{-1}$

**References:**

SM 5910 B Ultraviolet Absorption Method, "*Standard Methods for the Examination of Water and Wastewater*", 21<sup>th</sup> Edition, 2005.

Written By: Heather Craven  
Edited By: Lilian Reyes

Date: 06/09/14  
Date: 08/17/16

Approved By: \_\_\_\_\_

Date: \_\_\_\_\_

## Urea

### **Scope and Applications:**

The concentration of Urea Nitrogen is measured and reported in units of ug/L.  
This method applies to seawater, ground water, surface water and storm water or run off.  
The method has been modified to allow for analysis of 10 ml sample volumes.

### **Principle:**

The direct colorimetric determination of urea using Diacetylmonoxime Reagent.

### **Detection Limits:**

The detection level for reporting is 10µg/L as Urea Nitrogen.

### **Precision and Bias:**

Analysis of seven low level standards (10 ug/l) had an average of 10.9 ug/L with a standard deviation of 1.1 ug/L. The MDL was calculated as 3.3 ug/l. The PQL or reporting level was set at 10 ug/L and MDL set at 8 ug/L.

### **Acceptance criteria for a run**

ICV  
Spike recovery 80-120%  
Duplicates <20% RSD  
Instrument Calibration Verification Low (IVCL) 10µg/L std ± 20%  
Instrument Calibration Verification High (ICVH) 100 ug/L 80-120%  
Recovery of certified standard 47 µg/L std ± 20%  
Blank must not be negative but less than 10mg/L

### **Working range:**

10µg/L to 500µg/L Urea Nitrogen (Increase range with dilution). Report results to the whole number using bankers rounding, ND if <10mg/L and rerun if >500ug/L.

### **Interferences:**

Check for turbidity, filter if necessary, cuvettes often become smeared with H<sub>2</sub>SO<sub>4</sub> film, check cuvette before reading absorbance, clean with DI water when necessary.

### **Preservation and Holding times:**

Samples can be stored in the freezer to extend the hold time; otherwise samples must be analyzed within 24 hours. Studies have not been done to verify extension of hold time when samples are stored in the freezer, so analysis should be done as soon as possible. This test requires at least 20 mL of sample.

### **Reagents:**

Reagent A (expires in one month):

DAMO: Weigh out 3.4g of Diacetylmonoxime (DAMO) dilute with 90mL DI water in a beaker with stirring to dissolve. When dissolved transfer to a 100mL Volumetric Flask fill to 100mL with DI water.

Thiosemicarbazide Solution: weigh out 0.95g Thiosemicarbazide add to 100mL of DI water in a beaker with stir bar, stirring for 10 minutes, till dissolved.

Pour the 100mL of DAMO in to container add 4mL of Thiosemicarbazide solution. Store at ~4°C.

Reagent B (expires in one year):

H<sub>2</sub>SO<sub>4</sub> Solution: Weigh out 117mL of DI Water in a beaker, place beaker in ice water bath, add 150mL of conc. H<sub>2</sub>SO<sub>4</sub>. CAUTION! Reaction is extremely HOT!

Ferric Chloride Solution: shave off 0.15 g FeCl<sub>3</sub> into a small beaker. Dissolve in 10 ml DI. Add 0.25mL Ferric Chloride Solution to H<sub>2</sub>SO<sub>4</sub> Solution. Store at room temperature.

**Calibration Standards:**

Use 100mg/L Stock Urea standard (Fisher Scientific lot 015477) 0.0215 g/100 ml stored in ~4°C.  
Expiration 6 months  
Dilute stock to to prepare cal stds.  
500 ug/l Cal Std: 0.5mL Std diluted to 100mL in a Volumetric Flask with DI Water.  
100 /l Cal Std: 100µL Std diluted to 100mL in a Volumetric Flask with DI Water.  
50 ug/l Cal Std: 50µL Std diluted to 100mL in a Volumetric Flask with DI Water.  
10 Cal Std: 1mL of 1000ug/l Cal Std diluted to 100mL in a Volumetric Flask with DI Water.  
1000 Cal. Std: 1mL Std diluted to 100 mL in a Volumetric Flask with DI Water.

**Certified Reference Material: Absolute Standards 5000 ug/l Urea- Cat 93626**

Dilute reference material prepare aliquots with 10 mg/L urea and freeze. Thaw and prepare before analyses as directed.

**Quality Control:**

Prepare LCS and Matrix spikes by adding 1.0mL of 100 mg/L Std to 9mL DI water to create 10.0 mg/l Std. Add 0.1mL of 10.0mg/L to 9.9mL of sample for matrix spikes and 0.1 ml to 9.9 ml of DI water for the LCS. Prepare 47 ug/L Urea N control by adding 0.1 ml of 10 mg/L urea(4.66 mg/l as N) from Absolute to 9.9mL DI water. Analyze Matrix Spike in duplicates after every 10 samples. LCS must be performed at the beginning of the run and after every matrix spike duplicate. The certified reference material is analyzed at the beginning of the run. Create a QC packet of matrix spikes and LCS data to go along with reports, use template in Urea under QC on the NAS unit.

**Set Up Procedure:**

1. Wash out glass tubes with DI water.
2. Use an electronic pipette to fill tubes.
3. Measure 10mL of DI water into glass tube labeled B for the blank.
4. Measure 10mL of each Cal Std and put in their respective tubes.
5. Into tube labeled **1** add 10mL of 10 ug/L standard. Prepare 47 ug/L in tube 2.
6. Measure out at least 11mL of sample with a syringe and filter through a 1.0µm filter into a small plastic cup.
7. Measure 10mL of first sample put in tube **3**.
8. Repeat for all samples.
9. Every 10 samples set up matrix spikes and LCS.
10. To all tubes add 0.67mL Reagent A and 2.35mL Reagent B.
11. Vortex all tubes to ensure homogeneous mixture.
12. Put first set of tubes into water bath set at ~85°C for 21minutes with **8 pieces** parafilm covering tops of the tubes. Set dial on water bath to approx 6.2 **10**.
- 13.** At the end of 21minutes, take tubes out of water bath and put into cool water bath to cool to room temperature, place second set of tubes into hot water bath for 21minutes.
- 13.14.** **Vortex again before analyzing in spectrophotometer.**
- 14.15.** Perform analysis on samples immediately upon cooling to room temperature.

**Instrument Set Up Procedure:**

1. Turn on UV-1800 Spectrophotometer from Shimadzu (Serial no. A11455150458); allow warming up for at least 20 min at 520 nm.
2. Pour blank into **euve**~~et~~**cuvette** and zero the instrument, pour blank back into tube to use again if necessary. Take care to wipe any H2SO4 residue from cuvette.
3. Select Calibration Table and change absorbencies of the Cal Standards and repeat step two with each standard.

4. Enter Calibration and obtain r-value for a liner equation and verify intercept is a zero.
5. Pour blank into ~~euve~~cuvette and re-zero instrument.

**Analysis Procedure:**

1. Pour sample into 1cm path cuvet and take a reading. Report results as ug/L Urea Nitrogen.
2. Report only values that fall between lowest and highest standard. Dilute sample and reanalyze as necessary.
3. Dispose of sample in cuvette and rinse it out with DI water.
4. Repeat for all tubes.
5. Calculate % recovery of matrix spikes and LCS every 10 samples, to ensure the analysis is within control limits.

**Trouble Shooting:**

~~If high~~If high or low recovery is occurring check to see if standards are expired and precision of the pipettes being used. Clean the cuvette with alcohol and rinse well with water. The reaction in this experiment occurs rapidly so letting the finished samples sit out and react longer will result in low recoveries.

**Standards and Instruments Specifications:**

Water Bath: VWR Scientific, Shel Lab, Model 1202, Serial# 0903100  
Diacetyl Monoxime (CH<sub>4</sub>NO<sub>2</sub>) Cas#57-71-6  
Thiosemicarbazide 99% (CH<sub>5</sub>N<sub>3</sub>S) Cas#79-19-6  
Ferric Chloride 6-Hydrate, Lump (FeCl<sub>3</sub>) Cas#1996-1  
Urea Cas#57-13-6  
H<sub>2</sub>SO<sub>4</sub> ACS+ Grade Cas#7664-93-9

**Reference:**

Mulvenna, P. F. and Savidge, G., A Modified Manual Method For the Determination of Urea in Seawater using Diacetylmonoxime Reagent, *Estuarine, Coastal and Shelf Science* (1992) 34,429-438.

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Title:Laboratory Analyst

Date: November 13, 2014

Approved By:David Holland

\_Title:Laboratory Director

Date: December 1, 2015

## **Total Phosphorus / Colorimetric Phosphate**

### **Test 'N Tube Method**

#### **Scope and Applications:**

This method applies to drinking water, ground water, reagent water, and wastewater.

#### **Principle:**

Total phosphorus consists of reactive phosphorus and acid-hydrolyzable phosphorus. Reactive phosphorus is a measure of phosphates that readily react with the color reagent without digestion and consist primarily of orthophosphate. Therefore, non-digested samples that are reacted with the color reagent are reported in terms of  $\text{PO}_4\text{-P}$ . Samples for total phosphorus determination are acidified and digested with an oxidizer reagent before being neutralized and allowed to react with the color reagent. Absorbance of the reacted samples is measured at 890 nm.

#### **Detection Limits:**

The detection level for reporting is 0.03 mg/L P or  $\text{PO}_4\text{-P}$

#### **Acceptance Criteria:**

Low Level Calibration Verification (LCSL):  $\pm 50\%$

Instrument Calibration Verification, Continuing Calibration Verification (ICV, CCV):  $\pm 20\%$

Matrix Spike Recovery:  $\pm 30\%$

Duplicate RPD%:  $< 10\%$

Second Source Quality Control Sample (QCS):  $\pm 20\%$

Calibration  $r^2$ :  $\geq 0.9995$

#### **Working range:**

The working range is 0.03-1.0 mg/L P. This range can be extended if the sample is diluted.

#### **Interferences:**

- Alkaline or highly buffered samples may require additional acid during the acid addition in order to bring the pH to  $< 1$ .
- Highly turbid samples may interfere.
- Very high levels of metals may interfere. Dilute as necessary.

#### **Preservation and Holding Times:**

If samples cannot be analyzed immediately, acidify to  $\text{pH} < 2$  with  $\text{H}_2\text{SO}_4$  and store at  $4^\circ\text{C}$ .

Samples requiring dissolved phosphate or dissolved total phosphorus are to be filtered through a rinsed  $0.45\ \mu\text{m}$  filter upon receipt and then acidified to  $\text{pH} < 2$  with  $\text{H}_2\text{SO}_4$  and stored at  $4^\circ\text{C}$ .

Acidified samples must be analyzed within 28 days.

#### **Instrumentation/Equipment:**

Shimadzu UV-1800 UV Spectrophotometer

**Safety Precautions:**

- The Test 'N Tube vials contain acidic and corrosive solution. Avoid contact
- NaOH are both corrosive. Avoid contact.
- Potassium Persulfate reagent is an oxidizer. Avoid contact.

**Reagents:**

- 1.54N NaOH
- Potassium Persulfate for Phosphonate (Permachem Reagent) pillow packets (Hach cat#2084766 50/pack)
- PhosVer3 Phosphate Reagent (Permachem Reagent) pillow packets (Hach cat#32106069 100/pack, cat#2106046 50/pack)
- Test 'N Tube vials (Hach cat#2743645 50/pack; tubes and reagents)
- Absolute Organic Nutrients 1000ug/mL Total Phosphorus as P (cat#24152)
- Absolute Inorganic Nutrients 1000ug/mL O-Phosphate as P (cat#54153)
- Absolute 1000ug/mL Phosphate as P (cat#54105)

**Calibration Standards:**

Dilute the 1000 µg/mL P Organic Nutrients stock solution to 100 µg/mL P by adding 1.0 mL stock solution to 9.0 mL deionized water. Use this 100 µg/mL P solution to make the calibration as listed below.

| OC-CAL<br>Concentration (mg/L) | Volume of 100 µg/mL<br>Solution (mL) | Final Volume (mL) |
|--------------------------------|--------------------------------------|-------------------|
| 0.03                           | 0.030                                | 100               |
| 0.50                           | 0.100                                | 100               |
| 1.0                            | 0.200                                | 100               |
| 1.5                            | 0.500                                | 100               |
| 2.0                            | 1.000                                | 100               |

Pipette 5 mL of each calibration standard into labeled Test 'N Tube vials.

**Second Source Standard:**

Use a 1000 µg/L P Inorganic Nutrients stock solution that is from another source than the solution used to make the calibration standards. Dilute this second-source stock solution to 100 µg/mL P by adding 1.0 mL stock solution to 9.0 mL deionized water. Add 0.05 mL of this 100 µg/mL P solution to 4.95 mL DI to make a 1.0 mg/L P quality control sample (QCS). Use Phosphate as P stock for PO<sub>4</sub> as P analyses.

### **Quality Control:**

- Continuing Calibration Blank (CCB):
  - o Analyze the CCB at the beginning of each run, every 10 samples, and at the end.
- Low Level Calibration Verification (LCVL):
  - o A solution containing the same concentration as the lowest calibration solution is measured at the beginning of the batch.
- Second Source Quality Control (QCS):
  - o A mid-range solution made from a source that is different from that used to make the calibration is to be measured at least quarterly and every time that new calibration standards are prepared.
- Continuing Calibration Verification (CCV):
  - o A mid-range CCV should be analyzed every ten samples or at least once per batch.
- Matrix Spikes:
  - o A matrix spike and a matrix spike duplicate should be analyzed every ten samples or at least once per batch. If the matrix spikes do not meet the acceptance criteria, there may be matrix interference that warrants investigation.

### **Digestion Procedure:**

All calibration standards and quality control samples are to be digested along with samples requiring total phosphorus. Samples requiring  $\text{PO}_4\text{-P}$  are not to be digested.

1. Turn on the digestion block and allow it to warm up.
2. Neutralize at least 10 mL of sample to pH 6-8 using 5N NaOH.
3. Add 5 mL of the neutralized sample to a Test 'N Tube vial.
4. Add 1 packet of Potassium Persulfate reagent.
5. Cap and shake to mix and diffuse the heat generated and Vortex to thoroughly combine reagents and samples.
6. Samples may now be placed in the digestion block. Digest for 30 minutes at 150 °C.
7. Remove samples from the digestion block and allow them to cool to room temperature.
8. Add 2 mL of 1.54N NaOH

### **Instrument Warm-Up Procedure:**

1. Turn on the spectrophotometer. Do not open the cover while the instrument is initializing.
2. Press enter to get to the main menu and select "PC Control" at the top right.
3. Open the software and select "Connect" at the bottom of the screen (or F9).
4. Open the Phosphorus method file and allow the instrument to warm up for at least 30 minutes.
5. Set up the Standard Table for the calibration curve. Be sure to include the concentration of each calibration standard.
6. Add each sample to be analyzed into the Sample Table.

**Analysis Procedure:**

1. For samples requiring PO<sub>4</sub>-P, add 2 mL of 1.54 N NaOH to the Test 'N Tube vial, neutralize at least 10 mL of sample to pH 6-8 using 5N NaOH, and then add 5 mL of the neutralized sample to the Test 'N Tube vial.
2. Starting with the calibration blank, add 1 PhosVer3 packet to the sample and mix. Not all of the reagent will dissolve.
3. Allow the color-developing reaction to occur for 3 minutes and then read the absorbance in the 1 cm cuvette. Press "Read Std" or "Read Unk" at the bottom of the screen (or F9) to record data.
4. Repeat steps 4-5 for each calibration standard and then each sample.

**Shutdown Procedure:**

1. Disconnect the software from the instrument by selecting "Disconnect" or pressing F10.
2. Save data before closing.
3. Power off the spectrophotometer.

**References:**

Hach Method 8190 (DOC 316.53.01121)  
Standard Methods 4500-P E; 21<sup>st</sup> Edition

Written By: Heather Craven Title: Chemist Date: 04/21/2014

Updated By: Sarah McGinnis Title: Chemist Date: 12/10/2014

Approved By: David Holland Title: Lab Director Date 2/15/2015

### **HACH 8048 Orthophosphate/Ascorbic acid Method**

#### **Scope and Application**

This method covers the determination of orthophosphate in drinking water, surface and saline waters, domestic and industrial waters.

#### **Principle:**

Orthophosphate or inorganic phosphorus it is known to be reactive . Reactive phosphorus in presence of ascorbic acid (color reagent) is reduce to an intense blue color. The blue color is proportional to the total concentration of phosphorus. The developed color is measured at 890 nm on spectrophotometer.

#### **Detection limits:**

The detection level for reporting is 0.01 mg/L Phosphorus.

#### **Working range:**

The working range is 0.01-0.5mg/L P. This range can be extended if the sample is diluted.

#### **Acceptance Criteria:**

Laboratory Control Standard Low (LCSL) of 0.01 mg/L: 50- 150%

Laboratory Control Standard (LCS) 1 mg/L: 90-110%

Second-source solution (QCS) 1 mg/L: 80-120%

Matrix spike recovery 1mg/L: 70-130%

Matrix Spike Duplicate: <10% RSD

#### **Interferences:**

- Concentration as low as 0.1 mg /L of Arsenic as arsenate will cause a positive interference
- Concentration at 1 mg/L of Cr 6+ and NO<sub>2</sub><sup>-</sup> will cause a negative interference.
- Highly turbid samples may interfere  
A correction for turbidity should be analyzed by measuring a sample without the color reagent and after the reagent addition. Sample turbidity must be removed by filtration prior to analysis.
- The salt error for samples ranging from 5-20% salt content was found to be less than 1%
- Traces of phosphorus on glass ware can cause cross contamination. Avoid this by washing glassware, tubes and cuvette with HCL 1:1 and rinse with deionized water.

#### **Preservation and Holding Times:**

- Collect samples on 250 mL plastic bottles
- To asses dissolved orthophosphate, filter samples within 15 minutes of collection, using a 0.45 micron filter. The samples should be filtered on the field.
- Store samples <6 ° C
- Analyze sample within 48 hours of collection

- Let temperature to increase at room temperature before analysis.

### **Instrumentation and Equipment:**

- UV-1800 Spectrophotometer from Shimadzu (Serial no. A11455150458)
- Glass 5 cm cell
- Filter 0.45  $\mu\text{m}$  from Thermo Scientific (Cat no. F2500-1). Only for samples that for dissolved orthophosphate
- Test tubes 25 mL, rinsed with HCL 1:1
- Absolute Inorganic Nutrients 1000ug/mL O-Phosphate as P (cat#54153)
- Absolute 1000ug/mL Phosphate as P (cat#54105)

### **Safety Precautions:**

Wear safety glasses, glove and lab coat.

### **Reagents and Standards:**

#### **-Sulfuric Acid 5N:**

70 ml of H<sub>2</sub>SO<sub>4</sub> in 500 ml of water

#### **- Potassium antimonyl tartrate solution (Ricca, cat # 5872-16)**

#### **-Ammonium molybdate solution (Ricca, cat # 665-16)**

#### **-Ascorbic Acid (0.1M):**

1.76 g of ascorbic acid and dissolve in 100 mL distilled water.

Note: Should be use within a week after preparation

#### **-Combined reagent / Color reagent (100 mL):**

Mix above reagents at **room temparture** in the given **order**: 50 mL of 5N sulfuric acid, 5 mL of potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution.

**Note:** Mix after the addition of each reagent. This mixture is stable for 4 hrs.

### **Calibration Standards**

| Dilute the 1000  $\mu\text{g/mL}$  P Inorganic Nutrients stock solution to 100  $\mu\text{g/mL}$  P by adding 1.0 mL stock solution to 9.0 mL deionized water. Use this 100  $\mu\text{g/mL}$  P solution to make the calibration as listed below

| CAL Concentration (mg/L) | Volume of 100 µg/mL Solution (mL) | Final Volume (mL) |
|--------------------------|-----------------------------------|-------------------|
| 0.01                     | 0.100                             | 1000              |
| 0.03                     | 0.030                             | 100               |
| 0.05                     | 0.50                              | 100               |
| 0.1                      | 0.100                             | 100               |
| 0.3                      | 0.300                             | 100               |
| 0.5                      | 0.500                             | 100               |

**Notes:**

- For Analyses use 20 mL of each calibration standard into sample cell.

**Quality Control:**

- **Initial Calibration Blank (ICVB):**
  - A deionized water is to be analyze at the beginning of each batch, every ten samples and at the end of each batch.
- **Laboratory Control Standard Low(LCSL):**
  - A solution containing the same concentration as the lowest calibration solution is measured at the beginning of the batch.
- **Instrument Calibration Verification (ICV):**
  - A mid range standard should be analyzed at the beginning of each batch, every 10 samples and at the end of each batch. This is to verify if there any variation in the instrument. The ICV should not be more than 25 % of difference of the first ICV analyzed.
- Second Source Standard:**
  - Use a Absolute 1000ug/mL Phosphate as P (cat#54105)
  - A mid-range solution made from a source that is different from that used to make the calibration is to be measured at least quarterly and every time that new calibration standards are prepared.

**Matrix Spikes:**

- A matrix spike and a matrix spike duplicate should be analyzed every ten samples or at least once per batch. If the matrix spikes do not meet the acceptance criteria, there may be matrix interference that warrants investigation.

**Analysis Procedure:**

1. Add 20 mL of sample in an test tube.
2. Add 3.2 mL combined reagent and vortex.
3. Read sample after at least 13 min but no more than 30 minutes.

**Note:** To remove traces of phosphorus, make sure to wash glassware, tubes and cuvette with HCL 1:1 and rinse with deionized water.

**Instrument Setup Procedure:**

1. Turn on the spectrophotometer. Do not open the cover while it initializes.
2. Press Enter when prompted for a password.
3. Open the UV Probe software on the computer.
4. Select PC Control on the instrument (F4). Now all operations are controlled from the UV Probe Software.
5. Select Connect at the bottom of the screen.
6. Open the phosphorus standard: File/Open/Data/Phosphorus.std
7. Fill the standard table with your calibration standards name and concentrations, including the blank. Right click on the graph, select properties and mark the option of correlation coefficient square.
8. Fill the sample table with your samples IDs
9. To start with the instrument calibration, make active the standard table by clicking anywhere on the table.
10. Measure the absorbance of each calibration standard.
11. The linear r-value must be greater than 0.995.
12. If it is greater than 0.995, save the calibration and proceed with the sample and control measurements.

**Reporting:**

1. Report results as mg/L phosphate, report up to two decimal places.
2. Report only values that fall between lowest and highest standard. Dilute and reanalyze samples as necessary. Samples below the lowest standard are report as none detect.

**Note:** Data needs Lead Chemist approval before entering into the system.

**Calculations:**

1. QCS, LCS and LCSL %Recovery:  $(\text{Measured Value}/\text{Theoretical Value}) \times 100\%$
2. MS %Recovery:  $[(\text{Spiked Sample Measured Value} - \text{Sample Measured Value}) / \text{Theoretical Value}] \times 100\%$
3. MS %Difference:  $[|\text{MS} - \text{MSD}| / \text{Average (MS \& MSD)}] \times 100\%$

**References:**

Standard Methods 4500-P E; 20<sup>st</sup> Edition  
Method 365.1 EPA

| Written by: Lilian Reyes      Title: Lab Analyst I      Date: 03/31/15

## **Total Organic Carbon / Dissolved Organic Carbon**

### **Scope and Applications:**

This method applies to drinking water, ground water, reagent water, and wastewater.

### **Principle:**

Acidified sample is sparged to remove inorganic carbon (IC). The sample and a sodium persulfate oxidizing reagent then passes through the total carbon (TC) reactor where UV light and gentle heating is applied to convert the remaining organic carbon (OC) into carbon dioxide which is then measured with a non-dispersive infrared (NDIR) detector. This non-purgeable organic carbon (NPOC) measurement is reported as total organic carbon (TOC).

For dissolved organic carbon (DOC) determinations the sample is first passed through a rinsed 0.45  $\mu\text{m}$  filter and then submitted to the same process as above.

### **Detection Limits:**

The detection level for reporting is 0.20 mg/L OC.

### **Acceptance Criteria:**

Low Level Calibration Verification (ICVL):  $\pm 50\%$   
Continuing Calibration Verification (CCV):  $\pm 15\%$   
Matrix Spike Recovery:  $\pm 30\%$   
Duplicate RPD%:  $< 20\%$   
Second Source Quality Control Sample (QCS):  $\pm 20\%$   
Calibration  $r^2$ :  $\geq 0.995$

### **Working range:**

The working range is 0.20-10.0 mg/L OC. This range can be extended if the sample is diluted or if the instrument is recalibrated with a higher range of calibration standards.

### **Interferences:**

- Insufficient acidification will lead to incomplete release of  $\text{CO}_2$ .
- High levels of organic particulates can result in insufficient oxidation.
- Filtration for the determination of DOC can result in the loss or gain of DOC. Analyze filter blanks to check for this loss or contribution of DOC.

### **Preservation and Holding Times:**

Samples requiring TOC are to be collected in pre-preserved vials containing  $\text{H}_3\text{PO}_4$  and stored at  $\leq 6^\circ\text{C}$  until time of analysis. Samples requiring DOC are to be filtered in the field or laboratory within 48 hours of collection through a 0.45  $\mu\text{m}$  filter that has been rinsed with at least 250 mL deionized water. The sample is then to be acidified with  $\text{H}_3\text{PO}_4$  to  $\text{pH} \leq 2$  and stored at  $\leq 6^\circ\text{C}$  until time of analysis. Acidified samples are to be analyzed within 28 days of collection.

### **Instrumentation/Equipment:**

Shimadzu TOC-V<sub>WP</sub> Total Organic Carbon Analyzer Serial number: 41173528 with Shimadzu ASI-V Autosampler

### **Safety Precautions:**

- Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is corrosive. Avoid contact.
- Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is an oxidizing reagent and is corrosive. Avoid contact.
- Ultraviolet radiation is emitted from the UV lamp. Avoid prolonged viewing of this light even with the protective cover in place.

### **Reagents:**

- Persulfate Oxidizer Solution:
  - o Dilute 60 g of sodium persulfate and 15 mL  $\text{H}_3\text{PO}_4$  to 500 mL. This solution should be made at least 24 hours before use and kept in a cool, dark location. When stored in a cool, dark location it is stable for one month.
- Phosphoric Acid Solution:
  - o Add 100 mL of reagent grade  $\text{H}_3\text{PO}_4$  ( $\geq 85\%$ ) to 400 mL deionized water. This solution is stable for one month.
- Dilution water and rinse water:
  - o Acidify deionized water to  $\text{pH} < 2$  with  $\text{H}_3\text{PO}_4$  (1.5 mL per L is sufficient) for both the dilution water and the autosampler rinse water. The dilution water is to be replaced daily.

### **Calibration Standards:**

Use the 1000 mg/L stock solution Absolute Grade 59179 when making calibration standards as follows:

| Concentration (mg/L) | Volume of conc. $\text{H}_3\text{PO}_4$ (mL) | Volume of 1000 mg/L Solution (mL) | Final Volume (mL) |
|----------------------|----------------------------------------------|-----------------------------------|-------------------|
| 0.2                  | 0.150                                        | 0.020                             | 100               |
| 0.5                  | 0.150                                        | 0.050                             | 100               |
| 1                    | 0.150                                        | 0.100                             | 100               |
| 2                    | 0.150                                        | 0.200                             | 100               |
| 5                    | 0.150                                        | 0.500                             | 100               |
| 10                   | 0.150                                        | 1.00                              | 100               |

For the matrix spikes, add 0.060 mL of stock solution to 29.94 mL of sample.

### **Second Source Standard:**

Prepare a 500 mg/L second-source stock standard to be used to make the second-source standard (QCS). Dry potassium hydrogen phthalate (KHP) at 105-120 °C for about an hour and cool in a dessicator prior to use. Once cool, fill a clean 1 liter volumetric flask with 500-600 mL of deionized water and add 1 mL concentrated  $\text{H}_3\text{PO}_4$  and 1.063 g KHP and bring the total volume up to 1 liter. When stored in a cool, dark location, this solution is stable for 6 months.

