DETERMINATION OF TOTAL ORGANIC CARBON (TOC) AND DISSOLVED ORGANIC CARBON (DOC) USING THE SHIMADZU TOC ANALYZER

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1. SCOPE AND APPLICATION

1.1. This SOP details the analysis of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) in surface, salts, ground waters, effluents and influents. Tests covered by this SOP are W-DOC and W-TOC.

1.2. The sample concentration limit for TOC/DOC for this method is 100 mg C/L. Samples containing TOC/DOC levels higher than 100 mg C/L should be diluted prior to analysis. The method detection limit (MDL) is 0.50 mg C/L and the practical quantitation limit (PQL) is 1.0 mg C/L.

2. SUMMARY OF THE METHOD

2.1. The described procedure is based on Standard Methods 5310 B-2000.

2.2. The acidified samples are purged with ultra high purity (UHP) air prior to injection in order to remove the inorganic carbon fraction. Samples are introduced by the sample injector into a combustion tube.

2.3. The total carbon component of the sample is combusted/oxidized to form carbon dioxide, which is detected by infrared analysis.

2.4. This procedure is applicable only to homogeneous samples, which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

2.5. The method actually measures nonpurgeable organic carbon (NPOC). In many surface and ground waters, the purgeable organic carbon contribution to TOC is negligible. Therefore, in practice, the nonpurgeable organic carbon determination is substituted for TOC.

2.6. Interferences: Salt samples may impair the effectiveness of the catalyst and reduce its lifespan. Samples with a conductivity of 15,000 umhos/cm or greater and a salinity of 9 PPTh or greater are batched as salt samples and are diluted 1:2. A 2N hydrochloric (HCl) acid rinse (4.7.) is run every 5 cups in order to minimize residue build up on the catalyst. Salts are placed at the end of each run and no more than fifteen salt samples should be analyzed per run. The run should end with at least 1 acid rinse and 4 blanks to further minimize residue build up on the catalyst. Elemental carbon may not be oxidized at the furnace temperature of 680 ^{o}C, but it is not expected to be a constituent of the water samples analyzed. Gases of halide components may interfere with the detection system. They are eliminated by passing the reaction gas through a halogen scrubber.

3. EQUIPMENT AND SUPPLIES

3.1. Two Shimadzu Total Organic Carbon Analyzers each equipped with autosamplers

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are available:

3.1.1. TOC-L_{CPH}; Autosampler: ASI-L

3.1.2. TOC-V_{CPH}; Autosampler: ASI-V

3.2. Assorted volumetric flasks (Class A)

3.3. Eppendorf and Oxford pipettes

3.4. Fisher 24 mL Glass Shell Vials (03-339-30H)

3.5. 50 ml graduated cylinder (Class A)

4. CHEMICALS, REAGENTS, AND STANDARDS (SEE DEP SOPs NU-041 and NU-042)

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

Note: All reagent and standard preparations must be documented in the Reagent and Standard Logsheet for W-TOC analysis. This excel sheet (NU-RGTSTD-1.0_W-TOC) is located in the REAGENT_PREP folder for TOC analysis on the Nutrients drive. It needs to be updated whenever a reagent or standard is newly prepared. For every analysis file print the Reagent and Standard Logsheet and place it into the analysis folder.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard and reagent are generated in the module and documented in the reagent and standard sheet submitted with each analysis folder. If available, a Certificate of Analysis for each purchased reagent is also maintained in the REAGENT_PREP folder for TOC analysis. A Certificate of Analysis for the certified quality control standard (4.8.) is kept in a binder in C307. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: Prior to using the chemicals in this analysis, please read their MSDS and the safety notes found in Section 11 of this SOP.

4.1. Deionized (DI) water

4.2. UHP Grade Compressed Air

4.3. Concentrated sulfuric acid (H_2SO_4) and hydrochloric acid (HCl)

4.4. Potassium hydrogen phthalate (Fisher Scientific catalog # P243-100)

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Stock Standard Solution (1000 mg C/L) - This solution is used for the low spike (V1), laboratory fortified blank (LFB), and the continuing calibration verification (CCV/CHCK20) standard. Holding time for the Stock standard is 180 days.

4.4.1. Dry 5g of primary grade potassium hydrogen phthalate at 120 ^{o}C for 12 hrs. Cool in a desiccator.

4.4.2. Weigh out 2.1254 g of the dried potassium hydrogen phthalate into a weighing boat.

4.4.3. Add approx. 800 mL of DI water to a clean 1 L flask. Add 2 mL of H_2SO_4 and mix.

4.4.4. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Pour this solution into the reagent bottle labeled 'TOC STOCK: 1000 PPM'.