This second source stock solution is to be remade if the analyzed QCS standard does not meet acceptance criteria or at the end of 6 months, whichever comes first.

Use this stock solution to make the QCS standard. Dilute 0.400 mL QCS stock solution and 0.150 mL  $\text{H}_3\text{PO}_4$  to 100 mL in a volumetric flask.

### **IC Removal Efficiency Check Solution:**

Prepare a 1000 mg/L IC check solution by adding 0.350 g sodium bicarbonate ( $\text{NaHCO}_3$ ) that has been dried in a dessicator for 2 hours and 0.441 g sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) that has been heated at 280 °C and cooled in a dessicator for at least 1 hour to a 100 mL volumetric flask that contains about 50 mL deionized water. Bring volume to 100 mL and store in an airtight glass container in a cool, dark place for up to two months.

To spike a sample aliquot to check for IC removal efficiency, add 0.2 mL of the IC check solution to 39.8 mL sample.

### **Quality Control:**

- Laboratory Reagent Blank (ICVB):
  - o An acidified blank solution is to be analyzed at the beginning and end of each run to assess background contamination. Add 50  $\mu\text{L}$   $\text{H}_3\text{PO}_4$  to 40 mL deionized water.
- Filter Blank:
  - o A filter blank must be analyzed for each lot of filters used for DOC analyses. Add 50  $\mu\text{L}$   $\text{H}_3\text{PO}_4$  to 40 mL of the filtered deionized water.
- Low Level Calibration Verification (ICVL):
  - o A solution containing the same concentration as the lowest calibration solution is measured at the beginning of the batch. If the ICVL does not meet acceptance criteria, recalibration is necessary.
- Second-Source Quality Control (QCS):
  - o A mid-range solution made from a source that is different from that used to make the calibration is to be measured at least quarterly and every time that new calibration standards are prepared. If the QCS does not meet acceptance criteria, prepare new stock solution and re-analyze. If it still fails to meet acceptance criteria, recalibrate.
- Continuing Calibration Verification (CCV):
  - o A mid-range CCV should be analyzed every ten samples or at least once per batch. If the CCV does not meet acceptance criteria, recalibrate.
- Matrix Spikes:
  - o A matrix spike and a matrix spike duplicate should be analyzed every ten samples or at least once per batch. If the matrix spikes do not meet the acceptance criteria, there may be matrix interference that warrants investigation.
- IC Removal Efficiency Check (as needed):
  - o A sample of each matrix is to be spiked with a solution of inorganic carbon and compared to un-spiked aliquot of that sample to determine if IC removal conditions are sufficient. If the spiked sample produces a higher measured NPOC value, then the sparge conditions need to be adjusted until the spiked and un-spiked portions are  $\leq 10\%$  RPD.
  - o Re-analyze for each matrix whenever instrument settings are altered.

### **Instrument Warm-Up Procedure:**

1. Turn on the nitrogen gas supply. The supply pressure should be ~50 PSI.
2. Turn on the instrument.
3. Launch the software, open a new worksheet and select connect.
4. Check to make sure that the carrier gas supply indicator on the front of the instrument is reading at 200 PSI. Adjust if necessary.
5. Allow the instrument to warm up for at least 30 min before continuing with analysis. The instrument status should indicate that it is ready before analysis can begin.

### **Setup Procedure:**

1. Rinse out the instrument flow lines by selecting the Instrument menu, Maintenance, and Replace Flowline Content.
2. Run at least one acidified blank prior to analysis to clean the instrument. Then analyze the ICVB.
3. Samples are to be brought to room temperature prior to analysis. Wastewater samples are to be filtered through a 1.0  $\mu\text{m}$  filter prior to analysis to remove large particulates. Check pH.
4. Add all samples and QC samples to the worksheet. All samples are to be analyzed with the NPOC method and the current calibration curve.
5. Select the autosampler icon on the top right corner and assign each sample the appropriate space on the autosampler.
6. Once the worksheet is completed, begin the run by selecting Start at the top right. Be sure to select the appropriate action for the completion of the run (Keep Running, Sleep, or Shut Down).

### **Shutdown Procedure:**

If at the start of the run the Shutdown option is selected for the completion of the run, then after it is completed shut off the nitrogen gas supply. If it is not selected, then follow the steps below.

1. Select Shutdown from the top right of the software window and press OK.
2. Press the power button on the front of the instrument to turn it off.
3. Turn off the nitrogen gas supply.

### **Basic Instrument Maintenance:**

- Check the condition of the tubing, halogen scrubber, and syringe plunger tip daily. Replace as necessary according to the user manual.
- At the start of each run, select the Instrument menu, Maintenance, and Replace Flowline Content to draw new dilution water into the tubing and expel any previous dilution water.
- Periodically wash the IC sparge chamber and TC reaction chamber by selecting the Instrument menu, Maintenance, and Washing. From there, select the chamber and it will be washed with dilution water.
- If the signal drops off, check that there is adequate persulfate solution and that there are no leaks or sharp bends in any of the sample lines. If this does not correct the problem, the 8-port valve rotor may need to be cleaned or replaced per the instrument manual instructions. If the problem persists, the instrument needs to be serviced by a Shimadzu representative.

**Reporting:**

Report all results to the tenth.

**References:**

AWWA, APHA, WEF. (2005). 5310 C. Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method. In *Standard Methods for the Examination of Water and Wastewater* (21st ed., pp. 5-23 - 5-25). Baltimore, MD.

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Shimadzu Corporation, Analytical & Measuring Instruments Division. (2004). *TOC-VWP Total Organic Carbon Analyzer User's Manual*. Kyoto, Japan.

Written By: Heather Craven Title: Chemist Date: 12/30/2013

Approved By: David Holland

Title: Laboratory Director

Date: 11/24/2014

## CHROMOGENIC SUBSTRATE TEST (SM 9223)

Colilert is used for the simultaneous detection, specific identification, and confirmation of total coliforms and *Escherichia coli* in drinking water and recreational water. Colilert-18 reagent must be used for marine water for detection of *E. coli* and must be diluted 10fold.

### PRINCIPLE:

Colilert is a specially designed reagent formulation of salts, nitrogen, and carbon sources that are specific to total coliforms (Family Enterobacteriaceae, mainly: *Citrobacter*, *Enterobacter*, *Escherichia*, *Klebsiella*, along with *Hafnia*, *Serratia*). It provides specific indicator nutrients: ONPG (O-Nitrophenyl-B- d-galactopyranoside) and MUG (4-Methylumbeliferyl-B-d-glucuronide) for the target microbes, total coliforms and *Escherichia coli* respectively. As these nutrients are metabolized, yellow color (from ONPG) and fluorescence (from MUG) are released confirming the presence of total coliforms and *E. coli*, respectively. Non-coliform bacteria are suppressed and cannot metabolize the indicator nutrients.

### STORAGE AND SHELF LIFE:

Colilert: Store at 4-30°C, away from light in a cool, dry environment. Do not use beyond expiration date.

Comparator: Store at 4-30°C, away from light. Do not use beyond expiration date.

### QUALITY CONTROL PROCEDURES:

1. Sterility: check sterility of one bottle from each new lot of sample collection containers unless sterility check has been performed by supplier. Record the results on the Quality Control card kept in microbiology binder.
2. Performance Check: test each new lot of Colilert (Idexx Cat#WP200I) and Colilert-18 (Idexx Cat#WP200I-18) with positive and negative controls for ONPG and MUG reactions as follows:
  - a. Into three separate sterile vessels, aseptically empty contents of a tube of Colilert into each sterile vessel containing 100 mL sterile, distilled water. Mix thoroughly to aid dissolution.
  - b. Label the vessels "*Escherichia coli*", "*Klebsiella pneumoniae*", and "*Pseudomonas aeruginosa*" respectively.
  - c. Using a sterile inoculating loop, transfer the following viable cultures: *E. coli* (ATCC #11775), *K. varicola* (ATCC #31488), and *Ps. aeruginosa* (ATCC 10145) to the appropriately labeled Colilert vessel.

- d. Incubate the three vessels at  $35.0 \pm 0.5^{\circ}\text{C}$  for 24 hours.
- e. After 24 hours of incubation, the following results should be observed:

*E. coli* - Yellow and florescent

*K. varicola* - Yellow, no fluorescence

*Ps. aeruginosa* - No color, no fluorescence

- 3. If the results listed above are not obtained, repeat the test on additional reagents from the same lot. If again the proper results are not obtained, notify the laboratory director.

### **SAMPLE CRITERIA:**

- 1. Drinking water samples should be collected in pre-sterilized 125 ml capacity bottles containing sodium thiosulfate to dechlorinate the sample. Note:  $\text{Na}_2\text{S}_2\text{O}_3$  in IDEXX sample containers is sufficient to neutralize 15mg/L residual chlorine.
- 2. A 100 ml sample volume is required for finished drinking water. If the volume of finished drinking water is less than 95 ml, the sample may not be diluted to 100 ml. Report as "unsatisfactory, quantity not sufficient"
- 3. When sample dilution is required for quantitative testing (i.e. recreational water) use sterile water. Do not dilute sample in buffered water; Colilert is already buffered and additional buffer compounds can adversely affect the growth of the target microbes and test performance.
- 4. Samples which cannot be delivered to the laboratory within 2 hours should be transported in an ice cooler at  $4^{\circ}\text{C}$ . Samples should arrive within 2 hours of collection or at temperature  $<10^{\circ}\text{C}$ . Samples should be refrigerated upon arrival and processed as soon as possible. At no time should the elapsed time between collection and processing exceed 30 hours for drinking water, 6 hours for wastewater, or 8 hours for surface water.
- 5. All samples processed or received later than required hold time are to be brought to the attention of the senior chemist or laboratory director and a note should be made on the COC or result entry.
- 6. Some water samples containing humic material may have an innate color and/or turbidity. These samples are unsuitable for the Colilert method; finished drinking water samples with innate color and/or turbidity should be tested using the 10 tube multiple tube fermentation method. Inoculate 10 tubes of double strength lauryl tryptose with 10 ml of sample; incubate and read tubes as described in Standard Methods). Both total and fecal coliforms are to be reported between  $<1$  and  $>2420$  (unless diluted) and reported to the whole number.

## **SAMPLING PROCEDURE:**

1. Sterile containers provided by Monterey Bay Analytical Services must be used. If other containers are used the client will be notified that the container used instead cannot be guaranteed sterile. Do not touch or otherwise contaminate the inside of the container, the inside of the cap, or the treads of the container. Completely remove any seal on the lid or lip of the bottle. Do not rinse the container. If the container appears to be damaged discard it and select a new one.
2. Choose a faucet both based on the requirements of the sampling site plan and the quality of the sampling site. Do not take a sample from a faucet that is leaking around the handle. Do not take a sample from a dirty faucet or one that is equipped with an aerator and/or screen. Do not take a sample from a swing type faucet. Never take a sample from a hose or other device which is attached to the faucet, remove it first.
3. It is usually prudent to sterilize the faucet either with a bleach solution or by flaming with a torch to remove any bacteria that may reside at the sampling point. If using bleach be sure to flush the site so no residual chlorine remains. This step is not required but it is recommended.
4. Open the faucet just enough to produce a flow which can be collected without splashing. Let the water run until a stable chlorine level is attained, usually about 2 to 3 minutes. Carefully fill the container up to the 100-ml mark. Immediately replace the cap (tightly) and record the sample with site identification, description of sample point, date and time of collection, name of sample collector, and chlorine residual if appropriate.

## **PROCEDURAL NOTES:**

1. Avoid prolonged exposure of the inoculated Colilert to direct sunlight. The indicator compounds may be hydrolyzed, creating a false-positive (yellow) result.
2. Colilert is a primary water test. Colilert performance characteristic do not apply to samples altered by any form of pre-enrichment or concentration (e.g. membrane filter or growth in lactose broth).
3. High numbers of other heterotrophs (for example, *Flavobacterium*) can cause a false positive B-glucuronidase fluorescence and an inaccurate indication of *E. coli*. While one would not normally expect to encounter such extremely high levels of heterotrophs in a water sample, pre-enrichment could produce them.
4. High calcium salt concentrations in certain waters may cause a slight precipitate. This should not affect results.

### **PRESENCE/ABSENCE PROCEDURE (FINISHED DRINKING WATER):**

Samples are given unique identification numbers during the log in procedure. *The procedure below is based on the standard Colitag (Cat#4600-0013) reagent. If Colilert-18 reagent is substituted, the incubation period must be adjusted.*

1. Specimens are set-up on the day they arrive. Check each sample bottle for proper sample quantity. If the specimen bottle is overfilled, aseptically remove the excess water. If the bottle is under filled by more than 5 ml (less than 95 ml of sample is received), record the following on the lab form, "Quantity not sufficient; unable to test, please resubmit".
2. Aseptically open a tube of Colitag reagent and add the contents to the 100 mL water sample. Tighten the cap and write the time the Colitag was added on the worksheet.
3. Shake vigorously to dissolve the reagent. Some particles may remain undissolved. Dissolution will continue during incubation. Note: Upon mixing of Colitag reagent with the sample, a transient blue color may appear in samples containing 40-50 times the amount of free chlorine normally found in drinking water. The sample should be considered invalid and testing discontinued. Record the following on the report form, "Specimen highly chlorinated; unsuitable for Colitag testing, please resubmit".
4. Incubate reagent/sample mixtures at  $35^{\circ} \pm 0.5^{\circ}$  C for 24 hours. Note: If Colilert-18 reagent is used incubation time will be adjusted to 18-22 hours.
5. Read the reaction vessels at 24 hours. Color should be uniform throughout the vessel. If not, mix by inversion before reading. Use the comparator to read the sample bottles; the comparator is the lowest level of yellow and fluorescence which can be considered positive. A typical positive test is much more intense than the comparator.  
Note: If an inoculated Colitag vessel is inadvertently incubated over 28 hours - the following guidelines apply. No yellow color is a valid NEGATIVE TEST. A yellow color after this incubation period must be verified (see supplemental section for verification procedure).
6. Total Coliforms:
  - a. At 24 hours, compare each reaction vessel against the color comparator dispensed into an identical vessel.
  - b. If no yellow is observed, the test is negative for total coliforms and E. coli; report "Total Coliforms and E. coli absent".
  - c. If the sample has a yellow color greater or equal to the comparator, the presence of total coliforms is confirmed; report "Total Coliforms present" and go to the E. coli section.
  - d. If a sample is yellow after 24 hours of incubation, but slightly less than the positive comparator, it may be incubated up to an additional 4 hours (see note 3). If the sample is coliform positive, the color will intensify; report "Total Coliforms present" and go to the E. coli section. If it does not intensify, report "Coliforms absent".

Note: If the 28 hour reading period is exceeded, verify the specimen according to the supplemental procedure.

7. *E. coli*: if yellow is observed at 24 hours, check each vessel for fluorescence by placing it three to five inches from the U.V. lamp (use Woods'Lamp-365nm). Observe for fluorescence in a dark environment.
  - a. If the fluorescence is greater or equal to fluorescence of the comparator, the presence of *E. coli* is specifically confirmed; report "*E. coli* present".
  - b. If the fluorescence is less than the comparator, report "*E. coli* absent".
8. Record results on presence/absence worksheet including date/time of inoculation and date/time of reading and analysts initials.

### QUANTITRAY (MPN) ENUMERATION PROCEDURE

1. Samples are set up on the day they arrive. 6 hour hold time for wastewater, 8 hour hold time for surface water, 30 hour hold time for drinking water.
  - a. Recreational water samples should be diluted at least 10 fold in sterile dH<sub>2</sub>O (i.e. add 10 ml sample to 90 ml dH<sub>2</sub>O).
  - b. Non recreational water samples require dilution only if the sample volume is less than 100 ml. If the specimen bottle is overfilled, aseptically remove the excess water. If the bottle is under filled by more than 2.5 ml, prepare a 1:10 dilution in sterile dH<sub>2</sub>O.
2. Aseptically open a tube of Colilert reagent and add the contents to the 100 mL water sample.
3. Mix gently to dissolve the reagent. Once the reagent is dissolved, pour this sample directly into the tray avoiding contact with the foil tab. Then seal according to Quanti-tray instructions. Record date/time of inoculation, analyst's initials and sample dilution of quantitray.
4. Incubate reagent/sample mixtures for 24-28 hours if using Colilert reagent and 18-22 hours when using Colilert-18 reagent at  $35 \pm 0.5$  °C.
5. Read the tray at 24 or 18 hours. Compare each result against the comparator dispensed into an identical vessel.
  - a. Wells with yellow color greater or equal to the comparator are positive for total coliform. Count the number of small and large wells which are positive for total coliforms and record on the quantitray worksheet.
  - b. Examine all wells positive for total coliform for fluorescence by placing the tray three to five inches from the U.V. lamp (use Woods'Lamp-365nm) in a dark environment. Wells which fluoresce are positive for *E. coli*. Count the number of small and large wells which are positive for *E. coli* and record on the quantitray worksheet.
  - c. Use the Quantitray MPN table to convert the number of positive wells to the number of total coliforms and *E. coli* per 100 ml. Record date/time of inoculation, date/time of reading, analyst's initials, sample dilution and MPN on worksheet.

- d. If a quantitray is inadvertently incubated over 28 or 22 hours, the following guidelines apply: A yellow color after 24 or 22 hours is not valid and should be repeated or verified. If the 24 or 22 hour reading period is exceeded, verify the specimen according to the supplemental procedure.
- e.

#### **REPORTING:**

1. The analyst is responsible for notifying submitter within 24 hours of determining: 1) E. coli or Total coliforms are present in a sample; or 2) a sample is invalidated. Examples of sample invalidation include immediate production of color when colilert reagent is added to sample (i.e. chlorine interference). Phone the submitter and document notification on the worksheet; it should include the date, time, and client contacted.
2. The laboratory must report drinking water samples directly to the State Department of Public Health by the 10<sup>th</sup> day of the month following sample collection. Report:
  - a. All results (positive, negative, repeat, or replacement) from water systems that serve 15 to 10,000 service connections.
  - b. All positive, repeat, or replacement results from systems serving more than 10,000 service connections.
3. After results have been entered into the computer the worksheet is to be stored in the microbiology results binder including chlorine residual if applicable.

#### **Instruments:**

Shel Lab Incubator

Quanti-Tray Sealer Model 2X, Serial# 3628, Model# 89-10894-02

Water Bath: Polystat Model 1200-00 Circulator

Enterococcus incubator: VWR Scientific Model 2005 Low Temperature Incubator

Tuttunauer 2540E Autoclave Serial#9805314

#### **NOTES:**

1. For colilert information or assistance, please call 1-800-321- 0207.
2. If coliform is slightly less yellow than comparator and there is no staff available in four hours, mark sample as slight yellow and place back in incubator and check the next morning. If sample is still slightly yellow then count as negative, if sample is very yellow then mark indeterminate and have sample recollected.

#### **REFERENCES:**

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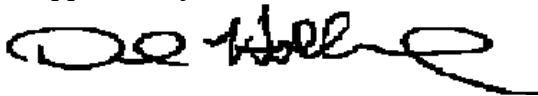
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5. EPA Office of Water. 2006. Total Coliform Rule: A Handbook for Small Noncommunity Water Systems serving less than 3,300 persons.  
[http://www.epa.gov/ogwdw/disinfection/tcr/pdfs/stepguide\\_tcr\\_smallsys-3300.pdf](http://www.epa.gov/ogwdw/disinfection/tcr/pdfs/stepguide_tcr_smallsys-3300.pdf)

Written by: David Holland

Date: August 1999  
Revised: April 2016  
Reviewed:

Approved by:



Laboratory Director

## **Ammonia-Nitrogen**

### **Ion Selective Electrode**

#### **1. Scope and Application**

This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.

#### **2. Detection Limits**

The detection limit (MDL) is 0.02 mg/L. The reporting limit (PQL) is 0.05mg/L.

#### **3. Precision and Bias**

In a single laboratory using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH<sub>3</sub>-N /L, standard deviations were +/- 0.038, +/- 0.017, +/- 0.007, and +/- 0.003, respectively. In a single laboratory using surface water samples at concentrations of 0.10 and 0.13 NH<sub>3</sub>—N /L, recoveries were 96% and 91%, respectively.

#### **4. Working Range**

The calibration range is 0.05 – 10.00 mg NH<sub>3</sub>-N/L. The working range of the Accumet Ammonia ISE is 0.05 to 1,400 mg NH<sub>3</sub>-N /L.

#### **5. Summary of Method**

The ammonia is detected potentiometrically using an ion selective ammonia electrode and a specific ion meter. The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

#### **6. Sample Collection, Preservation and Holding Times**

Collect 500 mL of sample in a screw capped plastic bottle.

Samples that are to be tested within 24 hours should be stored in the refrigerator at 4 degrees C.

Preserve samples high in organic and nitrogenous matter, and any other samples for a prolonged period, by lowering the pH to 2 or less with 2 mL 50% H<sub>2</sub>SO<sub>4</sub> / L (hold time is 28 days).

#### **7. Comments**

##### **7.1 Interferences**

- a) Volatile amines act as a positive interference.
- b) Mercury interferes by forming a strong complex with ammonia, thus the samples cannot be preserved with mercuric chloride.

##### **7.2 Helpful Hints**

- a) Color and turbidity have no effect on the measurement, thus distillation may not be necessary for turbid or highly colored samples.
- b) Do not record ammonia concentrations displayed on Orion 960, only record mV readings.
- c) If probe drifts, change fill solution and soak for a longer period of time.
- d) Measure the ammonia in aqueous solutions containing surfactants and non-aqueous media with the electrode suspended above the sample in a closed system.

#### **8. Safety Issues**

Sodium Hydroxide is very corrosive and reacts with water giving off large amount of heat.

#### **9. Instrumentation/Equipment**

- a) Accumet Ammonia Ion Selective Electrode (Cat. # 13-620-504)
- b) Orion Research 960 (Cat. # 096000)

## 10. Reagents and Standards

a) 10 N NaOH Soln:

Dissolve 200.0 g NaOH in 500 mL of DI water (use volumetric flask).

b) Ammonia-Nitrogen Standard Solution (1000 mg/L) (Absolute Part # 54153)

c) Ammonia ISE Fill Solution (RICCA Cat. # R3161200-120A)

d) Standards

Prepare the following standards in 250 mL volumetric flasks. Fill to volume with DI water.

(Prepare fresh each day).

| mL Standard Soln.<br>(1000 mg/L NH <sub>3</sub> -N) | NH <sub>3</sub> -N Concentration |
|-----------------------------------------------------|----------------------------------|
| 25 µL                                               | 0.1 mg/L                         |
| 250 µL                                              | 1.0 mg/L                         |
| 2.5 mL                                              | 10 mg/L                          |

e) Electrode Conditioning Soln: 0.02 M NH<sub>4</sub>Cl

Dissolve 0.5345g NH<sub>4</sub>Cl in 500 mL DI water to make 1000 mg/L concentration (Expiration 6 months).

## 11. Procedure

### 11.1 Sample Preparation

Bring all samples to room temperature before analysis.

### 11.2 Instrument Operating Conditions

Between measurements, the electrode can be stored; the electrode can be stored wet or dry.

- For short-term storage (< 1 week), store in 0.02 M NH<sub>4</sub>Cl soln.
- Change the internal filling solution every 2-3 weeks.
- For long-term storage, drain the internal solution, rinse the body and cap with DI water, and store disassembled unit dry.
- Electrode Assembly: Fill the membrane cap ½ full and screw the membrane cap onto the electrode body. Add approximately another 2 mL of the filling solution into the electrode body and tap the body to dislodge any air bubbles.

### 11.3 Calibration

- Soak electrode in 0.02 M NH<sub>4</sub>Cl for >3 hours or overnight.
- Measure ~50 mL of each standard in 100 mL beaker. (start with lowest standard concentration)
- Position electrode in the solution at an angle of approximately 20 degrees. Stir with small magnetic stirrer.
- Add 1 mL of 10 N NaOH, let stabilize.
- Enter calibration mV reading into meter.
- Repeat for each standard.
- Acceptable slope is -59 ± 4 mV/DEC.

### 11.4 Analysis

- Add 50 mL of each sample into 100 mL beaker with stir bar.
- Position probe at ~20 degrees
- Add 1 mL of 10 N NaOH and check the pH using litmus paper. If pH<10, add an additional mL of 10 N NaOH and check pH. Continue until the pH≥10. Record NaOH volume added on the worksheet.

- 4) If the volume of NaOH added is >10% of the sample volume, scale the result by the dilution factor:  
Result = calculated result\*(volume NaOH added + sample volume)/sample volume.
- 5) Let the probe stabilize, then record mV reading on the worksheet.

## 12. Q.A./Q.C. Requirements

### 12.1 QC Analysis

- a) One instrument calibration verification blank (ICVB) per set.
- b) One instrument calibration verification (ICV) per set (100 µl of 1000 mg/L NH<sub>3</sub>-N standard to 200 mL DI = 0.50 mg/L).
- c) One instrument calibration verification low (ICVL) per set (10 µL of 1000 mg/L NH<sub>3</sub>-N standard to 200 mL DI = 0.05 mg/L)
- d) One matrix spike (MS) and matrix spike duplicate (MSD) on 10<sup>th</sup> sample (spike = 25 µL of 1000 mg/L NH<sub>3</sub>-N Standard Soln to 50 mL sample = 0.50 mg/L NH<sub>3</sub>-N).

### 12.2 Acceptance Criteria

- a) ICVB < 0.05 mg/L NH<sub>3</sub>-N
- b) ICV: 90 – 110 % Recovery
- c) ICVL: 50 – 150 % Recovery
- d) Duplicates: <20 % Difference
- e) MS: 90-110 % Recovery
- f)  $r^2 \geq .995$   
(See calculations below)

## 13. Calculations

### 13.1 Using the NH<sub>3</sub> Electrode Worksheet

- a) Open the NH<sub>3</sub> Electrode worksheet template located in T:\NH3 Elect. Enter the slope in mV/DEC in the slope cell.
- b) Enter the measured mV for each calibration standard in the mV column in the calibration table. The worksheet will generate a calibration curve and display an  $r^2$  value and a logarithmic function in the form of  $y = m*\ln(x) + b$ .
- c) Enter the pre-logarithmic term (m) and the linear term (b) in the designated cells.
- d) Enter the measured mV for each sample in the mV column; report the calculated values in the final concentration column.

### 13.2 % Recovery and % Difference

- a) ICV and ICVL %Recovery: (Measured Value/Theoretical Value)\*100%
- b) MS %Recovery: ((Spiked Sample Measured Value – Sample Measured Value)/Spike amount)\*100%
- c) MS %Difference:  $(|MS - MSD|/(MS+MSD)/2)*100\%$

## 14. Reporting

### 14.1 Review

Always have the lead chemist review all data before reporting.

### 14.2 Reporting Units

The reporting units are mg NH<sub>3</sub>-N /L

### 14.3 Reporting Limits

The values are valid over a range from 0.05 to 1400 mg NH<sub>3</sub>-N /L.

### 14.4 Significant Figures and Reporting Values Below Detection Limit

Report to three significant figures, and to the nearest 0.01 mg/L. Results less than 0.05 mg NH<sub>3</sub>-N / L are reported as “ND” (“Not Detected”). If samples were diluted, multiply the PQL by the dilution factor.

**14.5 QC Data**

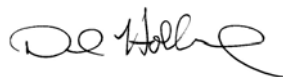
Report all QC data (ICVB, ICVL, ICV, MS % Rec, MSD % Diff) in QC folder located in Q:\NH3.

**15. Reference/Method Source**

- 1) Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, pages 4-106 to 4-107.

Written by David Holland

Approved by:



Laboratory Director

## Total Kjeldahl Nitrogen

### **Scope and Applications:**

Nitrogen plays a central role in a variety of chemical compounds and thus is an essential nutrient. The Kjeldahl method determines nitrogen in the trinegative state. It fails to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitro, nitroso, oxime, and semi-carbazone. If ammonia nitrogen is not removed in the initial phase of the procedure, the term "kjeldahl nitrogen" is applied to the result. Kjeldahl nitrogen minus the ammonia nitrogen is referred to as organic nitrogen. Many wastewater treatment facilities are required to monitor for total nitrogen discharged, this is calculated by adding the kjeldahl nitrogen to the nitrate and nitrite nitrogen.

### **Principle:**

In the presence of sulfuric acid,  $H_2SO_4$ , potassium sulfate and copper sulfate catalyst, amino nitrogen of many organic materials is converted to ammonium sulfate. Free ammonia and ammonium nitrogen are also converted to ammonium sulfate. Sodium hydroxide is added in excess, neutralizing the acid and making the solution alkaline. The alkalinity releases the ammonia. Steam is introduced into the mixture which drives the ammonia out of solution. The distillate is collected in boric acid. The ammonia forms ammonium borate, a weak base. The borate is titrated with 0.02 N sulfuric acid and the nitrogen is calculated.

### **Reporting Limits:**

0.50 mg/l for a 100 ml sample. Report levels below this as **Not Detected**. Adjust the PQL depending on the sample dilution.

### **Precision and Bias:**

MDL Study: A QC sample tested seven times averaged 5.28 mg/l N with a standard deviation of 0.19 mg/l, a RSD of 3.6% and a negative error of 0.32 mg/l or 6%.

**Note:** MDL study for this method should be performed once a year.

### **Working range:**

Nitrogen levels of 0.50 to 100 mg/l can be analyzed. Range can be extended by dilution.

### **Interferences:**

- Nitrate in excess of 10mg/l as N can cause a negative interference during the digestion procedure. Where  $NO_3$  would oxidize  $NH_3$  into  $N_2O$  resulting in ammonia lost. Also in the presence of sufficient reduced organic matter nitrate can be converted into ammonia and cause positive bias.
- Residual chlorine reacts with ammonia; remove by sample pretreatment with sodium thiosulfate.
- High levels of organic matter can react with  $H_2SO_4$  during digestion leading to an incomplete reduction of organic nitrogen to ammonia. To avoid this, add extra digestion reagent to samples believed to contain high levels of organic matter.
- High levels of salts can cause digestion temperature raise above 400 °C, point in which ammonia decompose. To avoid this excessive digestion add extra sulfuric acid ~1mL  $H_2SO_4$ /g salt. Too much acid will lower the temperature and result in an incomplete digestion

### **Sample collection, Preservation and Holding times:**

If an immediate analysis is not possible, preserve with sulfuric acid to pH 1.5 to 2. Usually 3 ml 50%

sulfuric solution is added per liter. For samples that are likely to contain residual chlorine, add a couple of drops of Sodium thiosulfate 10%. Refrigerate at 4°C. Holding time can be up to 28 days. A minimum of 100 ml of sample is required.

### Safety Issues

Sodium Hydroxide is very corrosive and reacts with water giving off large amount of heat. Use standard laboratory safety precautions (Safety glasses, lab coat and gloves).

### Instrumentation and Equipment

1. pH meter/ Titration apparatus (Serial # 1869001004148)
2. Two class A TD, 100 ml cylinder
3. Buchi K-350 Distillation Unit (Serial #500000033)
4. Buchi K-437

### Reagents:

2.0%Boric acid Receiver solution : 40 grams of boric acid (Fisher CAS# 10045-35-3) diluted to 2 liter with DI water. Once prepared transfer to a plastic container and add ~2 mL of mixed solution of Bromocresol Green-Methyl Red indicator solution (Hach CAT# 2329232).

Digestion Reagent: Combine 134 g Potassium Sulfate ( $K_2SO_4$ ) (Fisher CAS# 7778-80-5) and 7.3 g of Copper Sulfate (Fisher CAS# 7758-99-8)( $CuSO_4$ ) in 650 ml of water in a 1L beaker with a stir bar. Add 134 ml concentrated Sulfuric Acid (Fisher CAS# 7664-93-9)( $H_2SO_4$ ), **CAUTION! reaction becomes hot on addition of Sulfuric Acid, prepare in an ice water bath.** Dilute to 1 L with DI water, keep reaction stirring till it is cool enough to pour in to 1L plastic container and store @ 35°C. If it gets too cold salts will precipitate. Always wear goggles and work under the fume hood when preparing this reagent.

Sodium Hydroxide 30%: Dissolve 300 g (NaOH) Sodium Hydroxide (Fisher CAS# 1310-73-2) in water and dilute to 1L in a **plastic container**. **CAUTION reaction extremely hot, prepare inside an ice water bath!** When solution is cool pour in to distillation unit container labeled 30% Sodium Hydroxide. Always wear goggles and work under the fume hood when preparing this reagent.

### Set up Procedure:

1. Set up 20 Kjeldahl Digestion flasks in holding (Make sure that they don't have any cracks) apparatus from Buchi K-437 Digestion unit. Space for 16 samples, 1 blank, 1 QC and 2 Matrix Spikes.
2. Find 16 samples, determine amount of sample needed, up to 100 mL. (When possible, check  $NO_3^-$  concentrations and dilute samples over 10 mg/L  $NO_3^-$ -N.) If there are not enough samples to fill every digestion flask, replace unused flasks with Buchi glass plugs.
3. Pour 100 mL DI Water in to first two flasks
4. Pour each sample in to flasks 2-18. If less than 100mL sample used dilute to 100mL with DI Water.
5. In flasks 19 and 20 put sample chosen for matrix spike. (Use sample not needing dilution and with  $NO_3^-$  concentrations < 10mg/L  $NO_3^-$ -N if possible).
6. To flasks 2, 19 and 20 add 0.5mL Absolute Grade NIST Traceable Organic Nutrients TKN as N (part # 54152), (0.5mL of 1000mg/L spike creates a 5ppm spiking solution).
7. Add approximately 25mL Digestion Reagent and several boiling chips to each flask. Add extra digestion reagent to samples with high organic ~35mL.

### Digestion Procedure:

1. Turn on Buchi K-437 digestion unit and set temperature to 250°C.
2. Turn on water circulation baths (Chillers).
3. Wash top of digestion unit with water.
4. Place flasks in the holding apparatus on to the digestion unit, place top on the flasks.
5. Attach tube that goes to Buchi B414 Scrubber. Verify all seals are tight.
6. Digest samples till most flasks are full of fumes (~3 hours).
7. Reset temperature to 380°C, when unit reaches temperature set timer for 30 minutes. Take note not to let the digestion block exceed 380°C. Excess heat can result in loss of nitrogen by formation of nitrogen oxides.
8. At end of 30 minutes take flask holding apparatus off Buchi K-437 and allow cooling before distillation. To avoid shocking the glassware, set down holding apparatus on top of cement blocks such that the bottoms of the digestion tubes do not make contact with the countertop.
9. While still warm, add ~10mL DI to flasks to avoid crystallization.

### **Distillation Procedure:**

1. *Set up Buchi K350 Distillation Unit*  
Turn ON the Buchi Recirculating Chiller (pre-set temperature: 15 °C). To turn ON the Chiller, press the green switch following by the green start button. Then proceed to turn ON the Distillation Unit, the button to turn it ON is on the back right side. Wait until it beeps, that means that the distillation unit is ready to be use.
2. *Clean Distillation Unit*  
Distill approximately 100 mL of RO plus 5 drops of H<sub>2</sub>SO<sub>4</sub> 50% (1X), 100 mL of RO plus about 2 mls of NaOH 30% (1X) and 100 mL of DI (2X).
- 3.
4. Attach one flask at a time to left side behind cover of Buchi K350 Distillation unit, make sure to close cover, reaction will get hot. Start with flask 1.
5. On right side of unit place Buchi glass beaker with 50mL of 2.0% Boric Acid receiver solution (be sure end of tube is submerged into solution in beaker).
6. When flask and beaker are in place press Reagent button to add NaOH to flask until a color change is observed.
7. When instrument is finished dispensing, 4:00 should be on the screen in top right corner, at this time press start to begin distillation (Procedure takes 4 minutes).
8. Dispose of contents of digestion flask in to acid/base bucket in sink, rinse flask with DI water and return it to holding apparatus.
9. Repeat for all flasks, control, samples and matrix spikes.

### **Titration Procedure:**

1. Use Metrohm 877 Titrino Plus for the titration
2. Calibrate the pH electrode *Titrino Plus*.
  - a) Using the arrows [↓] [↑] sort through the list of the Titrino Plus screen. Select METHOD by pressing and releasing the [OK] key.
  - b) Sort through the list of methods, when the option of CAL\_PH is highlighted press and release the [OK] key.
  - c) Place the probe on the 801 Stirrer Base. Rinse the probe with DI, Introduce the probe into pH buffer (pH= 7.02 or pH =4.00), use 60 mL of buffer. Add a small agitator with the buffer.
  - d) Proceed to load the method by pressing the [START] key on the *Titrino Plus*.
  - e) *Titrino Plus* will ask you to introduce the next buffer. After introducing the next buffer

press the [OK] key.

- f) The percentage of the pH calibration will appear in the screen, record slope on worksheet

**Note:** The acceptable range for the slope is 98 -102%. Calibrate pH meter each day of use.

3. Load buret with 0.02N H<sub>2</sub>SO<sub>4</sub>. If the burette requires changing acid, perform a prep function after changing the acid. To do this follow the instructions below.
- Return to the main screen by pressing the [Back] key on the Titrino Plus
  - Using the arrows [↑] [↓] sort through the list of the screen, Select MENU by pressing and releasing the [OK] key.
  - Sort through the list, when the MANUAL CONTROL is highlighted press and release the [OK] key.
  - Using the arrows [↑] [↓] and [←] [→] sort through the list of the screen, when DOSING option in the list and the PREP option at the bottom of the screen are highlighted at the same time, press and release the [OK] key. Make sure that the tip of the titrant line is pointing an empty vessel.

Note: Flush the line when changing from one acid to another or when trying to remove air bubbles. To remove air bubbles tap the line during the flushing. Air bubbles will cause positive bias in the ammonia measurement.

4. Verify that the Titrino Plus is working properly, by running a low alkalinity ICV of ≤20 mg CaCO<sub>3</sub> /L. Follow steps listed that are listed below.
- Add 50 mL of the low Alk ICV into a 100 mL beaker. Place the beaker on top of the titrinostirrer platform.
  - Using the arrows [↑] [↓], sort through the list of the screen, select METHOD by pressing and releasing the [OK] key.
  - Sort through the list of methods, select the Low Alk option by pressing and releasing the [OK]. Or select ammonia for actual ammonia analyses.
  - Press and release the [START] key to begin with the titration.
5. By the end of the distillation procedure take the receiver beaker from right side of Buchi K350 Distillation unit. Note: Rinse with DI the distilled dispenser into the receiver beaker.
6. Place the receiver beaker on top of the titrino stirrer platform. Submerged the pH probe, with the acid dispenser tip into the liquid.
- Note:** The boric acid on it should be clear when measuring the blank or samples with low levels of ammonia, could be blue if the sample have a high ammonia content. The intensity of the blue color is proportional to the ammonia concentration.
7. From the home menu select Method > TKN.
8. Determine which endpoint you are going to use for the titration by checking the blank pH (pH~5.0). Set the endpoint one tenth lower than the blank. For instance if the pH is equal to 5.1 set up end point to 5.0. Do the change by going to: Menu/OK /Parameter/OK/Control parameters/OK/Endpoint/OK. Set up the desire new endpoint. Then highlight the *Accept* option and press OK.
9. When titration is completed, record mg NH<sub>3</sub>-N /L and titrant volume that is displayed on the instrument. Dispose of content of beaker and wash it out with RO water.

### Helpful Hints

1. Sometimes after digestion, the remaining salts in the digestion flasks can crystallize. When this happens, add ~10mL DI and reheat on the digestion block, stirring occasionally. **USE CAUTION!!!** Sometimes the solution can bump, expelling boiling sulfuric acid out of the digestion flask. Always stir in the fume hood with the opening of the flask pointed in a safe direction.

2. Measuring the pH of the blank to ensure the pH is slightly >4.9 (the titration endpoint) can help to determine the source of contamination when blank values are high.
3. Always check the pH after each titration. If the autotitrator passed the endpoint, the samples can be redistilled. Pour the distillate backing into an empty distillation flask, add sufficient NaOH until a color change is observed, and redistill into new Boric Acid.
4. Try to use fresh DI in the distillation unit. DI sitting for extended periods of time can absorb atmospheric ammonia.

#### **Calculations:**

- a)  $(X-Y)Z = \text{Results}$

X = Result given in ppm

Y = result of blank given in ppm

Z = dilution factor

- b) Liquid samples:  $\text{mg NH}_3\text{-N/L} = \frac{(A-B) \times 280}{C}$

A = volume of acid titrated for sample, mL and

B = volume of acid titrated for blank.

C = sample volume

- c) **% Recovery and % Difference**

a) LCS %Recovery:  $(\text{Measured Value} / \text{Theoretical Value}) \times 100\%$

b) MS %Recovery:  $(\text{Spiked Sample Measured Value} - \text{Sample Measured Value}) \times 100\%$

c) MS %Difference:  $(|\text{MS} - \text{MSD}| / (\text{MS} + \text{MSD}) / 2) \times 100\%$

#### **Quality Control:**

##### **QC Analyses**

- a) One Laboratory Control Blank (LCB) per set of 20 samples or less.
- b) One Laboratory Control Standard (LCB) per set of 20 samples or less (250  $\mu\text{L}$  of 1000 mg/L  $\text{NH}_3\text{-N}$  standard, 50 mL DI = 5.0 mg/L).
- c) One matrix spike (MS) on 20<sup>th</sup> samples (spike = 250  $\mu\text{L}$  of 1000 mg/L  $\text{NH}_3\text{-N}$  Standard Soln to 50 mL sample = 5.0 mg/L  $\text{NH}_3\text{-N}$ ).

##### **Acceptance Criteria**

- a) LCB < 0.5 mg/L  $\text{NH}_3\text{-N}$  (Preferred ~0.2 mg/L  $\text{NH}_3\text{-N}$  for blank subtraction purposes)
- b) LCS: 90 – 110 % Recovery
- c) MS: 80-120 % Recovery

#### **Reporting**

##### **Review**

Always have the lead chemist review all data before reporting. When possible, check to insure that TKN results are  $\geq \text{NH}_3$  results.

##### **Reporting Units**

The reporting units are mg  $\text{NH}_3\text{-N}$  /L

**Reporting Limits**

The values are valid over a range from 0.5 to 100 mg NH<sub>3</sub>-N /L. Range can be extended by dilution.

**Significant Figures and Reporting Values Below Detection Limit**

Report to three significant figures, and to the nearest 0.1 mg/L.

Results less than 0.5 mg NH<sub>3</sub>- N / L are reported as "ND" ("Not Detected").

Note: If samples were diluted, multiply the PQL by the dilution factor.

**QC Data**

Report all QC data (LCB, LCS, MS % Rec, MSD % Diff) in QC folder located in Q:\TKN.

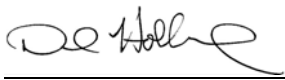
**Reference:**

Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition, 1998  
Nitrogen Determination according to Kjeldahl, Training Papers from BUCHI 1998 #97765

Written By Terren Chang Title: Chemist  
Modified By Lilian Reyes Title: Lab Analyst

Date 11/17/2014  
Date 8/17/2016

Approved By:

  
\_\_\_\_\_  
David Holland  
Laboratory Director

Date: May 9, 2016

## Total Kjeldahl Nitrogen

### **Scope and Applications:**

Nitrogen plays a central role in a variety of chemical compounds and thus is an essential nutrient. The Kjeldahl method determines nitrogen in the trinegative state. It fails to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitro, nitroso, oxime, and semi-carbazone. If ammonia nitrogen is not removed in the initial phase of the procedure, the term "kjeldahl nitrogen" is applied to the result. Kjeldahl nitrogen minus the ammonia nitrogen is referred to as organic nitrogen. Many wastewater treatment facilities are required to monitor for total nitrogen discharged, this is calculated by adding the kjeldahl nitrogen to the nitrate and nitrite nitrogen.

### **Principle:**

In the presence of sulfuric acid, potassium sulfate and copper sulfate catalyst, amino nitrogen of many organic materials is converted to ammonium sulfate. Free ammonia and ammonium nitrogen are also converted to ammonium sulfate. Sodium hydroxide is added in excess, neutralizing the acid and making the solution alkaline. The alkalinity releases the ammonia. Steam is introduced into the mixture which drives the ammonia out of solution. The distillate is collected in boric acid. The ammonia forms ammonium borate, a weak base. The borate is titrated with 0.02 N sulfuric acid and the nitrogen is calculated.

### **Reporting Limits:**

0.50 mg/l for a 100 ml sample. Report levels below this as **Not Detected**. Adjust the PQL depending on the sample size.

### **Precision and Bias:**

A QC sample tested seven times averaged 5.28 mg/l N with a standard deviation of 0.19 mg/l, a RSD of 3.6% and a negative error of 0.32 mg/l or 6%.

### **Working range:**

Nitrogen levels of 0.50 to 100 mg/l can be analyzed. Range can be extended by dilution.

### **Interferences:**

Nitrate in excess of 10mg/l as N can cause a negative interference or nitrate in the presence of reduced organic matter can be converted to ammonia and cause a positive bias.  
Residual chlorine reacts with ammonia; remove by sample pretreatment with sodium thiosulfate.  
High levels of organic matter can react with H<sub>2</sub>SO<sub>4</sub> during digestion leading to an incomplete reduction of organic nitrogen to ammonia. To avoid this, add extra digestion reagent to samples believed to contain high levels of organic matter.  
For saline samples, standards and blanks should be prepared in synthetic ocean water.

### **Sample collection, Preservation and Holding times:**

If an immediate analysis is not possible, preserve with sulfuric acid to pH 1.5 to 2. Usually 3 ml 50% sulfuric solution is added per liter. Refrigerate. Holding time can be up to 28 days, but sample should be tested within one week. A minimum of 100 ml of sample is required.

### **Reagents:**

**2.0%Boric acid Receiver solution** : (Prepare monthly) 20 grams of boric acid (Fisher CAS# 10045-35-3) diluted to <1 liter with DI water. Add ~2 mL of mixed solution of Bromcresol Green-Methyl Red indicator solution (Hach CAT# 2329232), bring up to 1 liter.

**Digestion Reagent:** Combine 134 g Potassium Sulfate (K<sub>2</sub>SO<sub>4</sub>) (Fisher CAS# 7778-80-5) and 7.3 g of Copper Sulfate (Fisher CAS# 7758-99-8)(CuSO<sub>4</sub>) in 650 ml of water in a 1L beaker with a stir bar. Add 200 ml concentrated Sulfuric Acid (Fisher CAS# 7664-93-9)(H<sub>2</sub>SO<sub>4</sub>), **CAUTION! reaction**

**becomes hot on addition of Sulfuric Acid.** Dilute to 1 L with DI water, keep reaction stirring till it is cool enough to pour in to 1L plastic container and store @ 35°C.

Sodium Hydroxide 30% Dissolve 300 g (NaOH) Sodium Hydroxide (Fisher CAS# 1310-73-2) in water and dilute to 1L in a plastic container. **CAUTION reaction extremely hot!** When solution is cool pour in to distillation unit container labeled 30% Sodium Hydroxide.

Always wear proper PPE and work under the fume hood when preparing these reagents.

#### **Set up Procedure:**

1. Set up 20 Kjeldahl Digestion flasks in holding apparatus from Buchi K-437 Digestion unit. Space for 16 samples, 1 blank, 1 QC and 2 Matrix Spikes.
2. Find 16 samples, determine amount of sample needed, up to 100 mL. (When possible, check  $\text{NO}_3^-$  concentrations and dilute samples over 10 mg/L  $\text{NO}_3^-$ -N.) If there are not enough samples to fill every digestion flask, replace unused flasks with Buchi glass plugs.
3. Pour 100 mL DI Water in to first two flasks.
4. Pour each sample in to flasks 2-18. If less than 100mL sample used dilute to 100mL with DI Water.
5. In flasks 19 and 20 put sample chosen for matrix spike. (Use sample not needing dilution and with  $\text{NO}_3^-$  concentrations < 10mg/L  $\text{NO}_3^-$ -N if possible).
6. To flasks 2, 19 and 20 add 0.5mL Absolute Grade NIST Traceable Organic Nutrients TKN as N (part # 54152), (0.5mL of 1000mg/L spike creates a 5ppm spiking solution).
7. Add approximately 25mL Digestion Reagent and several boiling chips to each flask.

#### **Digestion Procedure:**

1. Turn on Buchi K-437 digestion unit and set temperature to 250°C.
2. Turn on water circulation baths (Chillers).
3. Wash top of unit with water.
4. Place flasks in the holding apparatus on to the digestion unit, place top on the flasks.
5. Attach tube that goes to Buchi B414 Scrubber. Verify all seals are tight.
6. Digest samples till most flasks are full of fumes (~3 hours).
7. Reset temperature to 380°C, when unit reaches temperature set timer for 30 minutes. Take note not to let the digestion block exceed 380°C. Excess heat can result in loss of nitrogen by formation of nitrogen oxides.
8. At end of 30 minutes take flask holding apparatus off Buchi K-437 and allow cooling before distillation. To avoid shocking the glassware, set down holding apparatus such that the bottoms of the digestion tubes do not make contact with the countertop.
9. While still warm, add ~10mL DI to flasks to avoid crystallization.

#### **Distillation Procedure:**

1. Set up Buchi K350 Distillation Unit.
2. Distill ~3 blanks before distilling samples to clean the unit.
3. Attach one flask at a time to left side behind cover of Buchi K350 Distillation unit, make sure to close cover, reaction will get hot. Start with flask 1.
4. On right side of unit place Buchi glass beaker with 50mL of 2.0% Boric Acid receiver solution (be sure end of tube is submerged into solution in beaker).
5. When flask and beaker are in place press Reagent button to add NaOH to flask until a color change is observed.
6. When instrument is finished dispensing, 4:00 should be on the screen in top right corner, at this time press start to begin distillation (Procedure takes 4 minutes).
7. Dispose of contents of digestion flask in to acid/base bucket in sink, rinse flask with DI water and return it to holding apparatus.
8. Repeat for all flasks, control, samples and matrix spikes.

**Titration Procedure:**

1. For Titration use Metrohm 877 Titrino Plus (Serial # 1869001004148).
2. Be sure the 0.02N H<sub>2</sub>SO<sub>4</sub> burette is loaded. If the burette requires changing, perform a prep function to ensure the lines are free of air bubbles (Menu > Manual Controls > Dosing > Prep).
3. Calibrate to pH electrode according to the pH SOP.
4. From the home screen on the Metrohm 877 Titrino Plus, select Method > Low Alk.
5. Titrate a low alkalinity ICV to ensure the autotitrator is working properly.
6. When distillation procedure is completed take beaker from right side of Buchi K350 Distillation unit, place in front the Metrohm autotitrator with the probe submerged in the liquid.
7. From home menu select Method > TKN. Titrate to a pH endpoint of 4.9. When titration is completed, record ppm and titrant volume on the worksheet. Dispose of contents of beaker in acid/base bucket in sink and wash out with DI water.

**Helpful Hints**

1. Sometimes after digestion, the remaining salts in the digestion flasks can crystallize. When this happens, add ~10mL DI and reheat on the digestion block, stirring occasionally. **USE CAUTION!!!** Sometimes the solution can bump, expelling boiling sulfuric acid out of the digestion flask. Always stir in the fume hood with the opening of the flask pointed in a safe direction.
2. Measuring the pH of the blank to ensure the pH is slightly >4.9 (the titration endpoint) can help to determine the source of contamination when blank values are high.
3. Always check the pH after each titration. If the autotitrator passed the endpoint, the samples can be redistilled. Pour the distillate backing into an empty distillation flask, add sufficient NaOH until a color change is observed, and redistill into new Boric Acid.
4. Try to use fresh DI in the distillation unit. DI sitting for extended periods of time can absorb atmospheric ammonia.

**Calculations:**

$$(X-Y)Z=\text{Results}$$

X = Result given in ppm

Y = result of blank given in ppm

Z = dilution factor

$$\text{Liquid samples: mg NH}_3\text{-N/L} = \frac{(A-B) \times 280}{C}$$

$$\text{Sludge or sediment samples: mg NH}_3\text{-N/kg} = \frac{(A-B) \times 280}{C}$$

A = volume of acid titrated for sample, mL and

B = volume of acid titrated for blank.

C = sample volume

**% Recovery and % Difference**

- a) LCS %Recovery: (Measured Value/Theoretical Value)\*100%
- b) MS %Recovery: (Spiked Sample Measured Value – Sample Measured Value)\*100%
- c) MS %Difference: (|MS – MSD|/(MS+MSD)/2)\*100%

**Quality Control:**

Run a blank and a duplicate matrix spike and a method standard with set of analyses

Spike recoveries should be 80 to 120 % according to standard methods, however recoveries between 90 to 110% are desired.

Recovery of method standard must be 80 to 120 % according to standard methods, however recoveries between 90 to 110% are desired.

Each quarter an external reference sample must be analyzed. If results are not within acceptable range, perform corrective action and document.

## **Reporting**

### **Review**

Always have the lead chemist review all data before reporting. When possible, check to insure that TKN results are  $\geq$  NH<sub>3</sub> results.

### **Reporting Units**

The reporting units are mg NH<sub>3</sub>-N /L

### **Reporting Limits**

The values are valid over a range from 0.5 to 100 mg NH<sub>3</sub>-N /L. Range can be extended by dilution.

### **Significant Figures and Reporting Values Below Detection Limit**

Report to three significant figures, and to the nearest 0.1 mg/L. Results less than 0.5 mg NH<sub>3</sub>- N / L are reported as "ND" ("Not Detected"). If samples were diluted, multiply the PQL by the dilution factor.

### **QC Data**

Report all QC data (LCB, LCS, MS % Rec, MSD % Diff) in QC folder located in Q:\TKN.

## **Reference:**

Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition, 1998  
Nitrogen Determination according to Kjeldahl, Training Papers from BUCHI 1998 #97765

Written By: Sarah McGinnis Title: Chemist Date: 11/17/2014

Approved By: David Holland Title: Laboratory Director Date: 2/15/2015

## ***Ammonia-Nitrogen***

### **Distillation**

#### **1. Scope and Application**

The atmosphere contains 78% of Nitrogen gas, in this form Nitrogen cannot be used by plants or animals. In order to be use by plants have to be converted into ammonia or other forms of nitrogenous compounds. Rhizobium Leguminosaurum for example, is a prokaryote found in soils that lives symbiotically in the root nodules of legume plants and covert N<sub>2</sub> into ammonia. Ammonia is the preferred nitrogen containing nutrient for plant growth. Ammonia can be converted to nitrite (NO<sub>2</sub>) and nitrate (NO<sub>3</sub>) biologically, and then used by plants. In waters and wastewaters the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. All of these forms of nitrogen, and nitrogen gas (N<sub>2</sub>) can be converted from one to another biologically and are part of the nitrogen cycle. Nitrogen can be an important factor on controlling algal growth when other nutrients. Ammonia is present naturally in surface and wastewaters from deamination of nitrogen containing compounds and by the hydrolysis of urea. Ammonia can also come from industrial fertilizers, agricultural pollution, organic matter and fecal matter. Ammonia is also one of the most important pollutants because is relatively common but can be toxic, causing lower reproduction and growth, or death of animals and excessive plant or algal growth. The neutral, unionized form (NH<sub>3</sub>) is highly toxic to fish and other aquatic life. This method is applicable for the measurement of ammonia-nitrogen in , surface and saline waters, domestic and industrial wastes.

#### **2. Principle**

The sample is buffered at pH 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds and then distilled. During the distillation process ammonia will be converted into ammonia gas and then condensed and captured into a boric acid solution (~ pH 4.7). The distillation process is performed in order to avoid interferences when analyzing the sample. Immediately that ammonia arrives into the receiving solution will form ammonium borate, generating an increase in the pH. The ammonium borate then is titrated with a standardized sulfuric acid solution to a selected endpoint (~4.9). The amount of ammonia in the sample can be determined by a mathematical equation (see below).