4.5. Primary Grade Dextrose (Fisher Scientific catalog # D16-500)

Stock Standard Solution (10000 mg C/L) - This solution is used for the calibration, practical quantitation limit (PQL/PQCK4), and high spike (H1). Holding time for the Stock standard is 180 days.

4.5.1. Dry 5 g of primary grade dextrose at 120 ^{o}C for 12 hrs. Cool in a desiccator.

4.5.2. Weigh out 2.505 g of the dried dextrose into a weighing boat.

4.5.3. Add approx. 20 mL of DI water to a clean 100 mL flask. Add 0.2 mL of concentrated H_2SO_4 and mix.

4.5.4. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Pour this solution into the reagent bottle labeled 'TOC STOCK: 10000 PPM'.

4.6. Preparation of QC-Standards - Holding time, 30 days.

4.6.1. Blank Standard/Diluent (0 mg C/L) - To a 2 L volumetric flask containing approx. 1.5 L of DI water, carefully add 4.0 mL of concentrated H_2SO_4. Dilute to the mark and mix thoroughly. Used for the method blank (MBLK) and continuing calibration blank (CCB).

4.6.2. PQL and Calibration Standard (PQCK4, 1.0 mg C/L) - To a 1 L volumetric flask containing approx. 900 mL of diluent (4.6.1.), add 0.1 mL of the 10000 mg C/L stock standard (4.5.), fill up to the mark with diluent and mix thoroughly.

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4.6.3. CCV (CHCK20, 20 mg C/L) - To a 2 L volumetric flask containing approx. 1 L of diluent (4.6.1.), add 40 mL of the 1000 mg C/L stock standard (4.4.), fill up to the mark with diluent and mix thoroughly.

4.7. Acid Rinse (2N HCL) - To a 250 mL volumetric flask containing approx. 150 mL of DI water, carefully add 41 mL of concentrated HCL. Dilute to the mark and mix thoroughly. Holding time, 90 days.

4.8. ALTQC - A certified quality control standard is purchased (e.g., Inorganic Ventures Demand standard). For the expiration date of the purchased stock refer to the manufacturer's certificate. The stock ALTQC standard may be diluted appropriately so that the concentration falls within the calibration range. Holding time of the diluted standard, 30 days.

4.9. Working Calibration Standard (100 mg C/L) - To a 500 mL volumetric flask containing approx. 400 mL of diluent (4.6.1.), add 5 mL of the 10000 mg C/L Stock Standard Solution (4.5.). Fill up to the mark with diluent and mix thoroughly. Store this standard in a reagent bottle labeled 'WORKING CALIBRATION STANDARD: 100 PPM'. Holding time, 30 days.

4.10. Calibration Standard (0.80 mg C/L) - To a 1 L volumetric flask containing approx. 900 mL of diluent (4.6.1.), add 0.08 mL of the 10000 mg C/L stock standard (4.5.), fill up to the mark with diluent and mix thoroughly. Holding time, 30 days.

4.11. Sodium Carbonate; Certified A.C.S., Anhydrous (Fisher Scientific, catalog. # S263-500).

Inorganic Spiking Solution (1000 mg C/L):

4.11.1. Dry about 5 g of sodium carbonate at 120 ^{o}C for 12 hrs. Cool in a desiccator.

4.11.2. Weigh out 2.2125 g of the dried sodium carbonate into a weighing boat.

4.11.3. Add approx. 150 mL of DI water to a clean 250 mL flask. Rinse the contents of the weighing boat into the flask using DI water. Dilute to the mark and mix thoroughly. Pour this standard into a reagent bottle labeled 'INORGANIC SPIKING SOLUTION: 1000 PPM'. Do not acidify this standard. Holding time, 180 days.

5. SAMPLE HANDLING AND PRESERVATION

5.1. Samples are preserved with sulfuric acid at collection and stored on ice or at ≤ 6 °C (not frozen). All samples must be analyzed within 28 days of collection date for results to be reported unqualified.

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5.2. Samples are stored in the Nutrient refrigerators in the receiving room of the FDEP laboratory. Allow samples to come to room temperature before processing.

6. SAMPLE PREPARATION AND ANALYSIS (SEE DEP SOP NU-033)

6.1. Open program TOC-CONTROL-V/L.

6.2. Choose Sample Table Editor icon.

6.3. To start a new file and run: *File* → *New* → *Sample Table* → *TOCL-W / TOCV-W* → *OK*. To save the file, click *Save* and name the file YYMMDDW# or L# (where # is a number 1, 2, etc., that indicates the 1st, 2nd, etc., run of the day) depending on the instrument used (for TOC-V$_{CPH}$, Ex.: 120211W1; for TOC-L$_{CPH,}$ Ex.: 120211L1). → *Save*.