#### **3. Detection Limits**

The MDL and reporting limit is 0.50 mg/l for a50 ml of sample. Report levels below this as **Not Detected**. Adjust the PQL depending on the sample dilution.

Note: An MDL study should be realized once a year.

#### **4. Precision and Bias**

A QC sample tested seven times averaged 5.28 mg/l N with a standard deviation of 0.19 mg/l, a RSD of 3.6% and a negative error of 0.32 mg/l or 6%.

#### **5. Working Range**

The working range is 0.5 to 100 mg/L NH<sub>3</sub>-N can be analyzed. Range can be extended by dilution.

**Note:** Drinking, RO permeate or Surface Water samples with levels of ammonia below 0.5 mg/L, should by analyze by the *Ammonia by Electrode Method*. Since the detection limit for this method is 0.05 mg/L NH<sub>3</sub>-N.

#### **6. Sample Collection, Preservation and Holding Times**

-Collect 500 mL of sample in a screw capped plastic bottle.

-Samples that are to be tested within 24 hours should be stored in the refrigerator at 4 degrees C.

- Samples to be analyzed after 24 hours of collection should be preserved by lowering the pH to  $< 2$  or less with sulfuric acid ( $\sim 2$  mL 50%  $\text{H}_2\text{SO}_4$ ), and sodium thiosulfate of 10%. Once preserved the sample can be stored up to 28 days at 4 Celsius degrees.

## 7. Interferences

- At pH 9.5, 7% of the urea in the sample will hydrolyze, giving a positive interference.
- Residual chlorine reacts with ammonia; remove by sample pretreatment with excess sodium thiosulfate.

## 8. Safety Issues

Sodium Hydroxide is very corrosive and reacts with water giving off large amount of heat. Use standard laboratory safety precautions (Safety glasses, lab coat and gloves).

## 9. Instrumentation/Equipment

- pH meter/ Titration apparatus ( Metrohm 877, Serial # 11110554)
- Two class A TD, 50 ml cylinder
- Buchi K-350 Distillation Unit (Serial #500000033)
- Metal Clamps
- Buchi Recirculating Chiller

## 10. Reagents and Standards

- 2.0%Boric acid Receiver solution: 40 grams of boric acid (Fisher CAS# 10045-35-3) diluted to 2 liter with DI water. Add solution into a plastic container and add  $\sim 2$  mL of mixed solution of Bromocresol Green-Methyl Red indicator solution (Hach CAT# 23292-49).
- Sodium Hydroxide 30%: Dissolve 300 g Sodium Hydroxide (NaOH) (Fisher CAS# 1310-73-2) in water and dilute to 1L in a plastic container. **CAUTION reaction extremely hot!** When solution is cool pour in to distillation unit container labeled 30% Sodium Hydroxide.
- Borate Buffer: Add 44mL of 0.1N NaOH to  $\sim 200$ mL DI. Dissolve 4.75g Sodium Tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) (Baker Analyzed CAS# 1303-96-4). Bring up to 500mL.
- Phenolphthalein Indicator Soln.: Dissolve 1g phenolphthalein (Baker, CAS#2870) in 100 mL 95% ethyl or isopropyl alcohol (VWR Brand CAT# VW5540-4). Bring up to 200 mL with DI.
- 1.0 N Standardized Sulfuric Acid: purchased from RICCA (Cat no. 8300-32)
- 0.02 N Standardized Sulfuric Acid: Using a glass pipette and a volumetric flask, dilute 20.00 ml of 1.0 N  $\text{H}_2\text{SO}_4$  to 1 L with DI water. Standardized this acid before use. See Acid Standardization SOP.
- Low Alkalinity ICV, 20 mg  $\text{CaCO}_3$ /L solution: Add 1 mL of 1000 mg/L  $\text{NaHCO}_3$  solution ( use for Alkalinity method) into 50 mL of DI water.
- $\text{NH}_3$ -N ICV, 5 mg  $\text{NH}_3$ -N/L solution: Add 250  $\mu\text{L}$  of Inorganic nutrients 1000 mg/L  $\text{NH}_4$  as N. Standard purchased from Absolute(Cat No.54153).

## 11. Procedure

### 11.1 Distillation Procedure

- Set up Buchi K350 Distillation Unit*  
Turn ON the Buchi Recirculating Chiller (pre-set temperature:  $15^\circ\text{C}$ ). To turn ON the Chiller, press the green switch following by the green start button. Then proceed to turn ON the Distillation Unit, the button to turn it ON is on the back right side. Wait until it beeps, that means that the distillation unit is ready to be use.

2. *Clean Distillation Unit*

Distill approximately 100 mL of RO plus 5 drops of H<sub>2</sub>SO<sub>4</sub> 50% (1X), 100 mL of RO plus about 2 mls of NaOH 30% (1X) and 100 mL of DI (3X).

3. *Proceed to prepare the sample by following the directions below.*

Measure 50 mL sample and add to a digestion flask. On addition add to the digestion flask 3 mL of borate buffer and two drops of phenolphthalein indicator. Start adding drops of NaOH 30% until reaching a pH of 9.5. The phenolphthalein will turn the sample into a pink color once get basic. To make sure that the pH of the sample is not above or less than a pH of 9.5, compare against a vial comparator, which contains a solution of a pH of 9.5 with phenolphthalein indicator on it.

4. Attach the digestion flask to left side behind cover of Buchi K350 Distillation unit, make sure to close cover, reaction will get hot.
5. Place Buchi glass beaker with 50mL of 2.0% Boric Acid receiver solution on the right side of the distillation unit (be sure end of tube is submerged into solution in beaker).
6. Distill the sample by pressing the start button on the distillation unit. The distillation takes 4 minutes.
7. Dispose of contents of digestion flask in to acid/base bucket in sink, rinse flask with DI.
8. Repeat for all quality control samples, samples, and matrix spikes.

**11.2 Titration Procedure:**

1. Use Metrohm 877 Titrino Plus for the titration
2. Calibrate the pH electrode *Titrino Plus*.
  - a) Using the arrows [↓↑] sort through the list of the Titrino Plus screen. Select METHOD by pressing and releasing the [OK] key.
  - b) Sort through the list of methods, when the option of CAL\_PH is highlighted press and release the [OK] key.
  - c) Place the probe on the *801 Stirrer Base*. Rinse the probe with DI, Introduce the probe into pH buffer (pH= 7.02 or pH =4.00), use 60 mL of buffer. Add a small agitator with the buffer.
  - d) Proceed to load the method by pressing the [START] key on the *Titrino Plus*.
  - e) *Titrino Plus* will ask you to introduce the next buffer. After introducing the next buffer press the [OK] key.
  - f) The percentage of the pH calibration will appear in the screen, record slope on worksheet

**Note:** The acceptable range for the slope is 98 -102%. Calibrate pH meter each day of use.

3. Load buret with 0.02N H<sub>2</sub>SO<sub>4</sub>. If the burette requires changing acid, perform a prep function after changing the acid. To do this follow the instructions below.
  - a) Return to the main screen by pressing the [Back] key on the Titrino Plus
  - b) Using the arrows [↓↑] sort through the list of the screen, Select MENU by pressing and releasing the [OK] key.
  - c) Sort through the list, when the MANUAL CONTROL is highlighted press and release the [OK] key.
  - d) Using the arrows [↓↑] and [←→] sort through the list of the screen, when DOSING option in the list and the PREP option at the bottom of the screen are highlighted at the same time, press and release the [OK] key. Make sure that the tip of the titrant line is pointing an empty vessel.

Note: Flush the line when changing from one acid to another or when trying to remove air bubbles. To remove air bubbles tap the line during the flushing. Air bubbles will cause positive bias in the ammonia measurement.

4. Verify that the Titrino Plus is working properly, by running a low alkalinity ICV of  $\leq 20$  mg  $\text{CaCO}_3$  /L . Follow steps listed that are listed below.
  - a) Add 50 mL of the low Alk ICV into a 100 mL beaker. Place the beaker on top of the titrinostirrer platform.
  - b) Using the arrows [ $\uparrow$   $\downarrow$  ], sort through the list of the screen, select METHOD by pressing and releasing the [OK] key.
  - c) Sort through the list of methods, select the Low Alk option by pressing and releasing the [OK]. Or select ammonia for actual ammonia analyses.
  - d) Press and release the [START] key to begin with the titration.
5. By the end of the distillation procedure take the receiver beaker from right side of Buchi K350 Distillation unit. Note: Rinse with DI the distilled dispenser into the receiver beaker.
6. Place the receiver beaker on top of the titrino stirrer platform. Submerged the pH probe , with the acid dispenser tip into the liquid.  
**Note:** The boric acid on it should be clear when measuring the blank or samples with low levels of ammonia, could be blue if the sample have a high ammonia content. The intensity of the blue color is proportional to the ammonia concentration.
7. From the home menu select Method > Ammonia.
8. Determine which endpoint you are going to use for the titration by checking the blank pH (pH~5.0). Set the endpoint one tenth lower than the blank. For instance if the pH is equal to 5.1 set up end point to 5.0. Do the change by going to: Menu/OK /Parameter/OK/Control parameters/OK/Endpoint/OK. Set up the desire new endpoint. Then highlight the *Accept* option and press OK.
9. When titration is completed, record mg  $\text{NH}_3\text{-N}$  /L and titrant volume on the worksheet. Dispose of content of beaker and wash out with RO water.
10. Perform a blank correction for each result.

## 12. Q.A./Q.C. Requirements

### 12.1 QC Analysis

- a) One instrument calibration verification blank (ICVB) per set of 20 samples or less.
- b) One instrument calibration verification (ICV) per set of 20 samples or less (250  $\mu\text{L}$  of 1000 mg/L  $\text{NH}_3\text{-N}$  standard, 50 mL DI = 5.0 mg/L).
- c) One matrix spike (MS) on 20<sup>th</sup> samples (spike = 250  $\mu\text{L}$  of 1000 mg/L  $\text{NH}_3\text{-N}$  Standard Soln to 50 mL sample = 5.0 mg/L  $\text{NH}_3\text{-N}$ ).

### 12.2 Acceptance Criteria

- a) LCB < 0.5 mg/L  $\text{NH}_3\text{-N}$  (Preferred ~0.2 mg./L  $\text{NH}_3\text{-N}$  for blank subtraction purposes)
- b) LCS: 90 – 110 % Recovery
- c) MS: 80-120 % Recovery

## 13. Calculations:

### 13.1 Results

Results = (X-Y)\*Z

X = Result given in ppm

Y = result of blank given in ppm

Z = dilution factor

$$\text{Liquid samples: mg NH}_3\text{-N/L} = \frac{(\text{A-B}) \times 280}{\text{C}}$$

$$\text{Sludge or sediment samples: mg NH}_3\text{-N/kg} = \frac{(\text{A-B}) \times 280}{\text{C}}$$

A = volume of acid titrated for sample, mL and

B = volume of acid titrated for blank.

C = sample volume

**Note:** Perform a blank subtraction for each result

### 13.2 % Recovery and % Difference

- a) LCS and LCSL %Recovery: (Measured Value/Theoretical Value)\*100%
- b) MS %Recovery: (Spiked Sample Measured Value – Sample Measured Value)/(ICV true value)\*100%
- c) MS %Difference: (|MS – MSD|/(MS+MSD)/2)\*100%

## 14. Reporting

### 14.1 Review

Always have the lead chemist review all data before reporting.

### 14.2 Reporting Units

The reporting units are mg NH<sub>3</sub>-N /L

### 14.3 Reporting Limits

The values are valid over a range from 0.5 to 100 mg NH<sub>3</sub>-N /L, range can be extended by dilution.

### 14.4 Significant Figures and Reporting Values Below Detection Limit

- a. Report to three significant figures, and to the nearest 0.1 mg/L. Results less than 0.5 mg NH<sub>3</sub>-N / L are reported as “ND” (“Not Detected”). If samples were diluted, multiply the PQL by the dilution factor.
- b. Verify that Ammonia levels are lower than the TKN results. Verify that the TN calculation is displaying 3 significant figures, if not proceed to fix.

### 14.6 QC Data

Report all QC data (ICVB, ICVL, ICV, MS % Rec, MSD % Diff) in QC folder located in V:\NH3.

## 15. Reference/Method Source

- 1) Standard Methods for the Examination of Water and Wastewater, 21th Edition, 2005, Sections 4-108 to 4-110.

Written By Terren Chang Title: Chemist  
Modified By Lilian Reyes Title: Lab Analyst

Date 11/17/2014  
Date 5/13/2016

Approved by: \_\_\_\_\_  
David Holland  
Laboratory Director

Date:

## NH3 MDL Study 2016

| Replicate # | Analysis Date | True Value (mg/L) | Raw Value (mg/L) | Blank(mg/L) | Result-Blank(mg/L) | % Rec (50-150%) |
|-------------|---------------|-------------------|------------------|-------------|--------------------|-----------------|
| 1           | 8/10/2016     | 0.8               | 0.818            | 0.202       | 0.616              | 77%             |
| 2           | 8/10/2016     | 0.8               | 0.885            | 0.202       | 0.683              | 85%             |
| 3           | 8/10/2016     | 0.8               | 0.840            | 0.202       | 0.638              | 80%             |
| 4           | 8/25/2016     | 0.8               | 0.840            | 0.269       | 0.571              | 71%             |
| 5           | 8/25/2016     | 0.8               | 0.739            | 0.269       | 0.470              | 59%             |
| 6           | 8/25/2016     | 0.8               | 0.885            | 0.269       | 0.616              | 77%             |
| 7           | 9/8/2016      | 0.8               | 0.650            | 0.190       | 0.460              | 58%             |
| 8           | 9/8/2016      | 0.8               | 0.806            | 0.190       | 0.616              | 77%             |
| 9           | 9/8/2016      | 0.8               | 0.885            | 0.190       | 0.695              | 87%             |

**Average** 0.596  
**Standard Deviation** 0.083164663  
**RSD (10-20%)** 13.95%  
**MDL =  $t \times S$ , 2.896 X S** **0.241**  
**PQL=** 0.5 mg/L

**H<sub>2</sub>SO<sub>4</sub>:** 0.02NStandardized  
**Method:** NH3  
**Instrument:** Titrino Plus

**Note:** For 0.8 mg/L NH3-N, 400 uL of Abs std 1000 mg/L Inorganic Nutrients were dissolved into 500 mL of DI water.

## SM 4500-H+ B pH Procedure

### **Scope and Application:**

Application to drinking, surface, ground and saline waters as well as acid rain, and wastewater (domestic and industrial).

### **Principle of operation:**

pH is defined as the negative logarithm of the hydrogen ion concentration in moles per liter. The pH scale goes from zero to fourteen with a value of seven units to be considered neutral. Values below seven are acid; values above seven are basic. It is important to note that a one-unit change in pH represents a ten-fold change in the concentration of the hydrogen ion. As an example, if the pH is changed from six to five, a ten-fold increase in hydrogen ion concentration has occurred.

### **Precision and Bias:**

pH has a great impact on almost all biological and chemical processes used for water and wastewater treatment, and proper measurement of this value is critical. pH is measured using a pH meter consisting of a potentiometer, glass pH electrode, reference electrode and temperature compensating device. When calibrating the instrument, use two buffers, which bracket the expected pH value for greatest accuracy.

### **Sample Criteria & Acceptability:**

A minimum of 50 ml of sample should be submitted in a clean container provided by the laboratory. Sample should be analyzed within 6 hours of collection. If the sample does not meet the above criteria, document it on the worksheet but perform the test.

### **Sample Hold Time:**

Samples must be tested within 24-hours of being taken, best if pH is read the same day the sample was taken. Flag samples with H if measures > 15 minutes after collection.

### **Instrument Set Up**

- A. Open the Titration Base software
- B. Calibrate the *Titrimo Plus*.

1. Using the arrows [↓↑] sort through the list of the Titrimo Plus screen. Select METHOD by pressing and releasing the [OK] key.
2. Sort through the list of methods, when the option of CAL\_PH is highlighted press and release the [OK] key.

3. Place the probe on the *801 Stirrer Base*. Rinse the probe with DI, Introduce the probe into pH buffer (pH= 7.02 or pH =4.00), use 60 mL of buffer. Add a small agitator with the buffer.
4. Proceed to load the method by pressing the [START] key on the Titrino *Plus*.
5. Titrino *Plus* will ask you to introduce the next buffer. After introducing the next buffer press the [OK] key.
6. The percentage of the pH calibration will appear in the screen, record slope on worksheet

**Note:** The acceptable range is 98 -102%. Calibrate pH meter each day of use.

1. Return to the main screen by pressing the [Back] key on the Titrino Plus
2. Using the arrows [↓↑] sort through the list of the screen, Select MENU by pressing and releasing the [OK] key.
3. Sort through the list, when the MANUAL CONTROL is highlighted press and release the [OK] key.

1. Fill a 100 ml beaker with up to 50 ml of pH QC.
2. Set stirring to low.
3. Record pH as LCS on worksheet for results.
4. Acceptable results are Ph 6.76 to 6.96 depending on Temperature.

**Procedure:**

1. Fill a 100 ml beaker with ~50 ml of sample.
2. Set stirring to low.
3. Record pH on worksheet for results.
4. Repeat for all samples.

**Reporting:**

Report the result to the nearest tenth (0.1).

**Reference:**

SM 4500-H+ B, Standard Methods Standard Methods for the Examination of Water and Wastewater 21th Edition (2000), Edited by Clesceri, L. Greenberg, A. and Eaton, A., page 4-87.

Written LRH

Approved By: \_\_\_\_\_ Title: \_\_\_\_\_ Date: \_\_\_\_\_

## Settleable Solids

### **Scope and Applications:**

Settleable solid in surface and saline waters as well as domestic and industrial wastes are determined.

### **Detection Limits:**

Detection limit is 0.1mL/L.

### **Precision and Bias:**

Repeated analysis of a QC sample resulted in an average of 0.6mL/L with a standard deviation of 0.038mL/L. The QC sample contained 0.65mL/L of settleable solids.

### **Working range:**

0-1000mL/L

### **Summary of Method:**

Settleable matter is measured volumetrically with an Imhoff cone.

### **Sample collection, Preservation and Holding times:**

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C up to the time of analysis to minimize microbiological decompositions of solids. Preferably do not hold samples more than 48 hours. Do not hold sample more than 7 days. Bring samples to room temperature before analysis.

### **Equipment:**

Imhoff Cone

### **Procedure:**

1. Bring Sample to room temperature.
2. Fill an Imhoff cone to the 1L mark with well-mixed sample.
3. Record start time and allow to settle for 45 minutes.
4. Gently agitate sample near the sides of the cone with rod.
5. Record time and allow to settle for 15 minutes longer.
6. Record volume of settleable solids in the cone on the worksheet as mL.  
Note: If the settled matter contains packets of liquid between large settled particles, estimate the volume of these and subtract from the volume of settled solids.  
Note: When a separation of settleable and floating materials occurs, do not estimate the floating material as Settleable matter.

### **Calculations:**

Take mL of solid divided by L of sample used. Calculations when using 1L are mL of solid divided by 1, if less than 1L used convert mL of sample to L of sample, example 850mL=0.85L.

### **Reporting:**

Reporting units are mL/L, the minimum detection limit is 0.1mL/L, Report results to the tenths, any result below 0.1mL/L report that as ND. If there are some solids, but not enough to measure accurately report the result as Trace.

### **Reference:**

SM 2540F Settleable Solids, Standard Methods Standard Methods for the Examination of Water and Wastewater 20th Edition (1998), Edited by Clesceri, L. Greenberg, A. and Eaton, A., page 4-87.

Monterey Bay Analytical Services  
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SM 2540F Settleable Solids  
Revision Date: 11/6/2014  
Page 2 of 2

Written By:\_\_\_\_\_Title:\_\_\_\_\_Date:\_\_\_\_\_

Approved By:\_\_\_\_\_Title:\_\_\_\_\_Date:\_\_\_\_\_

## **Total Suspended Solids**

(Gravimetric, Dried at 103-105 °C)

### **Scope and Application:**

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The practical range of the determination is 2 mg/L to 20,000 mg/L.

### **Detection Limit:**

2 mg/L Verify detection limit by checking 2.0 mg reference weight prior to analyses. Record weight on worksheet.

### **Summary of Method:**

A well-mixed sample is filtered through a standard glass fiber filter. The residue retained on the filter is dried to a constant weight at 103 to 105 °C. The increase in weight of the filter represents the total suspended solids.

### **Sample Handling and Preservation:**

Analysis should begin as soon as possible. Refrigeration or icing to 4 C, to minimize microbiological decomposition of solids, is recommended. Preferably do not hold samples more than 24 hours. If the sample must be held longer than 7 days flag the result with [aan](#) "H" to indicate the sample was out of hold time. Bring samples to room temperature before testing.

### **Interferences:**

Exclude large floating particles or submerged agglomerates of heterogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Because excessive residue on the filter may form a water trapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

### **Equipment:**

1. TSS 47 mm ProWeigh Filters (Environmental Express #F93447MM)
2. VSS 47 mm ProWeigh Filters (Environmental Express #F93447VOL)
3. Two piece Millipore filter holder
4. Vacuum Flask, 1L
5. Fisher Scientific Isotemp Programmable Oven Model 818F
6. Dessicator
7. Ohaus Discovery Analytical Balance
8. Fisher Scientific Isotemp Muffle Furnace

### **Selection of filter and sample size:**

Choose sample volume to yield between 2.5 and 200 mg dried residue. Use 5 to 50 ml when testing influent; use 200 to 1000 ml when testing effluent. For aeration basin samples, use around 5 mL with a 5 mL pipette. If more than 10 minutes are required for filtration, decrease sample volume.

### **Quality Control:**

1. Analyze one Laboratory Control Blank(LCB) per batch. LCB is completed by filtering 1000ml of DI water through a filter. The results must be less than 2 mg/L before results can be reported.
2. Analyze every tenth sample in duplicate or once per batch, whichever is more frequent.
3. The duplicates must be within 10% of each other. If not within 10%, dry the filter for one more hour and reweigh. If the control is still out of range, notify the Chemist. Samples may require reanalysis.

**Procedure:**

**A. Total Suspended Solids:**

1. Verify accuracy of electronic balance with range of certified weights (2mg, 100mg, 50g) prior to analyses and record on the worksheet.
2. Set up vacuum flask with, filter holder and filters.
  - i. If only TSS is to be completed on the sample use a TSS ProWeigh Filter, if VSS is also required use the VSS ProWeigh Filter for both TSS and VSS.
3. Record filter weight on worksheet, set-up the filter in the filter holder.
4. Apply vacuum and wet filter with DI.
5. Shake sample container vigorously and transfer the proper amount of sample to the funnel by means of a graduated cylinder.
6. Record volume of sample filtered on the worksheet.
7. Filter sample and rinse with three 10-ml portions of distilled water; continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.
8. Transfer filter back to the aluminum dish; evaporate to dryness in the oven set at 103 to 105 °C for 1 hour.
9. Remove from oven and let cool in desiccators.
10. Weigh the filter.
11. Record weight on the worksheet.
12. Repeat the cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less.
13. Record all weights on worksheet.
14. Repeat for all samples.

**B. Fixed and Volatile Suspended Solids (If Necessary):**

1. After the final weight is determined for TSS, place the filter in a labeled crucible and record on the worksheet. The filter must be placed in the crucible and not left in the aluminum dish because the dish will become black in color and it will be difficult to distinguish between the other samples.
2. Place the crucible in the muffle furnace at 550°C for 30-60 minutes. The LCB should also be heated at this temperature.
3. Allow for the crucibles to cool significantly, approximately 1 hour and place in the desiccator.
4. Record the final weight of the filter on the worksheet.

**Calculations:**

$$\text{Total Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{D}$$

$$\text{Fixed Suspended Solids, mg/L} = \frac{(C - B) \times 1000}{D}$$

$$\text{Volatile Suspended Solids, mg/L} = \frac{(C - A) \times 1000}{D}$$

A = weight of dried residue + filter in mg.

B = weight of filter in mg.

C = weight of ashed residue + filter in mg

D = volume of sample used in ml

**Reporting:**

Report results to two significant figures for results below 100 mg/L, report results above 100 mg/L to 3 significant numbers. Units are mg/L. Report results of less than 2 mg/L as "Not Detected".

**References:**

"Methods for Chemical Analysis of Water and Wastes", EPA-600/479-020, Revised March 1983, pages 160.2-13 to 160.2-3.

SM 2540-D Total Suspended Solids Dried at 103-105°C, "Standard Methods for the Examination of Water and Wastewater", 20th Edition, 1998, pages 2-57 to 2-58.

Written By: Corey Hendrickson

Date: 11/23/2009

Revised By: Hayden Maccagno

Date: 10/8/2014

## **Total Dissolved Solids (Filterable Residue) (Gravimetric, Dried at 180 ° C)**

### **Scope and Application:**

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

### **Summary of Method:**

A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight to determine the amount of dissolved solids.

### **Accuracy/Precision:**

A 100 mg/L std measured 10 different days averaged 98.5 mg/L with a SD of 6.4 mg/L and a RSD of 6.5%.  
A 500 mg/L std measured 10 different days averaged 501.5 mg/l with a SD of 8.6 mg/L and a RDS of 1.7%  
A proficiency sample measured 210 mg/L and the true value was 227 mg/L, a 92.5% recovery.

### **Detection Limit:**

Detection limit for this test is 10 mg/L for a 250 ml sample. Increasing volume will lower DL.

### **Definitions:**

Filterable residue is defined as those solids capable of passing through a glass fiber filter.

### **Sample Handling and Preservation:**

Analysis should begin as soon as possible. Refrigeration or icing to 4 C, to minimize microbiological decomposition of solids, is recommended. Preferably do not hold samples more than 24 hours. If the sample must be held longer than 7 days flag the result with an "H" to indicate the sample was out of hold time. Bring samples to room temperature before testing.

### **Interferences:**

High concentrations of bicarbonate will require careful and possible prolonged drying. Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

### **Equipment:**

1. Whatman 4.7 cm glass membrane filters ( Cat. No. 1827-047)
2. Two piece Gelman Science filter (clear funnel with white base)
3. Vacuum Filtration flask, 1L
4. 50 ml Evaporation Crucibles
5. Fisher Scientific Isotemp Programmable Oven Model 818F
6. Dessicator
7. Ohaus Discovery Analytical Balance
8. Fisher Scientific Isotemp Muffle Furnace

### **Quality Control:**

1. Analyze one laboratory control blank (LCB) with each batch of samples. LCB should be less than 10mg/L.
2. A laboratory control standard (LCS) of 500mg/L and a laboratory control standard low (LCSL) of 100mg/L must also be analyzed with each batch of samples. The acceptance level for the LCS is 90-110% and the acceptance for the LCSL is 80-120%.
3. Analyze at least one sample in duplicate per batch or a 10% frequency for drinking water or a 5% frequency for wastewater. The results must be within 5% of the average before results can be reported.

**Scheduled Preventative Maintenance:**

- 1) Review heating and drying procedure including drying times.
- 2) Verify functioning of electronic desiccator, check humidity and reactivate desiccant periodically.
- 3) Verify accuracy of analytical balance, complete daily checks of the balance using 2mg, 1000mg, and 50g weights. A monthly check of the balance should also be completed.
- 4) Water quality should be completed monthly on water sources (RO and DI).
- 5) Oven and desiccators should be up kept and cleaned often to remove excess dust.

**Selection of filter and sample size:**

Choose sample volume to yield between 2.5 and 200 mg dried residue. A 35 ml size is common for drinking water. Use 10 ml or 25 ml for wastewater. If more than 10 minutes are required for filtration, increase filter size or decrease sample volume. Samples suspected of having low TDS may require up to 250 ml in order to meet the detection limits, collect samples in a dried and tared 400 ml beaker.

**Procedure:**

**A. Total Dissolved Solids**

1. Verify accuracy of electronic balance with range of certified weights (2mg, 100mg, 50g) prior to analyses and record on the worksheet.
2. Heat a clean evaporating dish to  $180 \pm 2^{\circ}\text{C}$  for 2 hours.
3. Cool, desiccate, and store in desiccator until ready for use. Dry for at least four hours.
4. Weigh immediately before use. Record the weight and number of the crucible on worksheet.
5. Set-up the filter and pre-rinse the unit by washing the filter with three successive 20 ml volumes of DI water. Remove all traces of water by continuing to apply vacuum after water has passed through. Rinse the flask with deionized water and discard the waste.
6. Shake sample container vigorously and transfer 35.0 ml to the filter with a 50 ml graduated cylinder.
7. Rinse with one to two 10 ml portions of distilled water and continue to apply vacuum for about 1 minute after filtration is complete to remove as much water as possible.
8. Transfer filtrate to a weighed evaporating crucible.
9. Rinse the collection tube with three small portions of deionized water, adding the rinse water to the evaporating crucible. Evaporate to dryness at  $99^{\circ}\text{C}$  overnight.
10. Dry evaporated sample for at least one additional hour at  $180 \pm 2^{\circ}\text{C}$ , preferably for 2 hours.
11. Using tongs cool in desiccator for approximately 4 hours and weigh.
12. Record the weight on worksheet.
13. Repeat drying cycle at  $180 \pm 2^{\circ}\text{C}$  until constant weight is obtained or until weight loss is less than 4% of the previous weight or 0.5 mg, whichever is less.
14. Record final weight on worksheet.

**B. Fixed and Volatile Dissolved Solids (If necessary)**

1. After final weight is determined for TDS, place crucible in the muffle furnace at  $550^{\circ}\text{C}$  for 30 – 60 minutes. The LCB, LCS, and LCSL should also be ignited at  $550^{\circ}\text{C}$  for Quality Control.
2. Allow for the crucible to cool significantly, approximately 1 hour and then place in the dessicator.
3. Record weight on the work sheet.

**Calculations:**

$$\text{Total Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{D}$$

$$\text{Fixed Solids, mg/L} = \frac{(C - B) \times 1000}{D}$$

$$\text{Volatile Solids, mg/L} = \frac{(C - A) \times 1000}{D}$$

A = weight of dried residue + dish in mg.

B = weight of dish in mg.

C = weight of ashed residue + dish in mg

D = volume of sample used in ml

**Reporting:**

Report results to three significant figures. Units are mg/L. Report results of less than 10 mg/L as “Not Detected”.

When entering values into Labworks verify the balance between the TDS and the SEC. This can be completed by selecting the TDS\_SEC option when entering data. In most cases the ratio should be between 0.5-0.7.

**Troubleshooting:**

1. Balances are out of range: If this occurs adjust the volume accordingly. Reanalyze the sample and if the weight does not change by more than 5% of the previous value use the original sample value. Document that the ratio is high/low and that the sample has been rechecked.
2. Low LCB value: If the LCB weighs less than the weight of the crucible before the analysis begun make sure that it has had adequate dry time in the desiccator and has had time to cool in temperature.

**References:**

“Methods for Chemical Analysis of Water and Wastes”, EPA-600/479-020, Revised March 1983, pages 160.3 to 160.3-2.

SM 2540 C Total Dissolved Solids Dried at 180°C, *Standard Methods for the Examination of Water and Wastewater* 20th Edition (1998), Edited by Clesceri, L. Greenberg, A. and Eaton, A., pages 2-56 to 2-57.

Written By: David Holland

Title: Laboratory Director

Date: 05/07/10

Revised By: Hayden Maccagno

Date: 10/8/14

## Conductivity

### **Scope and Application:**

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

### **Summary of Method:**

The specific conductance of a sample is measured by use of a self-contained conductivity meter, the YSI Model 3100. The conductivity meter is used in the temperature compensated mode.

### **Sample Criteria & Acceptability:**

A minimum of 100 ml of sample should be submitted in a clean container provided by the laboratory. Samples can be stored for up to 28 days at 4°C. The samples must be brought to room temperature (15-25°C) before testing. If the sample does not meet the above criteria document it on the worksheet but perform the test.

### **Reagents and Standards:**

- a) 147 µmhos/cm Standard: Dissolve 0.0746g of pre-dried potassium chloride in a 1 liter Class A volumetric flask using deionized water.
- b) 1412 µmhos/cm Standard: Dissolve 0.7455g of pre-dried potassium chloride in a 1 liter Class A volumetric flask using deionized water.
- c) 24800 µmhos/cm Standard: Dissolve 14.9103g of pre-dried potassium chloride in a 1 liter Class A volumetric flask using deionized water.

Reagent Grade potassium chloride (KCl) is dried for 4 hours at 105°C. Use immediately or store in a desiccator for later use.

### **QC Procedure:**

1. The cell constant must be checked on a daily basis. To check the cell constant turn the probe off and back on again, the cell constant will appear on the screen and should be 1.00. If the cell constant is not 1.00 follow the following procedure to correct it:
  - a. Press the down arrow and mode keys at the same time. The CAL symbol will appear on the bottom left and the slope will appear on the screen. It should read 1.91%.
  - b. Press the Mode key again and the temperature should appear on the screen and read 25.0 C.
  - c. Press the Mode key once again and the cell constant should appear on the screen. Adjust the value using the up and down arrows to the desirable value of 1.00.
  - d. Press Enter and this should result in the word save appearing on the screen.
2. Instrument must be standardized with KCl solution before daily use.
3. Pour 50 ml of the standard potassium chloride solution into a 250 ml beaker.
4. Immerse conductivity cell in sample and the bottom of the probe must be clear of the bottom of the beaker to allow free flow of sample underneath. The electrodes must be submerged and the electrode chamber must be free of trapped air. Tap the cell to remove any bubbles, and dip it two or three times to assure proper wetting.
5. The conductance value of the solution is displayed on the meter.
6. Record QC and temperature on worksheet.

### **Procedure:**

1. Pour ~50mL of sample in 250mL beaker.
2. Immerse conductivity cell in sample. The electrodes must be submerged and the electrode chamber must be free of trapped air and the bottom of the probe must be clear of the bottom of the beaker to allow free flow of sample underneath. Tap the cell to remove any bubbles, and dip it two or three times to assure proper wetting.
3. The conductance value of the solution is displayed on the meter.
4. Record conductivity and temperature on worksheet.

**Quality Controls:**

- a) Check deionized water. It should read less than 1 umho. If reading is higher, clean-cell and repeat reading of deionized water. If reading is still high, notify the Chemist.
- b) The standard solutions must be completed and have an accuracy of 95-105%.

**Reporting:**

Report results to three significant figures. Report in units of micromhos per centimeter at 25°C, PQL is 2μS/cm

**Conductance Meter Maintenance:**

- a) Store cell in deionized water. If the cell has been stored dry, soak in deionized water for 24 hours. Check the platinum black coating on the electrode. If the coating appears thin or if it is flaking off the electrode, the cell should be cleaned and the electrodes replatinized. See "Instruction Manual YSI Model 32 Conductance Meter" pages 11 and 12 for instructions. The electrode should be cleaned and replatinized every four months or when needed. Record the preventative maintenance on the "PM Worksheet".

**References:**

"Instruction Manual YSI Model 3100 Conductance Meter, Item 060818, PN A32018 R, October 88 EP.

"Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, pages 120.1-1 to 120.1-3.

SM 2510B Standard Methods for the Examination of Water and Wastewater 20th Edition (1998), Edited by Clesceri, L. Greenberg, A. and Eaton, A.

Revised By: Hayden Maccagno

Date: 11/14/2014

Approved By:

Date:

## ***Alkalinity***

### Titration Method

#### **Scope and Application:**

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Alkalinity is the capacity of the water to neutralize by itself when an acidic solution is added. It is the sum of all the titratable bases. Because the neutralizing capacity of many surface waters is primarily due the presence of bases, like bicarbonate, carbonate, and hydroxide, the alkalinity it is taken as an indicator of these constituents.

Alkalinity depends on the end-point pH used. According to Standard Methods, the end-point pH recommended for routine or automated analysis of total alkalinity is 4.5.

#### **Precision and Bias:**

No general statement can be made about the precision because of the great variation in sample characteristic. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg CaCO<sub>3</sub>/L can be achieved. Forty analysts in an interlaboratory study, analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mgCaCO<sub>3</sub>/L. Samples were analyzed using an end point of pH 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.

A total of seven replicates of 3 mg/l NaHCO<sub>3</sub> QC were analyzed in our laboratory on 3 different days, obtaining an average of 3.0 mg/L, a standard Deviation of 0.53 mg/L and a relative standard deviation of 17.56%.

#### **Minimum Reporting Limits:**

Based on 0.1 ml of 0.02 N titrant and 50 ml of sample the detection limit for total alkalinity is 2mg CaCO<sub>3</sub>/L and the reporting limit is 10 mg CaCO<sub>3</sub>/L.

#### **Working Range:**

**Alkalinity Method:** 20 mg CaCO<sub>3</sub>/ L to 5000 mg CaCO<sub>3</sub>/L, not exceeding more of 50 ml of titrant.

**Low Alkalinity Method:** 1 mg CaCO<sub>3</sub>/L to 19 mg CaCO<sub>3</sub>/L (Method use in samples with alkalinity < 20 mg CaCO<sub>3</sub>/L)

**Phenolphthalein Alkalinity Method:** 1 mg CaCO<sub>3</sub>/L to 5000 mg CaCO<sub>3</sub>/L (Method use in samples with pH >8.5)

### **Summary of Method:**

**Methyl orange or total alkalinity** is determined by titration of a sample to a pH of 4.5 with 0.1N H<sub>2</sub>SO<sub>4</sub> standardized; includes all carbonate, bicarbonate and hydroxide.

**Phenolphthalein alkalinity** is a method use when a sample have pH greater than 8.5 (pH>8.5 indicate that the sample is over saturated with CaCO<sub>3</sub>. The phenolphthalein alkalinity is determined by titration to a pH of 8.3 with 0.1 N H<sub>2</sub>SO<sub>4</sub> standardized.

**Low Alkalinity** is a method use when a sample has less than 20 mg CaCO<sub>3</sub>/L. The sample is titrated using a 0.02 N H<sub>2</sub>SO<sub>4</sub> standardized to the equivalent point (pH 4.5) and re-titrated to reduce pH exactly 0.30 pH units. This pH reduction will correspond to an exact doubling of hydrogen ion concentration.

### **Preservation and Holding Times:**

Samples should be analyzed as soon as possible after collection but can be stored at 4°C up to 14 days for regulatory purposes. Warm to room temperature before analyzing.

### **Interferences**

Soaps, oily matter, suspended solids or precipitates may coat the electrode and cause a sluggish response.

**Note:** Do not dilute, filter or alter the sample. Instead clean the electrode occasionally.

### **Safety Issues:**

Use standard laboratory safety precautions (Safety glasses, lab coat and gloves).

### **Instrumentation/Equipment:**

1. pH meter/ Titration apparatus ( *Metrohm 877, Serial # 11110554*)
2. Titration Vessels (120 ml)
3. Class A TD, 50 ml cylinder

### **Reagents:**

- 1) 1.0 N Standardized Sulfuric Acid: purchased from RICCA (*Cat no. 8300-32*)
- 2) 0.02 N Standardized Sulfuric Acid: Using a glass pipette and a volumetric flask, dilute 20.00 ml of 1.0 N H<sub>2</sub>SO<sub>4</sub> to 1 L with DI water.
- 3) 0.1 N Standardized Sulfuric Acid: Using a glass pipette and a volumetric flask dilute 100 ml of 1 N Sulfuric Acid to 1 L with DI.
- 4) Solution for ICV:  
Prepare 1000 mg/L NaHCO<sub>3</sub> QC solution by weighing 0.8265 g NaHCO<sub>3</sub> (previously dried). Dilute to 500 mL of DI water.  
Or use Alkalinity as Calcium Carbonate standard of 1000 mg/L CO<sub>3</sub> from Absolute standard Inc. (*Cat no. 54142*).

**Note:** These acids have to be standardized before their use. For Acid Standardization refer to Standard Methods 2320 B, section 3 or the SOP located in: Computer/Method/SOP/Acid Standardization

### **Q.A./Q.C. Requirements:**

- 1) Blank acceptance criteria, is less than 0.1 mL of acid. It is recorded as Not Detected. Analyze one blank per day.
- 2) Analyze one ICV every twenty samples. The acceptance criteria for the ICV is 95-105 recovery percent. Analyze an ICV every 20 samples.
- 3) Perform duplicate analysis every ten samples or at the end of each batch, whichever is more frequent. Duplicate analysis should be less than 10 % difference.

### **Instrument Set Up**

- A. Open the Titration Base software
- B. Calibrate the *Titrimo Plus*.

1. Using the arrows [↓↑] sort through the list of the *Titrimo Plus* screen. Select METHOD by pressing and releasing the [OK] key.
2. Sort through the list of methods, when the option of CAL\_PH is highlighted press and release the [OK] key.
3. Place the probe on the *801 Stirrer Base*. Rinse the probe with DI, Introduce the probe into pH buffer (pH= 7.02 or pH =4.00), use 60 mL of buffer. Add a small agitator with the buffer.
4. Proceed to load the method by pressing the [START] key on the *Torino Plus*.
5. *Torino Plus* will ask you to introduce the next buffer. After introducing the next buffer press the [OK] key.
6. The percentage of the pH calibration will appear in the screen, record slope on worksheet

**Note:** The acceptable range is 98 -102%. Calibrate pH meter each day of use.

- C. Flush the line of the *Torino Plus* with acid,

1. Return to the main screen by pressing the [Back] key on the *Titrimo Plus*
2. Using the arrows [↓↑] sort through the list of the screen, Select MENU by pressing and releasing the [OK] key.
3. Sort through the list, when the MANUAL CONTROL is highlighted press and release the [OK] key.
4. Using the arrows [↓↑] and [←→] sort through the list of the screen, when DOSING option in the list and the PREP option at the bottom of the screen are highlighted at the same time, press and release the [OK] key. Make sure that the tip of the titrant line is pointing an empty vessel.

Note: Flush the line when changing from one acid to another or when trying to remove air bubbles. To remove air bubbles tap the line during the flushing. Air bubbles will cause positive bias in the alkalinity measurement.

### Analysis

1. Allow sample to reach room temperature before analyses. Samples may be warmed in a water bath. Avoid over heating the samples
2. Keep sample sealed until analyses
3. Select titrant. Use 0.02 N H<sub>2</sub>SO<sub>4</sub> for low level alkalinities and 0.10 N H<sub>2</sub>SO<sub>4</sub> for > 20 mg/L CaCO<sub>3</sub> or phenol alkalinity.
4. Pour 50 ml of sample or ICV into a titration vessel. Fill the *Titrimo Sample Charger* with all the samples, including a vessel full of DI water in the position zero for automatic rinsing. Note: Keep track of the order of your samples. Every twenty sample change the rinsing DI for fresh one.
5. Select the Method to use in the *Titrimo Plus*.
6. Using the arrows [   ], sort through the list of the screen; select METHOD by pressing and releasing the [OK] key.
7. Sort through the list of methods, select the needed option by pressing and releasing the [OK]. ALK for Total Alkalinity, Low Alk for samples with <20 mg/L CaCO<sub>3</sub> or pal for phenolphthaleine Alkalinity). **Note:** Don't forget to switch acid if needed.
8. After loading the method proceed to the *Compact Sample Changer*. Using the arrows [   ], sort through the list of the screen of the *Compact Sample Changer*, select the RACK POSITION by pressing and releasing the [START] key. Select the NUMBER OF SAMPLE option by pressing and releasing the [OK] key. Add the number of samples to be analyzed. Select the NEXT SAMPLE Position by pressing and releasing the [OK] key. Add the number of the position of your first sample to be analyze.
9. Press and release the [START] key to begin with the titration.

### Blank and QC Analysis

1. Instrument Calibration Verification Blank (ICVB), pour 50 ml DI Water into vessel.
2. Verify that ICVB meets acceptance criteria above.
3. For Total Alkalinity ICV (Instrument Calibration Verification) add 2 ml of 1000 mg/L QC to 50 ml DI for a total concentration 40.00 mg/L CaCO<sub>3</sub>). For low alkalinity use a ICV of 20 mg CaCO<sub>3</sub>/L
4. Instrument will calculate results. Verify that ICV meets acceptance criteria above.
5. Acceptable RSD is < 10%
6. Duplicate Analyses frequency is 10% or once per batch whichever is more frequent.

### Helpful Hints:

#### A. When QC is over the acceptance criteria:

Check all the connections to make sure that they are well tight and there is any presence of bubbles.

#### B. Prepare Work sheet

- a) Open the Alkalinity worksheet template located in Computer/Method (\\NAS) (Z:)/ Alk/ TEMPLATE. Press [Save As], and save the excel worksheet with the date that the samples were analyzed (yyyymmdd).
- b) Enter the slope of your calibration in the slope cell. Enter your initials and the day that the samples were analyzed.
- c) Write samples ID in the order that were analyzed, including the ICV and excluding the blank. Write down the sample number of the first sample (the ICV) in the *Counter* column. *Note: The sample number can be found in the titration Base program, by highlighting the sample and opening the Determination tab ( located inside the information window). The samples # are in consecutive order, use the first sample determined the rest of samples number.*
- d) In the *Titrimo Base* program highlight the rows of analyzed samples. Copy and paste this rows in the sheet # 3.
- e) From sheet #3, copy and paste on sheet # 2 the alkalinity results in the *Alk (mg/L)* column and the volume of titrant use in the *Titrant (mL)* column.
- f) Fill the volume use for each sample in the *Volume (mL)* column.
- g) Copy and paste in sheet #1 the samples ID (delete ICV and duplicate samples), fill the analyte column with the ALK word for total alkalinity or low alkalinity and, ALK\_PHEN word for phenyl alkalinity.
- h) Copy and paste the samples Ids and results from sheet # 2, in sheet #1, change them to whole numbers. Fill the *Date* column with the day that the samples were analyzed (mm/dd/yyyy). *Note: Make sure that the rounding is correct for samples that end 0.5 mg CaCO<sub>3</sub>/L*
- i) Save changes and print sheet #2.

### C. Watch the counter number

Sometimes, some samples results may be skipped by the titration base program. If when preparing the worksheet you notice that there is a result missing check the titration base program. Look for the counter number of the first titrated sample (QC) and the rest of the samples numbers. The numbers are in consecutive order, find the number of the skipped sample, and write it down. In the Alkalinity worksheet accommodate your alkalinity results and volume of titrant, leave blank the alkalinity result and volume of titrant for the skipped sample. Eliminate the skipped sample row from the list and fix the counter number. Make sure that the counter numbers of the worksheet match with the ones in the titration program.

### D. Import data into Lab Work

- a) In Lab Work select the [Result Entry] option.
- b) Pinch the [Analyses Awaiting for Result] option.
- c) Perform an speed search for alkalinity.
- d) First press [View Selection ] option and then the *Enter Selection* option. ( A new window will appear).
- e) Close the new window and in the LabWORKS Result Entry window select [Import Instrument Results] option. The Intelligent Instrument Interface Result File will appear.
- f) Select the[ *Labworks Excel work book* ] option. Before importing the data, make sure that the file to import is open in the sheet #1.
- g) Press [Browse] find the file to enter in the following location: Computer /Method (\\NAS) (Z:)/ Alk/ mm/dd/yyyy
- h) Press [Ok], the interface will extract the samples ID with their results. Prees [Ok].

**Note:** Use the alkalinity worksheet to make sure that the entered results are correct, to write the average of those samples that have duplicates and to round according to laboratory rounding rule.

**Calculations:**

$$\text{Alkalinity, mg CaCO}_3/\text{L} = (\text{ml H}_2\text{SO}_4 \times N_{\text{H}_2\text{SO}_4} \times 50,000) / \text{mL}_{\text{sample}}$$

$$\text{Recovery \%} = ([\text{Alkalinity mg/L (measured)} - \text{Alkalinity mg/L (true value)}] / \text{Alkalinity mg/L (true value)}) \times 100$$

$$\text{Relative Difference \%} = [ |\text{Alkalinity mg/L (Sample)} - \text{Alkalinity mg/L (Dup)}| / \text{Average (Sample \& Dup)} ] \times 100$$

$$\text{Alk} < 20 \text{ mg CaCO}_3/\text{L} = 2 (\text{ml H}_2\text{SO}_4 [\text{pHEp1}] - \text{ml H}_2\text{SO}_4 [\text{pHEp2}]) / \text{ml sample}$$

Exception: if alkalinity < 20 mg/L use “low alkalinity calculation procedure (SM2320B Part 5, Page 2-28)

**Reporting:**

1) **Before entering Data make sure that is approved by the lead chemist**

2) **Reporting Units**

Alkalinity is reported as “Alkalinity = \_\_\_\_mg CaCO<sub>3</sub>/L”.

3) **Reporting Limits**

Results below the PQL are reported as “ND” (not detected). Samples using more than 50 ml of titrant are diluted and re-analyzed. Theoretical MDL = 1 mg/L.

4) **Significant Figures and Reporting Values Below Detection Limit**

**Reference/Method Source:**

SM 2320B Alkalinity Procedure, “Standard Methods for the Examination of Water and Wastewater”, 20<sup>th</sup> Edition, 1997.

Written By: Lilian Reyes

Title: Lab Analyst

Date: 4/14/16

Approved By: David Holland

Title: Laboratory Director

Date: 4/18/16

## Alkalinity MDL Study 2015

| Replicate # | Analysis Date | Value (mg/L) | Result | % Rec (50-150%) |
|-------------|---------------|--------------|--------|-----------------|
| 1           | 9/9/2015      | 3            | 2.76   | 92%             |
| 2           | 9/9/2015      | 3            | 3.08   | 103%            |
| 3           | 9/9/2015      | 3            | 4.20   | 140%            |
| 4           | 9/11/2015     | 3            | 2.84   | 95%             |
| 5           | 9/11/2015     | 3            | 2.68   | 89%             |
| 6           | 9/11/2015     | 3            | 2.72   | 91%             |
| 7           | 9/17/2015     | 3            | 2.96   | 98.7%           |

|                                              |                 |
|----------------------------------------------|-----------------|
| Average                                      | 3.03            |
| Standard Deviation                           | 0.532881        |
| RSD (10-20%)                                 | 17.56%          |
| <b>MDL</b> = $t \times S$ , where $t = 3.14$ | <b>1.673246</b> |
| PQL                                          | 10              |

**H<sub>2</sub>SO<sub>4</sub>:** 0.02 N Standardized  
Low Alk (Ep1=pH 4.5 &

**Method:** Ep2=pH=4.2)

**Instrument:** Titrino Plus

## Color

### **Scope and Applications:**

This method applies to drinking water, natural waters, and both industrial and domestic wastewater.

### **Principle:**

The color of the sample is visually compared to the color of a range of platinum-cobalt standards. The color of non-turbid samples may be measured on a pre-programmed spectrophotometer at 455 nm.

### **Working Range**

The working range using the nessler tubes or spectrophotometer is 3-30 CU. Higher values may be obtained if the sample is diluted. Samples with turbidity  $\geq 1$  NTU, should be analyzed using the nessler tubes. Adjust MDL and PQL by dilution factor.

### **Detection Limits:**

The method detection limit and the reporting limit is 3 CU.

### **Acceptance Criteria:**

- Recovery of 5 CU standard:  $\pm 20\%$
- Duplicates:  $<20\%$  RSD

### **Interferences:**

- Turbidity: remove by filtering sample through a rinsed 0.45  $\mu\text{m}$  filter or report results as "Apparent CU."
- When using the spectrophotometer, make sure the cuvette is clean and free from smudges. Clean with DI when necessary.
- Measure pH of each sample. Report the pH of the sample as Color may vary with pH. If necessary adjust pH to 7.6 and report color at pH 7.6.

### **Preservation and Holding Times:**

Samples are to be analyzed within 48 hours of collection. Samples should be kept cold until analyzed.

### **Instrumentation/Equipment:**

- UV-1800 Spectrophotometer from Shimadzu (Serial no. A11455150458)
- Glass 10 X 20 mm cuvette
- 50 mL nessler tubes or a pre-programmed

### **Reagents and Standards:**

- 500 Color units standard by Absolute Standards Inc. (Cat no. 54255).-Color Instrument Calibration Verification (ICV): Dilute 1000  $\mu\text{L}$  of stock solution (500 color units) with 100 mL of DI water in a volumetric flask to make a 5 CU standard.

### **Quality Control:**

**-Initial Calibration Verification Blank (ICVB):** A DI water is to be analyze at the beginning of each batch, every ten samples and at the end of each batch. A non zero absorbance of the blank means that the cell needs to be cleaned or there is variation in the spectrophotometer **response**. It may be necessary to allow additional warm-up time.

**-Duplicates analyses:** Analyzed every tenth samples a duplicate (i.e. repeating the entire procedure) or at least one per batch.

**-Instrument Calibration Verification (ICV):**

A 5 CU standard is to be analyzed at the beginning of each batch, every 20 samples and at the end of each batch. This is to verify if there any variation in the instrument. The ICV should not be more than 25 % of difference of the first ICV measurement.

### **Nessler Tubes, Calibration Standards:**

Calibration standards are to be prepared monthly and stored in the dark when not in use. Prepare calibration standards from a 500 CU stock solution. Prepare standard having CU of 3, 5, 7, 10, 15, 20, 25, and 30 by diluting 0.3, 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, and 3.0 mL of the stock color solution with deionized water in nessler tubes. (**Note:** The expiration period after preparation is one month. For measurements in the spectrophotometer , there is a calibration curve ready to use). Change calibration on the spectrophotometer when a new lot of color standard is to be used.

### **Nessler Tube Procedure:**

1. Fill a matched nessler tube with sample to the 50 mL line and place on the rack.
2. Look vertically downward into the tubes at an angle such that light is reflected upward through the tubes and compare the sample to the calibration curve.
3. If the color of the sample exceeds the calibration curve, dilute the sample until it is within range.

**Note:** Samples should be at room temperature to avoid smears on the nessler tubes.

### **Spectrophotometer Setup Procedure:**

1. Turn on the spectrophotometer. Do not open the cover while it initializes.
2. Press Enter when prompted for a password.
3. Select PC Control on the instrument (F4). Now all operations are controlled from the UV Probe Software.
4. Select Connect at the bottom of the screen.
5. To open the method, go to File, select open, and then change the file type at the bottom to Standards (\*.std). Select the Color\_140612.std file and open.
6. Allow the instrument to warm-up.
7. If the absorbance with nothing inside the cover is not reading at 0.000, press auto zero.
8. Fill the cuvette with DI H<sub>2</sub>O and zero the instrument by selecting Cell Blank

**Note:** Samples should be at room temperature to avoid smears on the cuvette.

**Reporting:**

1. Before entering data make sure that it is approved by the lead chemist
2. Report the mean of the duplicate readings.
3. Reporting Units:
  - a. Color is reported as CU, one CU is equivalent to one Pt-Co unit and to one Hazen unit
4. Reporting Limits:  
The PQL for this test is 3

Results are to be reported as integers with the unit CU or if samples are unfiltered, results are to be reported as "Apparent CU."

| CU      | Report to Nearest |
|---------|-------------------|
| 1-50    | 1                 |
| 51-100  | 5                 |
| 101-250 | 10                |
| 251-500 | 20                |

**References:**

APHA; AWWA; WEF. (1998). 2120 B. Visual Comparison Method. In *Standard Methods for the Examination of Water & Wastewater* (20th ed.).

Written By: \_\_\_\_\_ Title: \_\_\_\_\_ Date: \_\_\_\_\_

Approved By: \_\_\_\_\_ Title: \_\_\_\_\_ Date: \_\_\_\_\_



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Date: 12/05/16

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## Quote

### Detailed Quote Information

| Analysis Name                            | Quantity | Price          | Total           |
|------------------------------------------|----------|----------------|-----------------|
| <b>Total Nitrogen, inc NO3, NO2, TKN</b> | <b>2</b> | <b>\$70.00</b> | <b>\$140.00</b> |
| Ammonia Nitrogen                         | 2        | \$30.00        | \$60.00         |
| TDS                                      | 2        | \$25.00        | \$50.00         |
| Total                                    |          |                | \$250.00        |
| Prompt Payment Total (< 30 days)         |          |                | <b>\$225.00</b> |

Kind Regards

David Holland  
Laboratory Director

## ***Oil & Grease***

### Hexane Extraction

#### **1. Scope and Application**

This method is for determination of n-hexane extractable material (HEM) in surface and saline waters and industrial and domestic aqueous wastes. Extractable materials that may be determined are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials.