6.4. In some cases, it may be helpful to perform an optional rinse before the calibration. To add the rinse sequence to the beginning of the run (the rinse blank result will be calculated from a previous calibration), highlight line1 and select *Insert*→ *Multiple Samples*. This opens the Sample Group Wizard.

6.4.1. Page 1 Sample Source: Select *Calibration Curve* option and browse button. Then select calibration: for TOCV, select *Calibration_W-TOC.cal* → *Open*; for TOC-L, select folder icon → *Data* → *OK* → *TOC-KJ-1-50.cal* → *Open* → *Next*.

6.4.2. Page 2 Sample Parameters. Set options as follows:
Number of Samples = 1
Start Vial = 1
Sample Name = Enter file name (Ex. 120211W1 or 120211L1)
Sample ID = RINSE→ Finish→ Assign vial number as follows: Vial 1=0 (the 0 position indicates the DI water rinse reservoir)→ OK

6.5. To setup a calibration sequence, highlight line three and then for TOC-Vcph, select *Insert* →*Calibration Curve* →*Calibration*_W-TOC*.cal* →*Open*; for TOC-L, select *Insert* → *Calibration Curve* → Select folder icon → *Data* → *OK* → *TOC-KJ-1-50.cal* → *Open*.

6.6. After inserting the calibration, the Sparging/Acid Addition window will appear. Assign vial numbers as follows:
100 mg C/L standard = 1
20 mg C/L standard = 1 (Instrument dilution from vial 1)
5 mg C/L standard = 1 (Instrument dilution from vial 1)
1 mg C/L standard = 4 (prepared standard, 4.6.2.)
0.8 mg C/L standard = 2 (prepared standard, 4.10.)
0 mg C/L standard = 3 (diluent, 4.6.1.)
Select *OK* to complete. The vial column numbers should read 3, 2, 4, 1, 1, 1.

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6.7. To setup a sample sequence, highlight line four, select *Insert* → *Multiple Samples*. This will open the Sample Group Wizard.

6.7.1. Page 1 Sample Source; Select Calibration Curve option and browse button. Then select calibration file that was just created (6.5) and open → Next

6.7.2. Page 2 Sample Parameters; Set options as follows:
Number of Samples = 91
Start Vial = 3
Sample Name = Enter file name. (Ex. 120211W1 or 120211L1)
Sample ID = Leave blank
→ Finish → OK

6.8. Pour samples and QC-standards into labeled 24 mL Fisher glass shell vials according to the run sequence. Place them in the autosampler rack and return rack to turntable for realignment. Make sure that all vials are correctly seated.

6.8.1. For each batch: Prepare two 20 mg C/L matrix spikes (spike code V1) by adding 400 µL of the 1000 mg C/L stock standard solution (4.4.) to two 20 mL portions of a selected sample. Prepare one 40 mg C/L matrix spike (spike code H1) by adding 80 µL of the 10000 mg C/L stock standard solution (4.5.) to one 20 mL portion of a selected sample. Prepare a laboratory fortified blank (LFB) following the same procedure as the 20 mg C/L matrix spike by substituting blank standard (4.6.1.) for the sample. Effluents and salts are batched separately.

6.8.2. Inorganic spike (spike code IS): For each analytical run, prepare one inorganic sample spike. Add 400 µL of the 1000 mg C/L inorganic spiking solution (4.11.) to one 20 mL portion of a selected sample.

6.8.3. Each run begins with the following sequence:

Rinse (6.4) (optional)
Calibration (6.5)
MDL (Blank Standard, 4.6.1.)
PQCK4 (PQL, 1.0 mg C/L, 4.6.2.)
DEMAND (ALTQC#, 4.8.)
CHCK20 (CCV, 20 mg C/L, 4.6.3.) and **CCB** (Blank Standard, 4.6.1.) – these continuing calibration checks are scheduled to bracket every ten samples on the run
Batched samples including **MBLKs** (4.6.1.), **LFBs** (6.8.1.), and spiked samples (6.8.1. and 6.8.2.)
Final **CHCK20** and **CCB**
For salt samples: **Rinse_HCL** (2N HCL, 4.7.) and extra blanks as necessary (see section 2.6.)

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6.9. Connect Instrument: Click *Connect.* Wait for connection, then press *Start* to start the run.