#### **2. Detection Limits:** 3 mg/L

#### **3. Precision and Bias:**

This method was validated through both single laboratory and inter-laboratory studies where the results indicate that there was an average recovery of 93% for HEM and 89% recovery for SGT-HEM. There was an 8.7% difference for HEM recovery and a 13% difference for SGT-HEM.

#### **4. Working Range:** 3 to 1000 mg/L

#### **5. Summary of Method**

A 1-Liter sample is acidified to a pH<2 and extracted using a solid phase extraction filter. The extract is then eluted off the filter with hexane and collected in a round bottom flask. The solvent is filtered through a phase separation filter and then evaporated; the HEM is then desiccated and weighed.

#### **6. Sample Collection, Preservation and Holding Times:**

- a) Collect samples in two 1-L glass bottles with PTFE-lined screw cap. Pre-rinse bottle with sample before collection.
- b) If analysis is delayed for more than 4 hrs, adjust the sample pH to less than 2 with HCl or H<sub>2</sub>SO<sub>4</sub> at time of collection, and refrigerate at 0-4 °C.
- c) Samples must be collected as grab samples. If a composite analysis is required, individual grab samples are composited in the laboratory prior to analysis.
- d) All samples must be refrigerated at 0-4 °C from the time of collection until extraction.
- e) All samples must be analyzed within 28 days of collection.

#### **7. Comments**

##### **7.1 Interferences:**

- a) Solvents, reagents and glassware may yield artifacts that affect results. Specific selection of reagents and purification of solvents may be required.
- b) If samples consist of complex matrices containing substances (such as particulates or detergents) that may interfere with the extraction procedure, use a smaller sample size for analysis.
- c) The SPE filter must be properly conditioned or analyte can be lost.
- d) The sample must not flow too quickly through the SPE filter or analyte can be lost.

##### **7.2 Helpful Hints:**

Glassware is cleaned by washing in hot water containing detergent, rinsing with tap and DI water, and rinsing with solvent.

#### **8. Safety Issues**

- a) n-Hexane has an increased neurotoxic effect. Inhalation of n-hexane should be minimized by performing all operations in the fume hood.
- b) n-Hexane is highly flammable and reacts vigorously with oxidizing materials.
- c) Methanol is flammable and is a contact irritant.
- d) Unknown samples may contain volatile toxic compounds. Open containers inside the fume hood.

## 9. Instrumentation/Equipment:

- a) Analytical balance
- b) SPE Manifold with reservoirs and collection tubes and round bottom flasks
- c) Whatman Phase Separation filter paper 150mm Diameter (Cat. No. 2200-150)
- d) Horizon Solvent Trap-Solvent Recovery System
- e) Horizon Speed – Vap III
- f) Vacuum pumps with regulator
- g) SPE filter disks
  - i) CPI International SPE Disks 90mm (P/N 4350-139)
  - ii) CPI International SPE Disks 47mm (P/N 4350-13)
- h) Aluminum evaporating dishes

### 9.1 Operating Instructions

See Operating Instructions for Horizon Solvent Recovery System  
See Operating Instructions for Mettler Toledo B Balance Line

### 9.2 Scheduled Preventative Maintenance

- 1) Empty waste collection carboy
- 2) Prepare evaporation disks by placing in desiccator before use
- 3) Keep analytical balance clean at all times

## 10. Reagents and Standards

- a) 6 N HCl (1+1): Mix equal volumes of concentrated HCl and DI water (Used as preservative).
- b) n-Hexane (Fisher Cat. H303-1)
- c) Methanol (CAS 67-56-1)
- d) Hexadecane/stearic acid soln, 8 mg/L (Absolute Standards Part No. 91958)
- h) QC Solution, 40 mg/L: Using a pipet, spike 5 mL of the hexadecane/stearic acid solution into 1L of DI water and acidify to a pH<2 (QC Solution must be kept at 0-4 °C)

## 11. Procedure:

### 11.1 Sample Preparation

- 1) Verify that the pH of the sample is less than 2.
- 2) If the sample pH is at neutral, add 5-6 mL of 6 N HCl to the sample bottle (1L)  
Adjust the amount of acid for higher pH values or smaller sample size.
- 3) Replace cap and mix.

### 11.2 Analysis

Disk Conditioning

- 1) Center disk on the screen of the filtration apparatus with the ripple side pointed up. Attach sample reservoir and screw on snugly.
- 2) Wash the disk and sides of the reservoir with at least 10 mL of hexane. Pull 1-2 mL through the filter using a light vacuum and then allow the disk to soak for at least 1 minute. After at least 1 minute pull the rest of the hexane through and allow the filter to dry completely.
- 3) After washing the disk with hexane activate it using 15-20 mL of methanol (conditioning solvent). Again, pull about 1-2 mL through the disk and allow to soak for at least 5 minutes. Add more methanol if necessary and repeat. **DO NOT ALLOW THE DISK TO GO DRY AFTER IT HAS BEEN ACTIVATED.** If the disk does dry the conditioning process must be repeated.
- 4) Turn on the vacuum and rinse the disk with DI water. Be careful to leave a small amount of water on the surface of the disk so it does not dry.

#### Sample Extraction

- 5) If the sample does not contain a large amount of solid material pour it completely into the reservoir. Try to avoid pouring the sample directly on to the filter. If there are a large number of solids present allow them to settle into the bottom of the sample container and decant as much liquid as possible into the reservoir. Save the resulting leftover sample for later. Depending on the size of the particulate matter the use of a pre-filter should be considered.
- 6) Switch the manifold to the "waste" position and apply vacuum. Allow the sample to completely pass through the filter no faster than 100 mL per minute (10 minutes total for a liter sample). **PASSING THE SAMPLE TOO QUICKLY THROUGH THE FILTER CAN RESULT IN LOW RECOVERIES.**
- 7) Periodically wash down the sides of the reservoir with water. Before the entire sample has passed through the disk rinse the sample container using about 200 mL of water and add it to the reservoir.

#### Drying

- 8) After sample extraction is complete allow the disk to completely dry by pulling a vacuum through it. This can take anywhere between 30-120 minutes depending on how clogged the disk is.
- 9) Attach a sample tube or round bottom flask to the bottom of the reservoir in order to catch the eluent. The tube should be seated so the reservoir's drip-tip is below its neck.

#### Eluting

- 10) Wash the sides of the reservoir with at least 20 mL of Hexane.
- 11) Switch the manifold to the "elute" position and gently pull 1-2 mL through, with the vacuum if necessary. Allow the filter to soak for at least 5 minutes and then pull 1-2 mL through again and allow the filter to soak for another 5 minutes. Now filter the rest of the hexane by gravity. Apply a vacuum only if the hexane has not completely filtered after 10 minutes.
- 12) Allow the disk to dry with the vacuum on.
- 13) Repeat these steps at least 1 more time, until there appears to be no more analyte eluting off the filter (The analyte should appear clear in color).

#### Filtering, Concentration, and Weighing

- 14) Turn on the Solvent Trap and allow the temperature to reach approximately -20°C, the process typically takes 1hr to reach temperature. Follow daily operating instructions for preparing the Solvent Trap for use.
- 15) Remove the sample tube from the manifold and filter through a phase separation filter into a pre-weighed aluminum dish. Rinse the tube 1-2 times with hexane. The filter should also be rinsed to ensure proper recovery.
- 16) Place the aluminum dishes into the Speed-Vap III. Apply a vacuum and allow the hexane to evaporate.
- 17) Place the aluminum dishes into a desiccator and allow to equilibrate for 30 minutes, then weigh.

### 11.3 Identification of polar/nonpolar constituents (If required)

#### Scope and application

This method is for the determination of polar and non-polar hexane extractable material (HEM) via silica gel treatment (SGT). The non-polar portion of material, that which is not bound up by the SGT, is usually composed of petroleum based material while the polar fraction is primarily animal and vegetable oil.

#### Analysis

- 1) Add approximately 100mL of Hexane to redissolve the HEM in the aluminum drying dish from the HEM extraction.

- 2) Add the dissolved HEM and Hexane mixture to a clean round bottom flask.
- 3) Add 3+/-0.3g of silica gel for every 100g HEM present to the flask.
- 4) Add a stir bar, cover with parafilm, and stir for at least 5 minutes.
- 5) Filter solution through filter paper that has been moistened with hexane into a dried and tared aluminum dish.
- 6) Place the dish in the Speed-Vap III and evaporate.
- 7) Place the aluminum dishes into a desiccator and allow to equilibrate for 30 minutes, then weigh.
- 8) The portion remaining consists of the nonpolar constituents.

## 12. Q.A./Q.C. Requirements:

### 12.1 Q.C. Analysis

One Laboratory Control Blank (LCB), one Laboratory Control Standard (LCS) and a sample duplicate is analyzed daily with each batch of samples. The laboratory must also complete matrix spike and matrix spike duplicate monthly, primarily on CAWWD Final Effluent monthly testing.

### 12.2 Acceptance Criteria

LCB < MDL (3mg/L)

LCS Precision (s): <11%

LCS Recovery (X): 83-101%

Spike Recovery: 64-132%

If samples or QC solutions don't meet the acceptance criteria, correct the problem, document corrective action, and reanalyze affected samples and/or QC solutions.

## 13. Troubleshooting:

- 1) Increased recovery of LCS: Check for droplets of water that may have formed during the filter and extraction process. If present allow for increased time in the desiccator or place in analytical oven and at a temperature no greater than 99°C for 15-20 minutes.
- 2) Sample leakage from filtration manifold: If the sample is leaking from the filtration manifold try to tighten the apparatus to control the leakage. If the sample reservoir is being connected by a clamp insure that the clamp is not resting on the reservoir, this will create excessive pressure on one side of the reservoir and may result in additional leakage.

## 14. Calculations

$$\text{HEM (mg/L)} = \frac{[\text{wt (flask+extract), mg}] - [\text{wt (flask), mg}]}{\text{Sample volume (L)}}$$

$$\text{Nonpolar HEM (mg/L)} = \frac{[\text{wt (aluminum dish + extract)}] - [\text{wt (aluminum dish)}]}{\text{Sample volume (L)}}$$

$$\text{Polar HEM (mg/L)} = \text{HEM (mg/L)} - \text{Nonpolar HEM (mg/L)}$$

## 15. Reporting

### 15.1 Reporting Units: mg/L HEM

### 15.2 Reporting Limits: 3.0 mg/L

### 15.3 Significant Figures and Reporting Values Below Detection Limit

Report results to 3 significant figures above 10 mg/L and report results to 2 significant figures below 10 mg/L. Report results below 3.0 mg/L as "ND" (not detected).

## 16. Reference/Method Source

“Method 1664, Revision B: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry”, EPA-821-R-10-001, February 2010.

Operating Instructions, Mettler Toledo B Balance Line, Mettler Toledo, 1998.

Accuprep 7000 Extraction Manifold, CPI International

Method 1664 Oil&Grease Using CPI nu-phase Fiber SPE Disks and Fastflo Prefilter, CPI International

Improved Procedure with Optimized Prefilter in the Determination of n-Hexane Extractable Materials for EPA Method 1664 Revision A, CPI International

Written by: Daniel Cook

Revised by: Hayden Maccagno

Approved by: \_\_\_\_\_  
Laboratory Director

**Standard Total and Fecal Coliform Multiple-Tube Fermentation Technique**  
**Fifteen Tube Test (SM 9221B&E)**

The Standard Total Coliform Multiple-Tube Fermentation Technique is used to determine the most probable number of total and fecal coliforms in shellfish growing water or wastewater samples. For recreational samples and raw water samples use Colilert chromogenic substrate method.

Samples are collected in pre-sterilized 125 mL capacity sterile polypropylene bottles. Sample volume should be approximately 100 mL (larger volumes do not allow adequate mixing). Samples that cannot be delivered to the laboratory within one hour should be transported in an ice cooler at <10°C. The temperature should be recorded on the requisition form. Samples should be refrigerated at 1-4°C upon arrival and processed as soon as possible. At no time should the elapsed time between collection and processing exceed 30 hours for potable water, 6 hrs for wastewater and 8 hrs for source water. All samples processed or received later than required holding time are to be flagged and a notation made on the chain of custody and/or included on a final report if resampling is not possible. Notify the lead chemist or laboratory director.

**Quality Control**

**Media:** All media must be less than three months old, stored at room temperature (media racks and baskets should be labeled with date of expiration). Check media on each day of use with known positive fecal coliform (*E. coli*; ATCC 11775)-growth with production of gas in LTB, BG&EC broth), a total coliform (*E. aerogenes* ATCC 13048) - growth with gas production in the LTB and BG, no gas in EC media), and a negative control (*Pseudomonas aeruginosa* ATCC 10145)- no gas in LTB, BG or in EC media) A temperature profile must be performed on the incubator as needed.

- 1) 10 mL sterile Lauryl Tryptose broth in 19 x 150 mm slip-cap test tubes. Fifteen tubes are required for each water sample tested. Each tube must contain one inverted vial. 5 tubes of double-strength LTB, 10 tubes single-strength.
- 2) 10 mL sterile Brilliant Green Lactose Bile broth in 19 x 150 mm test tubes. One tube is required for each positive Lauryl Tryptose tube. Each tube must contain one inverted vial.
- 3) 10 mL sterile EC broth (or MUG-EC broth) in 19 x 150 mm test tubes. One tube is required for each positive Lauryl Tryptose tube. Each tube must contain one inverted vial.
- 4) 9.0 mL  $\pm$  0.2 mL sterile phosphate buffered dilution water in screw-capped test tubes. One dilution tube is required for each sample tested (only required for high dilutions).

**Equipment:**

- 1) Sterile 10.0 mL pipets in 0.1 mL subdivisions.
- 2) Sterile inoculating loops, 3 mm in diameter.
- 3) Incubator set at  $35^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ . Check and record incubator temperatures twice daily.
- 4) Water bath set at  $44.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ . Check and record water bath temperatures as needed.

**Procedure**

**Day One** (Set-up and Inoculation of Samples):

- 1) Match samples with forms.
- 2) Record on the lab form the day and time the samples were inoculated and analyst initials.
- 3) Check lab form to determine the tests requested.
- 4) Arrange samples in numerical order whenever possible.
- 5) Arrange fifteen test tubes per test of sterile Lauryl Tryptose broth in racks according to Figure 1. Do not use any tubes showing growth or gas inside the vial.
- 6) Insert sterile dilution blanks in the spot marked "A" (only when using high dilutions).
- 7) Shake samples vigorously in an arc 24 times. If samples are not processed within ten minutes they must be reshaken.
- 8) Transfer the sample number on the bottle to the an easily viewed place on the rack or tubes.
- 9) To inoculate Sample A, use a 10.0 mL pipet in 0.1 mL subdivisions to add 10.0 mL of the undiluted sample to each of the first five test tubes (#1-5) in the series of double-strength LTB.
- 10) Add 1.0 mL sample from the dilution tube to the next five test tubes (#6-10) in the series of single strength LTB.
- 11) Add 0.1 mL sample from the dilution tube to the last five test tubes (#11-15) in the series of single strength LTB.
- 12) Use only one pipet per sample for all dilutions when possible.
- 13) Incubate Lauryl Tryptose tubes at  $35^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$  for  $24 \pm 3$  hours.

FIGURE 1. ARRANGEMENT OF TEST TUBES

| Sample A                 |                        |                       |    |                        |
|--------------------------|------------------------|-----------------------|----|------------------------|
| 1                        | 2                      | 3                     | 4  | 5                      |
| 6                        | 7                      | 8                     | 9  | 10                     |
| 11                       | 12                     | 13                    | 14 | 15                     |
| E.coli<br>media<br>check | E. a<br>media<br>check | P.a<br>media<br>check |    | "A" (for<br>dilutions) |

**Day Two** (Reading and Subculturing Tubes):

- 1) Remove racks containing the Lauryl Tryptose tubes from the incubator and gently shake to liberate trapped gas and resuspend organisms.
- 2) Working from left to right read all Lauryl Tryptose tubes after  $24 \pm 2$  hours incubation, if gas is present in the vial record as positive on lab form and subculture to Brilliant Green Broth and EC Broth as outlined in steps 3 through 12 below. If no gas is present in the vial, record as negative on the lab form and reincubate for an additional  $24 \pm 2$  hours. Note: Record results of tubes as they actually occur (i.e. in the proper sequence). See Figure 2.
- 3) Remove the first positive 24 hour Lauryl Tryptose tube in the sample series.
- 4) Remove one tube each of Brilliant Green Broth and EC Broth from their storage baskets.
- 5) If tube #1 in the series is positive, transfer the specimen label from the Lauryl Tryptose tube to the Brilliant Green Broth tube. Using small adhesive labels make a copy of the sample number and attach it to the top of the EC tubes' caps.
- 6) Remove caps and with a sterile inoculating loop, transfer one loopful of the bacterial suspension from the Lauryl Tryptose tube to the EC tube.
- 7) Using the same inoculating loop, transfer a second loopful of the suspension to the Brilliant Green tube.
- 8) Discard loop, replace caps, and discard Lauryl Tryptose tube. Autoclave in small container for

disinfection of inoculating loops.

- 9) Place the inoculated Brilliant Green tube into the spot in the rack previously occupied by the positive Lauryl Tryptose tube. Place the inoculated EC tube into the first spot of a separate test tube rack.
- 10) Continue working from left to right and subculture all remaining positive Lauryl Tryptose tubes in the sample series.
- 11) Place all subsequent, inoculated EC tubes in the next available spot to the right of the first EC tube. Always leave one empty space between each sample series. Incubate all EC tubes within 30 minutes after inoculation.
- 12) Place racks containing negative Lauryl Tryptose and any inoculated Brilliant Green tubes into the incubator at  $35^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$  for  $24 \pm 3$  hours. Place racks containing EC tubes in the waterbath at  $44.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  for  $24 \pm 2$  hours.

**Day Three** (Reading and Subculturing Tubes):

- 1) Remove racks containing the 48 hour Lauryl Tryptose and 24 hour Brilliant Green tubes from the incubator and gently shake to liberate gas and resuspend organisms.
- 2) Remove the racks of EC tubes from the water bath and gently shake to liberate gas.
- 3) Read all EC tubes first. Record results on lab form and discard tubes. Record as positive only the tubes containing gas inside the inverted vial. (Turbidity alone does not constitute a positive result).
- 4) Read all 24 hour Brilliant Green tubes from all racks next. If gas is detected, record as positive on lab form and discard tubes. If negative, record results, place in a separate rack labeled "48 hour Brilliant Green tubes," and incubate for an additional  $24 \pm 3$  hours. Label cap of first tube in sample series with lab number using small adhesive labels. Note: Record date tubes were inoculated on the rack label.
- 5) Read all remaining 48 hour Lauryl Tryptose tubes last. If positive, record results and transfer to Brilliant Green and EC Broth and discard Lauryl Tryptose tubes. Label racks of Brilliant Green tubes as "24 hour Brilliant Green tubes." Label cap of first tube in sample series with lab number using small adhesive labels. If the Lauryl Tryptose tubes are negative after 48 hours of incubation, record results and discard. (See section on "Reporting and Interpretation" for reporting out results of completed tests.)
- 6) Place racks containing inoculated Brilliant Green tubes in the incubator for  $24 \pm 3$  hours. Place racks containing EC tubes in the water bath for  $24 \pm 3$  hours. Note: Record date tubes were inoculated on the rack label.

**Day Four** (Reading and Recording Results):

- 1) Remove racks containing the 24 and 48 hour Brilliant Green tubes from the incubator and gently shake to liberate gas and resuspend organisms.
- 2) Remove the racks containing the 24 hour EC tubes from the water bath and gently shake to liberate gas.
- 3) Read all EC tubes first. Record results on lab form and discard tubes.
- 4) Read all 48 hour Brilliant Green tubes next. Record results and discard tubes.
- 5) Read all 24 hour Brilliant Green tubes from all racks last. If positive, record results and discard tubes. If negative, record results, place in the rack labeled "48 hour Brilliant Green tubes," and incubate for an additional  $24 \pm 2$  hours. If necessary, transfer sample number label to first tube of sample series.

**Day Five** (Reading and Reporting Final Results):

- 1) Remove racks containing the 48 hour Brilliant Green tubes from the incubator and gently shake to liberate gas and resuspend organisms.
- 2) Record results of all tubes and discard.
- 3) After interpreting and recording final results, recheck form for accuracy, initial, date, and place lab form in laboratory director's office to be checked.

**Reporting and Interpretation**

- 1) If Lauryl Tryptose or Brilliant Green tubes are negative after  $48 \pm 3$  hours, report out as  $<2$  Total Coliforms/100 mL.
- 2) If EC tubes are negative after  $24 \pm 3$  hours, report out as  $<2$  Fecal Coliforms/100 mL.
- 3) If any Brilliant Green or EC tubes are positive after  $48 \pm 3$  hours, proceed as follows to determine the MPN counts:
  - a) Record results of tubes as they actually occur, and in the proper sequence within each dilution. See Figure 2 for an example of the actual reading, interpretation, and recording of results.
  - b) Count separately the number of positive tubes within each of the three dilutions. This will give a three digit number. Sample A in Figure 2 would be 3-1-1 for Total Coliforms, and 0-0-0 for Fecal Coliforms.
  - c) Find the sequences on the MPN chart in the current edition of Standard Methods. For shellfish growing water use table from "Recommended Procedures for the Examination of

Shellfish." See Supplemental Information.

- d) After determining the correct sequence, look to the right side of the column for a MPN number.
- e) The correct interpretation of the MPN count for Sample A is 14 Total Coliforms per 100 mL and <2 Fecal Coliforms per 100 mL.
- f) Round using bankers rounding and report to the whole number.

**Instrument and Media:**

Water Bath: Precision Circulator

Difco Lauryl Tryptose Broth Ref# 224150

Difco Brilliant Green Bile Broth 2% Ref# 273000

Difco Ec Medium Ref# 231420

Written by: David Holland

Date: July 1999

Reviewed Sept 2003

Revised June 2014

Approved by: \_\_\_\_\_  
Laboratory Director's Signature



## **Anionic Surfactants as MBAS**

### Extraction & Colorimetric Method

#### **1. Scope and Application**

This method is applicable to the measurement of methylene blue active substances (MBAS) in drinking waters, surface waters, domestic and industrial wastes. It is not applicable to measurements of surface-type materials in saline waters.

#### **2. Detection Limit:** 0.05mg/L

#### **3. Precision and Bias**

A synthetic sample containing 270 ug LAS/L in DI was analyzed in 110 laboratories with a relative deviation of 14.8 % and a relative error of 10.6%.

#### **4. Working Range:** 0.05 – 100 mg/L LAS

#### **5. Summary of Method**

The dye, methylene blue, in aqueous solution reacts with anionic-type surface-active materials to form a blue colored salt. The salt is extractable with chloroform and the intensity of color produced is proportional to the concentration of MBAS.

#### **6. Sample Collection, Preservation and Holding Times:**

MBAS samples are collected in 500 mL plastic or glass collection bottles. Samples have to be refrigerated upon arrival and analysis should to be performed within 48 hrs of collection.

#### **7. Comments**

##### **7.1 Interferences**

- Positive interferences result from all other MBAS species present. If a direct measurement of any individual MBAS species, such as LAS, is sought, all others interfere.
- Negative interferences can result from the presence of cationic surfactants.
- Particulate matter may give negative interference through adsorption of MBAS.
- Sulfides may react with methylene blue to form a colorless reduction product, making the analysis impossible. Eliminate this interference by prior oxidation with hydrogen peroxide.

##### **7.2 Helpful Hints:**

- Clean the separatory funnels with 1+1 HCL after each use to remove methylene blue dye.

#### **8. Safety Issues**

Chloroform is highly toxic when inhaled. It is a suspect carcinogen. Take appropriate precautions against inhalation and skin exposure, analysis must be completed in the hood.

#### **9. Instrumentation/Equipment:**

- Separatory funnels, 125 ml
- UV-1800 Spectrophotometer (Serial no. A11455150458)
- Glass Wool
- 50 ml Graduated Cylinder

#### **10. Reagents and Standards:**

- Stock LAS Solution, 1000 mg/L (Absolute Standards)
- Standard LAS Solution  
LCSL 10 mg/L - Dilute 1.00 mL of Stock LAS Solution to 100 mL  
LCS 50 mg/L - Dilute 5.00 mL of Stock LAS Solution to 100 mL
- Methylene Blue Reagent
- MBAS Wash Solution
- Chloroform

**11. Procedure:**

- a) Select a sample volume on the basis of expected MBAS concentration.
- b) Add sample to separatory funnel and bring to 100mL with DI.
- c) Add 10 mL of chloroform and 20-25 mL methylene blue reagent. Rock funnel vigorously for 1 minute and let phases separate.
- d) Draw off chloroform into a second separatory funnel. Repeat extraction procedure two additional times, using 10 ml of chloroform each time. If blue color in water phase disappears, discard and repeat, using a smaller sample.
- e) Combine all chloroform extracts in the second separatory funnel. Add 25 - 50 mL of wash solution and shake for 30 sec. Let settle, swirl, and draw off chloroform layer through a funnel containing a plug of glass wool into a 50-mL volumetric cylinder.
- f) Rinse glass wool with chloroform and bring to volume to 50 mL.
- g) Analyze with UV-1800 Spectrophotometer at a wavelength of 652 nm.
- h) Repeat for all samples

**12. Q.A./Q.C. Requirements:**

**12.1 Q.C. Analysis**

- a) Analyze a blank solution with each set of samples daily.
- b) Analyze the LCS and the LCSL daily with each set of samples.
  - i) The LCS is prepared by placing 0.5 mL of the 50mg/L LAS solution in a separatory funnel with 100 mL of DI water, the result should be 0.250mg/L.
  - ii) The LCSL is prepared by placing 0.5 mL of the 10mg/L LAS solution in a separatory funnel with 100 mL of DI water, the result should be 0.05mg/L.
- c) A matrix spike and matrix spike duplicate should also be completed with each set of samples.
- d) Analyze each 10<sup>th</sup> sample in duplicate and spike with LAS standard solution.

**12.2 Acceptance Criteria**

Recoveries for the LCS, LCSL, and the sample spike must fall between 80 to 120 %. The percent difference for the duplicate sample analysis must be less than 10%.

**13. Trouble Shooting:**

- a) If emulsion forms gently shake the separatory funnel until the emulsion clears. If the emulsion does not clear restart the analysis and gently shake the funnel instead of vigorously shaking it.
  - ii) Emulsions are common with samples that are high in salt content and samples that have dirt and other particles present.

**14. Calculations**

Adjust for dilution factors if necessary.

**15. Reporting**

**15.1 Reporting Units:** mg/L LAS

**15.2 Reporting Limits:** 0.05 mg/L

**15.3 Significant Figures and Reporting Values Below Detection Limit:**

Results are reported to two significant numbers. Values below 0.05 mg/L are reported as "ND" (not detected).

**16. Reference/Method Source**

- 1) Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> Edition, 1992.
- 2) Instruction Manual, Cyanide Ion Electrode, Model 94-06, Orion Research
- 3) Instruction Manual, Model 90-01 Single junction Reference Electrode, Orion Research

Written by: Sigrid Weidner-Holland

Revised by: Hayden Maccagno

Approved by: \_\_\_\_\_

## ***Heterotrophic Plate Count***

### SM 9215 B Pour Plate Method

#### **1. Scope and Application**

The heterotrophic plate count (HPC), formerly known as the standard plate count, is a procedure for estimating the number of live heterotrophic bacteria in water and measuring changes during water treatment and distribution or in swimming pools. Colonies may arise from pairs, chains, clusters, or single cells, all of which are included in the term “colony-forming units” (CFU).