6.10. Post-run Procedure: Results are exported as an ASCII file and converted into a raw file in the QC manager for performing calculations and uploading to LIMS.

6.10.1. *File* → *ASCII Export Setting* → *Detail* → *Data.* Check the following export options; Sample ID, Dilution, Date/Time, Mean Conc., and Vial. Also make sure the export data box is checked.

6.10.2. To export file: *File* → *ASCII Export* → *Detail* (Include Injection Data) → *Filename* → *S*

6.10.3. Export to C:\TOC3201\Data for TOC-V, or to C:\TOC-L\Data for TOC-L. This is the local drive for the instrument workstation.

6.10.4. Open Windows Explorer and copy file from the local drive above to the appropriate instrument folder (TOC-L or TOC-V) in the current year's subfolder located at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Tocv\.

6.10.5. Print a copy of the final report and data table containing injection peaks by selecting: *File* → *Print* → *Sample Report –All*, then *File* → *Print* → *Sample Table.*

6.11. Quantitation/Calculations:

6.11.1. The instrument will give the values for organic carbon in mg C/L. The value given by the instrument is the average of three injections for a given sample that have a percent relative standard deviation of less than 5 %.

6.11.2. The QC Manager will calculate spike and standard recoveries and RPDs. For general calculations including RPDs and spike recoveries, see the FDEP Quality Manual Section 5.9.

6.11.3. The high calibration standard is prepared according to section 4.9. Two of the other standards used in the calibration are auto-diluted by the instrument from the high standard, and two of the calibrants are prepared manually (see 4.6.2. and 4.10.). See section 6.6. for calibration protocol. The correlation coefficient for the calibration is calculated by the instrument software.

7. DATA ARCHIVAL

7.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder

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is labeled with the test (W-TOC, W-DOC), filename/s (YYMMDDW# or L#), and initials of the analyst.

7.2. Each report folder should contain the following items - run report including raw data and calibration curve, results report method parameters, bench sheet, Reagent and Standard Logsheet, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.3. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

7.4. TOC instrument data excel transfer files for upload to QC manager are stored in electronic format in appropriate instrument folder (TOC-L or TOC-V) in the current year's subfolder located at \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Tocv\.

8. MAINTENANCE/TROUBLESHOOTING

Note: Make sure all maintenance performed is documented in the instrument's maintenance log.

8.1. Maintenance:

8.1.1. Before beginning sample analysis, conduct a general inspection of the instrument to ensure that everything is in order, and that there is sufficient UHP Air to complete the run.

8.1.2. The Humidifier and dehumidifier vessels should be filled with DI water to the fill line on the vessel. Once a month, this vessel should be drained and refilled with fresh DI water. This prevents contamination.

8.1.3. Keep the rinse water bottle filled with DI water. If running samples overnight, fill the bottle with DI water before starting the run.

8.1.4. The diluent bottle should be changed with fresh Blank Standard/Diluent (4.6.1.) at least once per month.

8.1.5. Make sure the HCL Intake is changed with fresh 2N HCL (4.7.) at least once every three months.

8.1.5.1. Regeneration of TC catalyst should be performed on a case by case basis (e.g., most sample results are based on four and five injections). See instrument manual for regeneration procedure. Regeneration should be followed with a run of at least 20 CCBs and a few CCVs.

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8.1.6. Check the waste line daily to ensure proper flow. Waste backup will damage autosampler. Dump waste down the drain as need.

8.2. Troubleshooting:

8.2.1. To stop the run at any point and delete the calibration, Click *Stop* button → *Stop* (stop all processes immediately).

8.2.2. To interrupt the run at any point and save the calibration, Click *Stop* button → *Stop* (after current sample is completed).

8.2.3. In order to restart a run in progress (for example, if there is a QC failure at the beginning of a run) and keep the sample table set up for a new run, previous data gathered or attempted must be deleted prior to restart. Highlight the lines to delete, go to *Edit* → *Clear Measured Data* → *Highlighted* → *Yes*, then click *View Vial Settings* → Assign the vial numbers for rerun samples.

8.2.4. Autosampler lid must be in place for run to proceed properly.

9. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE NU-038 AND NU-043)

9.1. A new calibration must be performed at the beginning of the analysis and the LCR must be verified (see 9.2.). Consecutive runs on one day may use the same calibration. The linear calibration consists of five standards (100 mg C/L, 20 mg C/L, 5 mg C/L, 1 mg C/L, and 0.8 mg C/L) and a blank. It is followed by a sequence of initial quality control standards as described in section 6.8.