#### **2. Detection Limits:** 1 CFU/mL

#### **3. Precision and Bias:** Not applicable

#### **4. Working Range:** 0 to unlimited

#### **5. Summary of Method**

The pour plate method is simple to perform and can accommodate volumes of sample or diluted sample ranging from 0.1 to 2.0 mL. The colonies produced are relatively small and compact, showing less tendency to encroach on each other than those produced by surface growth. On the other hand, submerged colonies often are slower growing, are difficult to transfer, and are not described in published studies. A thermostatically controlled water bath is essential for tempering the agar, but even so, significant heat shock from the transient exposure of the sample to 45 to 46 °C agar may occur.

#### **6. Sample Collection, Preservation and Holding Times:**

Collect samples for heterotrophic plate count in clean, sterile bottles or presterilized plastic bags. Add sodium thiosulfate to containers intended for the collection of water having residual chlorine or other halogen.

Initiate analysis as soon as possible after collection to minimize changes in bacterial population. The recommended maximum elapsed time between collection and examination of sample is 8 h (maximum transit time 6 h, maximum processing time 2 h). When analysis cannot begin within 8 h, maintain sample at a temperature below 4°C but do not freeze. Do not let maximum elapsed time between collection and analysis exceed 24 h.

Hold or transport bottled water samples obtained from retail outlets unrefrigerated under the same ambient conditions as those found in the retail store until tested. Examine freshly bottled samples (less than 48 h old) within 6 h of collection if unrefrigerated and within 24 hours if refrigerated.

#### **7. Comments**

##### **7.1 Interferences:** Chlorine Residual – Dechlorinate after sampling

##### **7.2 Helpful Hints**

Use a sterile pipet for initial and subsequent transfers from each container. If pipet becomes contaminated, replace with a sterile pipet. Use a separate pipet for transfers from each different dilution

When discharging sample portion, hold pipet at an angle of about 45° with tip touching bottom of petri dish or inside neck of dilution bottle. Lift cover of petri dish just high enough to insert pipet. Touch tip once against a dry spot on the petri dish bottom. Remove pipet without retouching it to the dish.

#### **8. Safety Issues:** Standard safe laboratory practices apply.

#### **9. Instrumentation/Equipment:**

##### **9.1 Operating Instructions**

see Shel Lab Incubator Manual

see Tuttnauer Autoclave Manual

## 9.2 Scheduled Preventative Maintenance

Replace the water in the autoclave on a weekly basis.

## 10. Reagents and Standards

### a) Plate Count Agar (Difco Cat. 0479-15.)

Suspend 23.5 grams of the dehydrated agar in 1 L DI water and boil to dissolve completely.

Dispense 12 mL of plate count agar into loosely capped culture tubes. Sterilize at 121-124 °C for 15 minutes. The pH should be 7.0 +/- 0.2 after autoclaving. Let cool, tighten cap and store in the refrigerator.

### Melting Plate Count Agar

Melt sterile solid agar medium in capped culture tube in boiling water, transfer melted agar in culture tube to a water bath between 44 to 46 °C.

## 11. Procedure:

### 11.1 Sample Preparation

Mark each plate with sample number, dilution, date, and any other necessary information before examination. Prepare at least duplicate plates for each volume of sample or dilution examined.

Use glass (65 cm<sup>2</sup>) or disposable plastic (57 cm<sup>2</sup>) petri dishes.

Thoroughly mix all samples or dilutions by rapidly making about 25 complete up-and-down (or back-and-forth) movements.

### 11.2 Instrument Operating Conditions

Incubator set to 35 °C with an incubation time of 48 h. The incubation time for bottled water is 72 hours.

Use an approved counting aid, such as the Quebec colony counter, or any other counter provided that it gives equivalent magnification and illumination.

### 11.3 Calibration

Not applicable.

### 11.4 Analysis

a) Select sample dilutions that will yield 30 to 300 colonies/plate.

b) Transfer sample with a sterile pipet to petri-dish. Usually 1 and 0.1 for potable water samples.

c) Pour culture medium (maintained at 44 to 46 °C) by gently lifting cover just enough to pour and mix carefully. Do not let more than 20 min elapse between starting pipetting and pouring plates.

d) Let medium solidify, invert plates and place in incubator.

e) Incubate samples for 48 hours (bottled water for 72 hours).

### Counting & Reporting Rules

Count all colonies on selected plates promptly after incubation. If counting must be delayed temporarily, store plates at 5 to 10 °C for no more than 24 h, but avoid this as a routine practice. In preparing plates, plant sample volumes that give from 30 to 300 colonies/plate. The aim is to have at least one dilution giving colony counts between these limits, except as provided below. For most potable water samples, plates suitable for counting will be obtained by plating 1 mL and 0.1 mL undiluted sample and 1 mL of the 10<sup>-2</sup> dilution.

Do not plant more than 2.0 mL of sample; therefore when the total number of colonies developing from 2.0 mL is less than 30, disregard the rule above and record result observed. With this exception consider only plates having 30 to 300 colonies in determining the plate count. If there is no plate with 30 to 300 colonies, and one or more plates have more than 300 colonies, use the plate(s) having a count nearest 300 colonies. Compute the count by multiplying average count per plate by the reciprocal of the dilution used and report as estimated CFU per mL.

## **12. Q.A./Q.C. Requirements:**

### **12.1 Q.C. Analysis**

Record results of sterility controls on the report for each lot of samples.

Prepare a replicate plate for each sample lot.

Test each lot of plate count agar for suitability.

Check sterility of medium and dilution water blanks by pouring control plates for each series of samples. If contamination is present, prepare additional controls to determine contamination of plates, pipets, and room air.

### **12.2 Acceptance Criteria**

Plate Count results are acceptable if sterility controls are negative and suitability is determined.

## **13. Calculations**

Compute bacterial count per mL by multiplying average number of colonies per plate by the reciprocal of the dilution used.

< 10 colonies/cm<sup>2</sup>: count colonies in 13 representative squares, multiply sum by 5.

>10 colonies/cm<sup>2</sup>: count 4 representative squares and multiple the sum by 57 for disposable plates and by 65 for glass plates.

## **14. Reporting**

### **14.1 Reporting Units**

Report counts as CFU/mL or estimated CFU/mL if > 300 colonies per plate.

Include in the report the method used, incubation temperature, time and medium

Example: CFU/mL, pour plate method, 5°C/48 h, plate count agar.

### **14.2 Reporting Limits**

If plates from all dilutions of any sample have no colonies, report the count as less than one (< 1) times the reciprocal of the corresponding lowest dilution. For example, if no colonies develop on the 1:100 dilution, report the count as less than 100 (< 100) estimated CFU/mL.

When bacterial counts on crowded plates are greater than 100 colonies/cm<sup>2</sup>, report results as greater than (>) 6500 times the reciprocal of the highest dilution plated for glass plates or greater then (>) 5700 times the reciprocal for plastic plates. Report as estimated colony-forming units per mL.

### **14.3 Significant Figures and Reporting Values Below Detection Limit**

Round off counts to two significant figures when converting to colony-forming units.

## **15. Reference/Method Source**

Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> Edition, 1992. 9215B

Operation Manual for Table Autoclave Electronic Models EZ10, Tuttnauer.

Written by: David Holland

Approved by: \_\_\_\_\_  
Laboratory Director

## **Orthophosphate/Ascorbic acid Method**

### **Scope and Application**

This method covers the determination of orthophosphate in drinking water, surface and saline waters, domestic and industrial waters.

### **Principle:**

Orthophosphate or inorganic phosphorus it is known to be reactive . Reactive phosphorus in presence of ascorbic acid (color reagent) is reduce to an intense blue color. The blue color is proportional to the total concentration of phosphorus. The developed color is measured at 890 nm on spectrophotometer.

### **Detection limits:**

The detection level for reporting is 0.03 mg/L Phosphorus.

### **Working range:**

The working range is 0.03-2.0 mg/L P. This range can be extended if the sample is diluted.

### **Acceptance Criteria:**

Laboratory Control Standard Low (LCSL) of 0.03 mg/L: 50- 150%

Laboratory Control Standard (LCS) 0.30 mg/L: 90-110%

Second-source solution (QCS) 0.30 mg/L: 80-120%

Matrix spike recovery 1mg/L: 70-130%

Matrix Spike Duplicate: <10% RSD

### **Interferences:**

- Arsenates react with the color reagent to produce a blue color. Concentration as low as 0.1 mg AS/L interfere with the phosphorus determination.
- Chrome 6 and NO<sub>2</sub>- are negative interferences.
- Highly turbid samples may interfere. A correction for turbidity should be analyzed by measuring a sample without the color reagent and after the reagent addition.
- The salt error for samples ranging from 5-20% salt content was found to be less than 1%
- Sample turbidity must be removed by filtration prior to analysis.

### **Preservation and Holding Times:**

- Samples should be collected in plastic or glass bottles and immediately filter (*Filter 0.45  $\mu$ m* ).
- Samples should be analyzed as soon as possible after collection. If immediate analysis is not possible, immediately filter and keep samples at 6oC for a maximum of 48 hours.
- Let temperature to increase at room temperature before analysis.

### **Instrumentation and Equipment:**

- UV-1800 Spectrophotometer from Shimadzu (Serial no. A11455150458)
- Glass 1 cm cuvette
- Filter 0.45  $\mu\text{m}$  from Thermo Scientific (Cat no. F2500-1). Only for samples that for dissolved orthophosphate
- Sample Cell 10 mL

#### **Safety Precautions:**

Phos Ver 3, contains Sodium Molybdate that can cause slight irritation with eye or skin contact. Wear safety glasses, glove and lab coat when using this powder.

#### **Reagents and Standards:**

- PhosVer3 Phosphate Reagent (Permachem Reagent) pillow packets (Hach cat#32106069 100/pack, cat#2106046 50/pack)
- Absolute Inorganic Nutrients 1000ug/mL (cat#54153)
- Absolute 1000ug/mL Phosphate as P (cat#54105)

#### **Calibration Standards**

Dilute the 1000  $\mu\text{g/mL}$  Phosphate as P stock solution to 100  $\mu\text{g/mL}$  P by adding 1.0 mL stock solution to 9.0 mL deionized water. Use this 100  $\mu\text{g/mL}$  P solution to make the calibration as listed below

| CAL Concentration (mg/L) | Volume of 100 $\mu\text{g/mL}$ Solution (mL) | Final Volume (mL) |
|--------------------------|----------------------------------------------|-------------------|
| 0.03                     | 0.030                                        | 100               |
| 0.10                     | 0.100                                        | 100               |
| 0.30                     | 0.300                                        | 100               |
| 0.50                     | 0.500                                        | 100               |
| 1.00                     | 1.000                                        | 100               |

#### **Notes:**

- Prepare a calibration per batch of PhosVer3 Phosphate Reagent.
- For Analyses use 10 mL of each calibration standard into sample cell.

#### **Quality Control:**

- **Initial Calibration Blank (ICVB):**
  - A deionized water is to be analyze at the beginning of each batch, every ten samples and at the end of each batch.
- **Laboratory Control Standard Low(LCSL):**
  - A solution containing the same concentration as the lowest calibration solution is measured at the beginning of the batch.
- **Instrument Calibration Verification (ICV):**

- A mid range standard should be analyzed at the beginning of each batch, every 10 samples and at the end of each batch. This is to verify if there any variation in the instrument. The ICV should not be more than 25 % of difference of the first ICV analyzed.

**-Second Source Standard:**

- Use Absolute Inorganic Nutrients 100 ug/ mL
- A mid-range solution made from a source that is different from that used to make the calibration is to be measured at least quarterly and every time that new calibration standards are prepared.

**Matrix Spikes:**

- A matrix spike and a matrix spike duplicate should be analyzed every ten samples or at least once per batch. If the matrix spikes do not meet the acceptance criteria, there may be matrix interference that warrants investigation.

**Analysis Procedure:**

1. Starting with the initial calibration blank, add 1 PhosVer3 packet to the cell. Immediately close the sample cell. Shake vigorously for 20-30 seconds. Not all of the reagent will dissolve.
2. Allow the color-developing reaction to occur for 3 minutes and then read the absorbance in the 2 cm cuvette. Press "Read Std" or "Read Unk" at the bottom of the screen (or F9) to record data.
3. Repeat steps 1-2 for each calibration standard and then each sample.

**Instrument Setup Procedure:**

1. Turn on the spectrophotometer. Do not open the cover while it initializes.
2. Press Enter when prompted for a password.
3. Open the UV Probe software on the computer.
4. Select PC Control on the instrument (F4). Now all operations are controlled from the UV Probe Software.
5. Select Connect at the bottom of the screen.
6. Open the phosphorus standard: File/Open/Data/Phosphorus.std
7. Fill the standard table with your calibration standards name and concentrations, including the blank. Right click on the graph, select properties and mark the option of correlation coefficient square.
8. Fill the sample table with your samples IDs
9. To start with the instrument calibration, make active the standard table by clicking anywhere on the table.
10. Measure the absorbance of each calibration standard.
11. The linear r-value must be greater than 0.995.
12. If is greater than 0.995, save the calibration and proceed with the sample and control measurements.

**Reporting:**

1. Report results as mg/L phosphate, report up to three significant figures.

2. Report only values that fall between lowest and highest standard. Dilute and reanalyze samples as necessary. Samples below the lowest standard are report as none detect.

**Note:** Data needs Lead Chemist approval before entering into the system.

**Calculations:**

1. QCS, LCS and LCSL %Recovery:  $(\text{Measured Value}/\text{Theoretical Value}) \times 100\%$
2. MS %Recovery:  $[(\text{Spiked Sample Measured Value} - \text{Sample Measured Value}) / \text{Theoretical Value}] \times 100\%$
3. MS %Difference:  $[|\text{MS} - \text{MSD}| / \text{Average (MS \& MSD)}] \times 100\%$

**References:**

Hach Method 8048 (DOC 316.53.01119)

Standard Methods 4500-P E; 20<sup>st</sup> Edition

Method 365.1 EPA

| Writen by: Lilian Reyes      Title: Lab Analyst      Date: 01/27/15

## DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY (EPA METHOD 300.0)

Instrument Dionex ICS 2000

### PRINCIPLE

This method determines the following inorganic anions: fluoride, chloride, nitrite, nitrate, bromide, sulfate and phosphate. A small volume of sample (approx. 3 ml) is loaded into the ion chromatograph. The injection valve injects 10 ul of the sample into the flow of eluent. The eluent (KOH) flows continuously through the I.C. and serves as a carrier for the 10 ul of sample.

The anions of interest are separated and their concentrations are measured. The major parts of the system are the guard column, the separator column, the eluent generator, the suppressor, and the conductivity detector. The guard column protects the separator column which separates the anions based on their size and charge. The function of the suppressor is to chemically reduce the background conductivity of the electrolytes in the eluent and to convert the sample anions into a more conductive form. The detector then detects the conductivity of the solution which varies depending on the concentrations of the anions (higher conductivity indicates a greater concentration of the anion).

### SAMPLE CRITERIA

The holding times for drinking water samples are as follows:

|                              |          |
|------------------------------|----------|
| Cl <sup>-</sup>              | 28 days  |
| NO <sub>2</sub> <sup>-</sup> | 48 hours |
| NO <sub>3</sub> <sup>-</sup> | 48 hours |
| SO <sub>4</sub> <sup>-</sup> | 28 days  |
| Br <sup>-</sup>              | 28 days  |
| PO <sub>4</sub> <sup>-</sup> | 48 hours |
| F <sup>-</sup>               | 28 days  |

Samples submitted for I.C. testing routinely should be run within 48 hours of collection. If testing needs to be delayed the sample can be preserved with sulfuric acid; preserved samples can be held for up to 28 days and the nitrate results reported as combined Nitrate/Nitrite. Any samples not tested within specified holding times should be identified on the worksheet.

Samples bottles dedicated for IC testing only are placed in the area by the IC bench. As soon as a sample is setup, place sample in the refrigerator. After analysis is reported remove the samples from the refrigerator and store them for 2 months. After 2 months, the containers should be emptied and discarded. Nondedicated samples (i.e. those also submitted for additional testing) are kept in the refrigerator.

## QUALITY ASSURANCE

**Operator competency** - Ion chromatography may be performed only by analysts who have been trained and who have demonstrated competency with the procedure. One check consists of preparing the calibration standards and calibrating the I.C. An r-value of 0.995 or higher in the linear fit type must be attained for each analyte of interest. Another way to demonstrate competence is to run a minimum of four replicate analyses of an independently prepared sample. Each analyte of interest in the sample should have a known concentration between 5 and 50 times the MDL. Acceptable recovery is 95-105% with < 10% RSD. Each operator must perform MDL study.

**Blank** – An instrument reagent blank (ICVB) consisting of DI water should be included at the beginning of each run. The results for the blank must be below the MDL for each analyte.

**Control standard(s)** - Controls representing two concentration levels for each analyte, the Instrument Calibration Check (ICV), Continuing Calibration Verification (CCV) and the Instrument Calibration Verification Low (ICVL) must be analyzed as described below. The source of the analytes used to prepare these controls must be different from the source used to prepare the calibration standards. A 50 ml stock solution of the ICV is prepared using volumetric glassware with the following concentrations: F: 2.00 mg/L; Cl: 20.0 mg/L; NO<sub>2</sub>-N: 2.00 mg/L; NO<sub>3</sub>-N: 2.00 mg/L; Br: 2.00 mg/L; PO<sub>4</sub>-P: 2.00 mg/L and SO<sub>4</sub>: 20.0 mg/L. These are prepared using 1000 ug/L standard stock solution (10000ug/L for SO<sub>4</sub> and Cl). Use this prepared standard undiluted at the beginning of the run and after every tenth sample. For each run sequence prepare an ICVL solution from the ICV as follows: Using a 1 ml pipette add 0.5 ml of ICV to an empty sample vial. Add 4.5 ml of DI water to create a 1:10 dilution. Acceptance range of ICV/CCV is 90-110%. Acceptance range for the ICVL is 50-150%.

**Duplicate spikes (MS and MSD)** – Duplicate spikes should be run after every tenth sample. The spike should not be less than four times the MDL, and it should increase each anion concentration by more than 25% of the background value. A suitable spike can be prepared by adding one part ICV to 1 part sample and 2 parts DI water. The average percent recovery for each anion should be between 80 and 120%. The duplicate spikes should be within 10% of each other. Record average percent recovery of spikes and duplicate percent difference on worksheets. Note: if the concentration of the spike is less than 25% of the background concentration, the spike recovery should not be calculated.

**Corrective Action:** If any of the above control criteria are not met, do not report sample results until the problem has been resolved. Verify dilutions and other method parameters, if necessary, recalibrate instrument and re-integrate QC. If problem persists, perform column cleanup or replace column.

**External controls & chart analysis** - In addition to the control standards tested with each batch of samples, an external reference standard (i.e. SPEX IC standard) should be tested on a quarterly basis. Furthermore, control values should be entered into the QC chart program and data reviewed for potential problems.

## CALIBRATION PROCEDURE:

Calibration should be performed whenever: 1) controls are out of range; 2) the KOH eluent cartridge is changed; 3) when a column, suppressor or detector is changed. Make sure to run an LCS control prior to calibration whenever there is a change that may affect retention times; modify retention times and timed events if necessary.

1. Four standards should be prepared with the following analyte concentrations (numbers are given in mg/l):

|     | Std 1 | Std 2 | Std 3 | Std 4 |
|-----|-------|-------|-------|-------|
| F   | 0.1   | 0.5   | 1.0   | 5.0   |
| Br  | 0.1   | 0.5   | 1.0   | 5.0   |
| PO4 | 0.1   | 0.5   | 1.0   | 2.0   |
| NO2 | 0.1   | 0.5   | 1.0   | 4.0   |
| NO3 | 0.1   | 1.0   | 10.0  | 50.0  |
| SO4 | 1.0   | 10.0  | 100.0 | 500.0 |
| Cl  | 1.0   | 10.0  | 100.0 | 500.0 |

2. Before the calibration run begins run a blank sample to ensure the baseline is consistent.
3. Run calibration standards beginning with the first standard (the lowest analyte concentrations).
  - a) See section on routine testing for instructions on system startup and setting up a sequence.
4. After all four calibration standards have been run, check the calibration curve.
  - a) Go to Chromeleon Data sequence by clicking on the far left tab for "DATA." In the Sequence label all calibration samples as "calibration standard" and apply the appropriate level to each. Double click on a calibration standard to open "Chromeleon Studio" to review the curve.
  - b) Click on the first analyte and then click "calibration plot" and view the linear calibration plot for each analyte.
  - c) Record the  $r^2$  values and retention times on worksheet. The  $r^2$  value should be 0.995 or higher for each anion. The  $r^2$  value can be found in the report designer under the calibration tab. See the principal analyst if the result is a lesser value.
  - d) Save all changes to the sequence.

### **PREPARE MDL STUDY**

The Method Detection Limit is the lowest concentration of a substance that can be identified with accuracy and confidence by a certain method or analysis.

- 1) Prepare a 1:10 dilution of the ICV standard.
- 2) Make at least two replicates of this dilution and run through the Ion Chromatograph using the method it was calibrated with. Repeat this on 3 non-consecutive days (adding one more replicate of the ICV on one day) resulting in a total of 7 results.
- 3) Collect data and calculate the standard deviation for the replicates. Multiply the standard deviation values by the correct student T value at the 99% confidence level. These values and more information about the MDL study can be found in appendix B of 40 CFR Part 136. The calculated number will be the Method Detection Limit.

### **SAMPLE PREPARATION**

**All Water Samples are to be filtered through 0.45 um membrane filters before injection:**

- 1) Rinse the syringe with the sample water. Then fill syringe with at least 3 ml of sample water.
- 2) Filter a minimum of 3 ml of sample through the 0.45 membrane into a sample vial.
- 3) If applicable use an appropriately sized pipette to create a dilution of the sample in a sample vial. Record the dilution in Chromeleon when creating the sequence.
- 4) Place sample in autosampler rack. The order in the rack must match that on the sequence.
- 5) Include a CCVB, CCV and MS/MSD for every 10<sup>th</sup> sample.

### **SYSTEM START-UP:**

- 1) Ensure the eluent bottle is full (1/2 liter will last over 8 hours). If it is not full fill it with DI water only.
- 2) Open the Chromeleon software. Click on "Instrument" tab.
- 3) Open the face of the ICS 2000, and turn knob to open the waste valve.
- 4) On the Chromeleon Instrument window click "Prime." Click "OK" at the top of the screen when you check that the waste valve is open.
- 5) Let instrument prime for at least 2 minutes. Click "Pump Off," and turn knob to close the waste valve.
- 6) Click "Pump On," set suppressor to 80 mA, the eluent generator to 32 mmol, and the column heater to 30 C. Turn the CRTC to the on position.
- 7) The system should equilibrate for at least 1 hour before proceeding.

### **CREATE SEQUENCE**

- 1) From Chromeleon Instrument panel select the "Data" tab.
- 2) Click "create" from the top of the screen.
- 3) Select the instrument method (Iso 32mmol, 30 deg, 80mA) and the processing method (isocraticmethodfasttest). Save the sequence according to date.
- 4) Copy and paste the newest calibration standards (usually from previous run).
- 5) Enter the list of samples into the new sequence in the order they are in the autosampler. Include an "end" method (Shutdown) at the end of the run to shutdown the instrument.
- 6) Load the samples into the autosampler. Push the "Hold/Run" button on the autosampler.

- 7) Click “resume” at the top of the sequence screen. Record pressure, conductivity, date of run, analyst and date ICV was made in log.
- 8) Review and record ICV and continuous calibration verifications (CCV) values as they are run. If the readings are not within the range notify principle analyst.

### **REPORTING RESULTS**

- 1) When the run is complete the analyst performing the run is responsible for recording and reporting results. To retrieve results go to the chromatogram window in Chromeleon Studio. The analyte peaks for every sample should be examined to insure they have been correctly integrated by the Chromeleon software. If the software has made an error in peak integration the chromatogram must be manually manipulated to provide accurate results.
  - a) Record the ICV, CCV, and MS/MSD values for all analytes on the sequence’s worksheet. Ensure they are all within proper QC recovery ranges.
  - b) Any samples with readings above the calibration range need to be diluted and repeated in the next run. List these samples on a new worksheet with the appropriate dilution.
- 2) Do not report results if control/spike values do not fall within limits (refer to section on quality control) if a valid reason for the error cannot be given. If controls, spikes, etc. are out of range, notify the principal analyst. If controls are within limits, report results. The printouts for the QC data are placed in the binder after review.
- 3) Report NO<sub>3</sub>-N, PO<sub>4</sub>, NO<sub>2</sub>, Br, F to one decimal place and NO<sub>3</sub>, Cl and SO<sub>4</sub> to the whole number.

### **PREVENTIVE MAINTENANCE:**

- 1) The column needs to be cleaned when retention times decrease. See supplemental procedures for instructions. Log, date and initial preventative maintenance chart.
- 2) Replace the bed supports on guard column whenever other methods of troubleshooting do not solve any problems.
- 3) Maintain the following spare parts. These items are considered consumables:
  - a) Column (part no. AS18)
  - b) Guard column (part no. AG18)
  - c) SRS suppressor (064554)
  - d) Conductivity cell (057985)

### **Instrument:**

Dionex ICS-2000 Serial number: 08121014

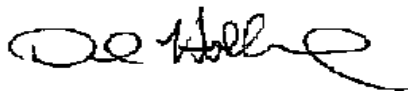
Conductivity Cell Serial number: 08120896, Cell Constant 152.06

**REFERENCES:**

- 1) ICS 2000 Ion Chromatograph Operator's Manual, Dionex Corporation
- 2) Methods for the Determination of Inorganic Substances in Environmental Samples, Method Number 300.0, Determination of Inorganic Anions by Ion Chromatography, John D. Pfaff, U.S. Environmental Protection Agency, 1993.
- 3) Standard Methods, 18th Edition, p. 1-4.

Written by: David Holland (Laboratory Director)  
Update by: Hayden Maccagno  
Date: 12/6/2016

Approved by:

A handwritten signature in black ink, appearing to read "De Holland", written over a horizontal line.

(Lab Director's signature)

## MDL Study

| CONC    | Date       | NO3    | %Rec (+/- 50%) | Date       | Br     | %Rec (+/- 50%) | Date       | NO3-N  | %Rec (+/- 50%) | Date       | NO2    | %Rec (+/- 50%) |
|---------|------------|--------|----------------|------------|--------|----------------|------------|--------|----------------|------------|--------|----------------|
| 0.01    | 20150205   | 0.009  | 93.1           | 20150309   | 0.006  | 61.0           | 20150309   | 0.009  | 87.0           | 20150309   | 0.013  | 126.0          |
| 0.01    | 20150205   | 0.008  | 83.0           | 20150309   | 0.007  | 72.0           | 20150309   | 0.010  | 95.0           | 20150309   | 0.013  | 130.0          |
| 0.01    | 20150205   | 0.008  | 83.7           | 20150309   | 0.006  | 61.0           | 20150309   | 0.007  | 72.0           | 20150304   | 0.011  | 108.4          |
| 0.01    | 20150304   | 0.011  | 114.4          | 20150304   | 0.006  | 55.0           | 20150304   | 0.011  | 114.4          | 20150304   | 0.011  | 112.8          |
| 0.01    | 20150304   | 0.009  | 86.4           | 20150304   | 0.005  | 50.0           | 20150304   | 0.009  | 86.4           | 20150304   | 0.010  | 98.7           |
| 0.01    | 20150303   | 0.010  | 101.6          | 20150304   | 0.006  | 55.0           | 20150305   | 0.011  | 110.0          | 20150305   | 0.014  | 142.0          |
| 0.01    | 20150303   | 0.008  | 81.8           | 20150305   | 0.008  | 80.0           | 20150305   | 0.009  | 89.0           | 20150205   | 0.013  | 131.7          |
| StDev   |            | 0.0012 |                |            | 0.0011 |                |            | 0.0015 |                |            | 0.0015 |                |
| Average |            | 0.01   |                |            | 0.01   |                |            | 0.01   |                |            | 0.01   |                |
| %RSD    | 10%-20%    | 13.2   |                | 10%-20%    | 17.0   |                | 10%-20%    | 15.7   |                | 10%-20%    | 12.5   |                |
| MDL     | StDev*3.14 | 0.004  | 0.001-0.01     | StDev*3.14 | 0.003  | 0.001-0.01     | StDev*3.14 | 0.005  | 0.001-0.01     | StDev*3.14 | 0.005  | 0.001-0.01     |
| Cal PQL | 10/4*MDL   | 0.010  |                | 10/4*MDL   | 0.008  |                | 10/4*MDL   | 0.011  |                | 10/4*MDL   | 0.012  |                |
| PQL     |            |        |                |            |        |                |            |        |                |            |        |                |

| CONC    | Date       | Cl      | %Rec (+/- 50%) | Date       | SO4    | %Rec (+/- 50%) | Date       | PO4    | %Rec (+/- 50%) |
|---------|------------|---------|----------------|------------|--------|----------------|------------|--------|----------------|
| 0.1     | 20150515   | 0.1107  | 110.7          | 20150309   | 0.1175 | 117.5          | 20141022   | 0.1271 | 127.1          |
| 0.1     | 20150515   | 0.1195  | 119.5          | 20150309   | 0.1127 | 112.7          | 20141022   | 0.1078 | 107.8          |
| 0.1     | 20150515   | 0.1015  | 101.5          | 20150309   | 0.1098 | 109.8          | 20141022   | 0.1042 | 104.2          |
| 0.1     | 20150515   | 0.1025  | 102.5          | 20150304   | 0.0935 | 93.5           | 20141024   | 0.1009 | 100.9          |
| 0.1     | 20150309   | 0.1137  | 113.7          | 20150303   | 0.1268 | 126.8          | 20141024   | 0.0993 | 99.3           |
| 0.1     | 20150304   | 0.14388 | 143.9          | 20150304   | 0.0935 | 93.5           | 20141028   | 0.0913 | 91.3           |
| 0.1     | 20150305   | 0.1457  | 145.7          | 20150304   | 0.097  | 97.0           | 20141028   | 0.1014 | 101.4          |
| StDev   |            | 0.018   |                |            | 0.013  |                |            | 0.011  |                |
| Average |            | 0.12    |                |            | 0.11   |                |            | 0.10   |                |
| %RSD    | 10%-20%    | 15.3    |                | 10%-20%    | 12.1   |                | 10%-20%    | 10.7   |                |
| MDL     | StDev*3.14 | 0.06    | (0.01-0.1)     | StDev*3.14 | 0.04   | (0.01-0.1)     | StDev*3.14 | 0.04   | (0.01-0.1)     |
| Cal PQL | 10/4*MDL   | 0.143   |                | 10/4*MDL   | 0.102  |                | 10/4*MDL   | 0.088  |                |
| PQL     |            |         |                |            |        |                |            |        |                |

| CONC    | Date       | F       | %Rec (+/- 50%) |
|---------|------------|---------|----------------|
| 0.05    | 20150520   | 0.0585  | 117.0          |
| 0.05    | 20150520   | 0.0581  | 116.2          |
| 0.05    | 20150520   | 0.058   | 116.0          |
| 0.05    | 20150521   | 0.0724  | 144.8          |
| 0.05    | 20150521   | 0.07334 | 146.7          |
| 0.05    | 20150521   | 0.07437 | 148.7          |
| 0.05    | 20150528   | 0.0579  | 115.8          |
| StDev   |            | 0.008   |                |
| Average |            | 0.06    |                |
| %RSD    | 10%-20%    | 12.6    |                |
| MDL     | StDev*3.14 | 0.03    | (0.005-0.05)   |
| Cal PQL | 10/4*MDL   | 0.064   |                |
| PQL     |            |         |                |

Perkin Elmer Elan 6100  
Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)

## Principle:

In the multi-element determination of trace elements by ICP-MS, sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where the energy transfer processes causes desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier detector and the ion information processed by a data handling system.

## Sample Collection/Handling:

Use metal free collection bottles to collect samples. Collect 250mL of sample. Smaller volumes (not less than 50 ml) can be used if necessary. On collection, acidify samples to pH <2 with 1:1 nitric acid, usually ~2mL per 125mL. If samples are not acidified at time of collection, they should be preserved within two weeks of collection or upon receipt in the lab and then held for minimum of 16 hours before analysis. [40 CFR 141.23(K)]. Preserved samples can be held up to 6 months after collection.

## Sample Preparation:

Samples containing particulate or organic material require pretreatment before analysis. Drinking water samples with a turbidity <1 NTU may be analyzed directly. Digest wastewater samples and samples with a turbidity >1 NTU. For determination of dissolved metals, filter samples with a 0.45µm filter.

## Digestion Procedure for total metals:

Samples with turbidity >1 NTU and wastewater samples must be digested with nitric and hydrochloric acids. Turn on the digestion hood, set the controller for the digestion block to 113 for 85°C to 95°C. Put a 50mL aliquot of preserved (~1% HNO<sub>3</sub>) sample in a plastic digestion tube, add 0.5mL 1:1 HCl, cover with a plastic reflux cap. Once samples reach temperature, record the time and temperature, and digest for 2 hours. Remove from the block, record the time and temperature and let cool, rinse caps into the digestion tube and bring volume up to 50mL (or original volume). Refer to EPA 200.8 Section 11.2 for the digestion procedure. Each digestion batch (≤ 20 samples) must have a laboratory control blank (LCB), a laboratory control standard (LCS) and a laboratory control standard duplicate (LCSD).

## Sample criteria:

Except as noted, specimens that do not meet the criteria below should be immediately reported as "no test" with an explanatory note:

1. Samples submitted in improper collection container.
2. Sample inadequately identified. (Sample has no identification, or cannot be matched to a laboratory request form).
3. Sample quantity insufficient.
4. Sample container broken or leaked in transit.

## Special Instructions:

All glassware and pipettes used in this procedure must be cleaned using glassware-cleaning procedure, i.e. nitric acid wash and DI water rinse.

## 2

## Standards and Reagents:

1. Nitric Acid ( $\text{HNO}_3$ ). Use high purity (trace metal grade) nitric acid 1:1
2. Gold Rinse: 2%  $\text{HNO}_3$  with a minimum of 100ug/L Gold
3. Calibration Standards: Absolute Standards ICP-MS Calibration Standard 1 (Part#52333), Absolute Standards EPA Method Calibration Standard 2 (Part#52334), Absolute Standards Strontium (Part# 57038), Absolute Standards Iron (Part#57026), Absolute Standards Mercury (Part#57880), Fisher Lithium Chloride (Cat#L121-100)
4. Second Source Standards: Absolute Standards ICP-MS Verification Standard #1 (Part#59472A), Absolute Standards ICP-MS Verification Standard #2 (Part#52101A), Absolute Standards Mercury (Part#57880), Ricca Lithium (Cat#MSLI1KN-100)
5. Internal Standard Solutions: Absolute Standards EPA Method 200.8 Internal Standard (Part#52332), Absolute Standards Scandium (Part#57221), Absolute Standards Gold (Part#56079), Elements Germanium (Part#Ge1000-50)
6. Tuning Solution: Absolute Standards ICP-MS Tuning Solution #1 EPA 200.8 (Part#52122); Dilute 1:1000
7. Mass Calibration Solution: CPI ELAN 6100/9000 Setup/Stability/Masscal Solution (Cat#4400-010403)
8. Deionized Water from laboratory system

## Instrument Set-up:

1. Turn on exhaust hood. Switch is located on the wall by the stairs.
2. Turn on argon gas cylinders and set pressure to ~60PSI (51PSI at the back of the instrument).
3. Turn on chiller set at 50PSI and 15°C.
4. Turn on Auto Sampler.
5. Launch software (ELAN) on the computer, click 'Instrument' on the top banner and then click the 'Start' button under Vacuum.
6. Check to see that drain hose, is inserted into the waste container (Empty container as needed).
7. To start the peristaltic pump, click 'Devices' on the top banner, click the 'Connect' button and set speed to 24 and click the counter-clockwise arrow. Place the Auto Sample needle in the rinse solution.
8. To light the plasma, click 'Instrument' on the top banner and once the vacuum pressure is in the Green, light the plasma by pressing the 'Start' button under Plasma. Aspirate rinse solution for about 30 minutes. This will allow the plasma to stabilize.
9. Click the Green 'R' on the side panel and check that the Tuning file is 2008TUNE, the DAC file is DEFAULT and that the Sample and Results files are correct.
10. Nebulizer Flow: Click 'Method' on the top banner, then 'File', 'Open', 'Optimize'. Click 'Optimize' on the top banner, select Nebulizer Gas Flow in the box on the left, click 'Get Analyte List', select 'Formula' and set the formula to  $\text{CeO } 155.9 / \text{Ce } 139.905 < 0.03$ , aspirate Mass Cal Solution and click 'Optimize'. Save DEFAULT.dac file when completed.
11. Lens Voltage: Click 'Optimize' on the top banner, select Lens Voltage in the box on the left, set 'Analyte' to Rh 102.905, select Max Intensity, aspirate Mass Cal Solution and click 'Optimize'. Save DEFAULT.dac file when completed.
12. Auto Lens: Click 'Method' on the top banner, then 'File', 'Open', 'Auto Lens Calibration'. Click 'Optimize' on the top banner, then the Auto Lens tab. Click 'Clear Calibration' and confirm, click 'Get Analyte List', aspirate Tuning Solution and click 'Calibrate'. Save DEFAULT.dac file when completed.
13. Tune: Click 'Method' on the top banner, then 'File', 'Open', 'EPA 2008 TUNING'. Click 'Tuning' on the top banner, aspirate Tuning Solution and click 'Tune'. Save DEFAULT.dac file when completed.
14. Daily: Click 'Method' on the top banner, then 'File', 'Open', 'DAILY 2008'. Click 'Sample' on the top banner, then the 'Manual' tab, type 'Daily' in the 'Sample' box, aspirate Mass Cal Solution and click 'Analyze Sample'. The Report will print automatically.

Note: Steps 10-14 can also be performed by using the SmartTune Wizard and running EPA2008 SmatTune Daily.swz

## 3

## Calibration Standard prep:

Li, Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Mo, Ag, Cd, Sb, Ba, Tl, Pb and U 10, 50 and 100 ug/L  
Fe 20, 100 and 1000 ug/L  
Se 50, 250 and 500 ug/L  
Hg 1.0, 2.5 and 5.0 ug/L

## Quality Control:

1. Analyze an Initial Calibration Blank (ICVB).
2. Analyze a Laboratory Control Blank (LCB), Laboratory Control Standard (LCS) and a Laboratory Control Standard Duplicate (LCSD) with each batch of digested samples.
3. Instrument Calibration Verification (ICV) and Continuing Calibration Verification (CCV) - Analyze a known reference sample after initial calibration (ICV) and after every ten samples (CCV) along with a Continuing Calibration Verification Blank (CCVB).
4. Matrix Spike and Matrix Spike Duplicate (MS and MSD) – spikes and duplicate spikes are to be performed on 10% of samples. Spike level should be the same concentration as the calibration verification and should not exceed MCL for the analyte. Spike an appropriately selected sample with the same solutions and concentrations as the mid-range calibration standard.
5. Quality Control Sample (QCS) – Analyze at least once quarterly and when a new lot of stock solutions are used to make calibration standards.

## Criteria for Acceptability of the Run:

1. Initial Calibration Blank (ICVB) and Prep Blank - No more than 10% of the analyte in the sample or 2.2xMDL, whichever is greater, report as not detected.
2. Laboratory Control Sample (LCS) – 70-130% recovery.
3. Calibration Verification (ICV and CCV) – 85-115% recovery and <20% precision.
4. Matrix Spike and Matrix Spike Duplicate (MS and MSD) – 70-130% recovery and <20% precision.
5. Quality Control Sample (QCS) – 85-115% recovery.
6. The  $r^2$  value for the calibration must be at least 0.995.

NOTE: If the acceptance criteria are not met, the analyst must address the problem and retest the samples.

## Out of Control Plan:

No sample should be reported until the all acceptance criteria have met. Or the out-of-control condition has been corrected and any problems or departure from protocol identified.

## Trouble Shooting:

1. PROBLEM - poor precision  
Check relative intensities and compare to expected levels. Check auto sampler and tubing for wear or blockage.
2. PROBLEM - error message  
Refer to instrument service manual
3. PROBLEM - contamination  
Check supplies associated with sample collection for contamination. Check rinse water, sample diluent, pipettes, sample cups. Make sure work area is free from dust.

4

Shutdown Procedure:

1. Rinse with approximately 50mL Deionized water, approximately 20mL while plasma is still lit, and the remainder with the plasma off.
2. To turn plasma off, click 'Instrument' on the top banner press the 'Stop' button under Plasma and press the 'Stop' button under Vacuum.
3. Auto sampler arm will return to 'Park'.
4. Run the peristaltic pump to empty spray chamber and tubing.
5. Release tubing on peristaltic pump and auto sampler.
6. Turn off chiller, auto sampler, argon and exhaust hood.
7. Exit software.

Calculations:

The results can be printed in a report from the software. The dilution factor must be shown and considered in the calculations.

Reporting:

1. The data from the printout should be transferred to the QC worksheet to verify that controls were within acceptable range and that duplicates are within range.
2. The lab analyst enters the results into the computer. Results are reported in units and number of significant figures consistent with MDL of method.

Instrument:

Manufacturer/ Model: Perkin Elmer ELAN 6100

Serial#: 0049901

References:

1. "Inductively Coupled Plasma Mass Spectrometry with ELAN Software" N0220008 Rev. C
2. "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry" Method 200.8 Revision 5.4 EMMC Version, USEPA
3. "Standard Methods for the Examination of Water and Wastewater" 18th Edition 1992 by APHA, AWWA, and WEF.

Attachments:

Datasheet

Preventative Maintenance Worksheet

Sample Digestion Log

Masses reported, MDL and PQL

Reviewed by: Sarah McGinnis, Lead Chemist

Date: April 19, 2016

Approved by: David Holland, Laboratory Director

Date:

1

Varian 715-ES  
Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

## Principle:

In inductively coupled optical emission spectrometry, a sample is aspirated into argon plasma and ionized. The ion is then excited and as it decays, it emits a photon. Each atom has its own characteristic wavelength of photon emission, and the intensity at the specific wavelength is proportional to the concentration of the element of interest.

## Sample Collection/Handling:

Use metal free collection bottles to collect samples. Collect 250 mL of sample. Smaller volumes (not less than 50 ml) can be used if necessary. On collection, acidify samples to pH <2 with 1:1 nitric acid, usually 2mL per 125mL. If samples are not acidified at time of collection (samples have 2 weeks to be preserved) add acid upon receipt in lab and hold for minimum of 16 hours before analysis. [40 CFR 141.23(K)]. Samples are held up to 6 months after preservation.

## Sample Preparation:

Samples containing particulate or organic material require pretreatment before analysis. Drinking water samples with a turbidity <1 NTU may be analyzed directly. Digest samples with a turbidity >1 NTU. For cation determinations of turbid samples, filter samples with a 1.0µm filter. For determination of dissolved metals, filter samples with a 0.45µm filter.

## Digestion Procedure for total metals:

Drinking water samples with turbidity >1 NTU and wastewater samples are to be analyzed following digestion with nitric and hydrochloric acids. Turn on hood. Set the controller for the digestion block to 113 for 85°C to 95°C. Put an aliquot of preserved (1% HNO<sub>3</sub>) sample (usually 50mL) in a plastic digestion tube, add 0.5mL 1:1 HCl, cover with a plastic reflux cap and digest in the digestion block for 2 hours. Remove from the block and let cool to the touch, rinse caps into the digestion tube and bring volume up to 50mL (or original volume). Refer to EPA 200.7 Section 11.2 for the digestion procedure. Each digestion batch (≤ 20 samples) must have a digestion blank, a laboratory control spike and a laboratory control spike duplicate.

## Sample criteria:

Specimens that do not meet the criteria below should have the client notified and suggested a recollection or as "no test" with an explanatory note:

1. Samples submitted in improper collection container.
2. Sample inadequately identified. (Sample has no identification, or cannot be matched to a laboratory request form).
3. Sample quantity insufficient.
4. Sample container broken or leaked in transit.

## Special Instructions:

All glassware and pipettes used in this procedure must be cleaned using glassware-cleaning procedure, i.e. using same matrix as sample, nitric acid wash or clean DI water.

## Reagents:

1. Nitric-Acid (HNO<sub>3</sub>). Use high purity (trace metal grade) nitric acid 1:1.
2. Manitol Rinse: (2%) Dissolve 9.5g D-Manitol in 1L of DI and 20mL 1:1 HNO<sub>3</sub>
3. Standard solutions: Standard solutions are prepared from standards purchased from Absolute, Ricca Chemical Company, Fisher Scientific or VWR

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4. Tuning Solution: 500ppm K; 50ppm Al, As, Ba, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sr, Zn in 5% Nitric from Varian (SVTUNSOL-500N); Dilute 1:10
5. Deionized Water from laboratory system

**Instrument Set-up:**

1. Turn on exhaust hood. Switch is located on the wall by the stairs.
2. Turn on argon gas cylinder and set pressure to ~92PSI (80-100PSI)
3. Turn on chiller set at 8-45PSI.
4. Turn on Auto Sampler before launching software.
5. Launch software (ICP Expert II), click 'Instrument' and check Casting (approx 35°C) and Peltier (approx -30°C) temps. The Casting takes about 6 hours to come up to temperature if the instrument has been turned off. The Peltier needs the chiller on and argon pressure to cool.
6. Check to see that drain hose, is inserted into the drain bottle. (Empty container as needed).
7. Light the plasma by pressing the 'Plasma On' button (or Shift+F4). In order to flush the lines of any introduced gas other than argon turn off plasma at hissing sound (before it is lit) at least twice before actually lighting on the third lighting. This prevents torch issues. Aspirate rinse solution for about 20-30 minutes. This will allow the plasma to stabilize.
8. Aspirate the tuning solution and perform a 'Torch Scan'; record the peak shift and the intensity of the peak. (Torch Align tab)
9. Aspirate DI and measure the dark current (background electrical "noise" in the detector) by pressing the 'Calibrate Detector' button. (W/L Calib tab)
10. Aspirate the tuning solution and press 'Calibrate Wavelength'; record range. (W/L tab)

**Standard prep:**

B 0.01, 0.05, 0.2, 1.0, 2.0 and 5.0 mg/L  
Ca 0.5, 2.5, 10.0, 50.0, 100 and 250 mg/L  
Cu 10.0, 50.0, 200 and 1000 µg/L  
Fe 10.0, 50.0, 200 and 1000 µg/L  
K 0.1, 0.5, 2.0, 10.0, 20.0 and 50.0 mg/L  
Mg 0.5, 2.5, 10.0, 50.0, 100 and 250 mg/L  
Mn 10.0, 50.0, 200 and 1000 µg/L  
Na 0.5, 2.5, 10.0, 50.0, 100 and 250 mg/L  
Si 0.5, 2.5, 10.0, 50.0, 100 and 250 mg/L  
Zn 10.0, 50.0, 200 and 1000 µg/L

**Quality Control:**

1. Analyze an Initial Calibration Blank (ICVB) and Prep Blank after calibration.
2. Analyze a Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCSD) with each batch of digested samples.
3. Calibration Verification (ICV and CCV) - Analyze a known reference sample after initial calibration (ICV) and after every ten samples analyze a continuing calibration verification (CCV) along with a continuing calibration verification blank (CCVB).
4. Spectral Interference Check (SIC) – Analyze on an annual basis. See EPA Method 200.7 section 7.14 for required concentrations.
5. Matrix Spike and Matrix Spike Duplicate (MS and MSD) – spikes and duplicate spikes are to be performed on every 10th sample. There must be one spike per run, if there are 14 samples only one spike is necessary. If there are 15 samples two spikes will be performed. Spike level should be the same concentration as the calibration verification and should not exceed MCL for the analyte. Spiking solutions are available from Absolute, Ricca Chemical Company, Fisher Scientific or VWR
6. Quality Control Sample (QCS) – Analyze at least once quarterly and when a new lot of stock solutions are used to make calibration standards.

## 3

## Criteria for Acceptability of the Run:

1. Initial Calibration Verification Blank (ICVB) and Prep Blank (LCB) - No more than 10% of the analyte in the sample or 2.2xMDL, whichever is greater, report as not detected.
2. Laboratory Control Sample (LCS) – 85-115% recovery.
3. Calibration Verification (ICV and CCV) – 95-105% recovery after calibration (ICV) and 90-110% recovery after subsequent determinations (CCV).
4. Matrix Spike and Matrix Spike Duplicate (MS and MSD) – 70-130% recovery and <20% difference.
5. Quality Control Sample (QCS) – The average of three analyses of the QCS must be within 5% of the stated value.
6. The  $r^2$  value for the calibration must be at least 0.995, linear max% error 25.0, Excess % curvature 25, and max upward % curvature 400.

NOTE: If any of the acceptance criteria are not met, the analyst must correct the problem and retest the samples.

## Out of Control Plan:

No sample should be reported until the all acceptance criteria have met for that batch. Or the out-of-control condition has been corrected and any problems or departure from protocol identified.

## Trouble Shooting:

1. PROBLEM - poor precision  
Check relative intensities and compare to expected levels. Check auto sampler and tubing for wear or blockage, rinse with mannitol.
2. PROBLEM - error message  
Refer to instrument service manual
3. PROBLEM - contamination  
Check supplies associated with sample collection for contamination. Check rinse water, sample diluent, pipettes, sample cups. Make sure work area is free from dust.

## Shutdown Procedure:

1. Rinse with approximately 50mL Deionized water, approximately 20mL while plasma is still lit, and the remainder with the plasma off.
2. Turn plasma off by pressing the 'Plasma off' button (or F4).
3. Return auto sampler arm to 'Park'.
4. Run the peristaltic pump to empty spray chamber and tubing.
5. Release tubing on peristaltic pump and auto sampler.
6. Turn off chiller, auto sampler, argon and exhaust hood.
7. Exit software (If the software stays open the Filament will stay on)

## Calculations:

The results can be printed in a report from the software. The dilution factor must be shown and considered in the calculations.

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Reporting:

1. The data from the printout should be transferred to the QC worksheet to verify that controls were within acceptable range and that duplicates are within range.
2. The lab analyst enters the results into the computer. Results are reported using the instrument method to choose which wavelength each result will be reported from. Results will be reported to the whole number except for boron which will be reported to two decimal places and potassium which will be reported to one decimal place.

Instrument:

Manufacturer/ Model: Varian 715-ES  
Serial#: IP0910 M173

References:

1. "Techniques for Simultaneous ICP-OES 700-ES Series" Prepared by Dr. Hilton Greenberg and updated by Alan Lynch, Varian Inc., October 2007.
2. "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry" Method 200.7 Revision 4.4 EMMC Version, USEPA
3. "Standard Methods for the Examination of Water and Wastewater" 18th Edition 1992 by APHA, AWWA, and WEF.

Attachment:

Preventative Maintenance Worksheet

Written by: Sarah McGinnis  
Date: August 10, 2010  
Reviewed: 4/19/16 Mollie Wooden

Approved by:

David Holland  
Laboratory Director  
Date:

## **TURBIDITY**

### **Scope and Applications:**

This method is applicable to drinking, surface, and saline waters.

### **Summary of Method:**

The turbidity method compares the intensity of the light scattered by the sample with the intensity of the light scattered by a standard reference suspension. It is measured using a Nephelometer that measures scattered light at 90° to incident light with a photo detector. The higher the intensity of the scattered light the higher the turbidity. High levels of turbidity interfere with disinfection of water.

### **Precision and Bias:**

A total of seven replicates of 0.10 NTU QC were analyzed in 3 different days, for an average 0.139, a standard deviation of 0.0006 and a relative standard deviation of 4.495 %.

### **Working Range:**

The working range is 0.05 to 40 NTU. Samples higher than 40 NTU should be diluted. Adjust MDL and PQL by dilution factor

### **Minimum Reporting Limits:**

The detection limit for turbidity is 0.03 NTU and the reporting limit is 0.05 NTU.

### **Sample Collection, Preservation and Holding Times:**

Samples should be analyzed as soon as possible after collection but can be stored up to 48 hours for regulatory purposes by cooling to 4 °C +/- 2°C. Refrigerating, help to minimize microbiological decomposition of solids, is recommended.

### **Interferences:**

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 will cause turbidities to be low, although this effect is generally not significant with finished waters. The cuvette must be kept scrupulously clean and free of scratches; carefully wipe the surface of the tube with lens paper to remove fingerprints and moisture.

### **Instrumentation/Equipment:**

*Turbidimeter 2100 N* by Hach company (Serial no. 13090930C030590). **Note:** Needs calibration every three months.

### **Reagents and Standards:**

1. Formazin Turbidity Standard 4,000 NTU: purchased from RICCA (Cat. No. 8830-16)
2. Turbidity Standard 1NTU: Dilute 25 µ L of stock solution (4,000NTU) with 100 mL of DI water in a volumetric flask. Prepare fresh each day.

### **Q.A./Q.C. Requirements:**

-Blank acceptance criteria, should be less than 0.05 NTU and is recorded as Not Detected.

- The acceptance criteria for the percent recovery of the Turbidity Standard solution is between 95 to 105.
- Analyze one blank and one QC before start with the turbidity measurements.
- Analyze a QC every 20 samples.
- Perform duplicate analysis on 10 % of samples. Duplicate analysis is less than 10 % difference.
- To verify if there any instrument variation, at the end of the analysis re-read standard and blank. The standard should not be more than 25 % of difference of the first standard measurement.

#### **Analysis Procedure:**

1. Clean cuvette with a soft cloth to remove water spots
2. Apply 1 or two drops of oil to the surface of the cuvette and use an oiling cloth to disperse.
3. Fill cuvette with DI water for the blank. Verify blank reads less than 0.05 NTU.
4. Pour out blank and rinse with 1.0 NTU standard.
5. Gently mix the standard by inverting the container several times.
6. Fill cuvette with 1.0 NTU STD.
7. Verify standard is within required parameters.
8. Proceed to analyze samples. Note: Before reading the sample invert sample container slowly.
9. Pour small amount of sample in to vial to wash out previous sample.
10. Fill cuvette with sample. Dry cuvette with a Kimwipe tissue.
11. Place cuvette in the turbidimeter.
12. Take reading, record on worksheet.
13. Repeat for all samples.

**Note:** Make sure to turn on the [**Signal Average**] button when measuring a sample. This option will make an average of three consecutive measurements of your sample. Turn off the [**Signal average**] option before introducing the next sample.

#### **Calculations:**

Multiply sample readings by appropriate dilution to obtain final reading.

Recovery % =  $\left( \frac{\text{Turbidity NTU (measured)} - \text{Turbidity NTU (true value)}}{\text{Turbidity NTU (true value)}} \right) \times 100$

Relative Difference % =  $\left( \frac{|\text{Turbidity NTU (Sample)} - \text{Turbidity NTU (Dup)}|}{\text{Average (Sample \& Dup)}} \right) \times 100$

#### **Reporting:**

1. Before entering data make sure that is approved by the lead chemist
2. Reporting Units:
  - a. Turbidity is reported as NTU.
3. Reporting Limits:
  - a. Results below the PQL are reported as "ND" (not detected). Samples measuring more than 40 NTU are diluted and re-analyzed. Adjust MDL and PQL by dilution factor.
4. Record data according to the following table:

Drinking water systems should be immediately notified by telephone if turbidity exceeds 5.0 NTU.

| NTU      | Record to Nearest |
|----------|-------------------|
| 0.0-1.0  | 0.05              |
| 1-10     | 0.1               |
| 10-40    | 1                 |
| 40-100   | 5                 |
| 100-400  | 10                |
| 400-1000 | 50                |
| >1000    | 100               |

**References/Method Source:**

*Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 180.1*

*2100 N Turbidimeter Laboratory Turbidity Instruction Manual, Hach Company, 1999*

Written By: Lilian Reyes

Date:10/2/14

Approved By:\_\_\_\_\_

Date:\_\_\_\_\_