9.2. Linear Calibration Range (LCR): See the FDEP Quality Manual Appendix B, Section 7.0, 'Protocol for Determining the Test Method Range of Applicability'. The correlation coefficient of the linear regression (r^2) must be equal to or larger than 0.995.

9.3. Each analytical run contains a number of sample batches, which consist of no more than 20 samples per batch. Each batch generally contains one LFB and one sample that has been spiked three times - low matrix spike, low matrix spike duplicate and one high matrix spike. Effluent batches contain a sample batched in duplicate and one high spike. Salt batches contain two low spikes. The spikes are prepared according to section 6.8.1. Acceptance limits for the LFB and matrix spike recoveries are 85-115 %.

9.4. On every analytical run, one sample is selected for an inorganic spike. The spike is prepared according to section 6.8.2. The relative percent difference (RPD) between the sample result and the spiked sample result must be below 20 %. If the RPD is 20 % or greater, no data from the run may be used. The instrument should be checked to ensure that it is operating correctly, with special attention

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being paid to the purging process.

9.5. The AltQC standard (DEMAND#, 4.8.) is a second source standard with acceptance limits supplied by the manufacturer.

9.6. One PQL (PQCK4, 4.6.2.) level standard is analyzed for every analytical run or at least one is analyzed every 24 hrs. Acceptance limits for the PQCK4 recovery are 70-130 %.

9.7. A CCV (CHCK20, 4.6.3.) and a blank (CCB, 4.6.1.) standard are run at the beginning of every run, after analysis of every set of 10 samples, and at the end of the run. The CCV is prepared from a source material other than the calibration standard. Acceptance limits for the recoveries of the check standard are 90-110 %.

9.8. The sample/matrix spike precision should be less than 20 % RPD for results over the practical quantitation limit (PQL).

9.9. Acceptance limits for the blanks (MDL, MBLKs, CCBs) are < 0.50 and > -0.50 mg C/L.

9.10. For general method performance and acceptance criteria for QC measures and corrective action for out-of-control data and contingencies for handling out-of-control or unacceptable data, refer to DEP SOPs NU-038 and SOP NU-043. If there are any anomalous results (e.g., differing results for multiple analyses of same sample) or any unusual events (spilled sample, cannot locate sample, etc.), see supervisor for further instruction.

10. SAFETY/WASTE MANAGEMENT

10.1. Refer to the MSDS notebook for information on safe handling of samples and reagents used with instrument.

10.2. Flush sample waste (as long as no other known hazards are present) down the sink with plenty of water.

10.3. Review the laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/system/files/Division-of-Environmental-Assessment-and-Restoration/governing-documents/Health%20%20Safety%20Plan_0.docx).

10.4. Safety glasses, gloves and lab coats should be worn at all times whilst handling samples and reagents.

11. REFERENCES

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time

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of use. Method validation data is on file with the supervisor. The limit of detection (LOD) is verified on every run based on the PQCK4.

11.1. Standard Methods Online, 5310 B-2000.

11.2 Shimadzu TOC-V/L Manual.

11.3. Quality Manual, Bureau of Laboratories, FDEP.

11.4. DEP SOP NU-033, Summary of Analysis Procedures for the General Chemistry and Nutrients Workgroups.

11.5. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

11.6. DEP SOP NU-041, Reagent Preparation Procedure.

11.7. DEP SOP NU-042, Standard Preparation Procedure.

11.8. DEP SOP NU-043, General Chemistry Quality Assurance and Data Authorization Guidelines.

11.9. Laboratory Health and Safety Plan.

11.10. DEP SOP LB-006, Standard operating procedure for records maintenance and storage.

Appendix of Significant Changes

02/19/2008 Section 4: Added an inorganic spike. Organic spike solution and CCV prepared from a different stock to the calibration standard.

05/15/2008 Reference method changed from EPA 415.1 to SM 5310 B.

04/23/2010 Section 2.6: Clarified the treatment of salt samples, Sections 4.6, 7.2 and 9.2: Added the high (H1) matrix spike which is prepared from a different stock to the calibration standard.

04/21/2010 Sections 4.6 and 4.1.2: Changed the volumes made for the high and inorganic spike: Changed the CCV stock standard from the 1000 mg C/L to the 10000 mg C/L stock standard (4.7.3).

09/17/2012 MDL changed from 1.0 mg C/L to 0.40 mg C/L. Section 3: Updated instrument information. Section 4: Modified to indicate changes in calibration and QC standards, per method update. Section 6: Modified to reflect instrument calibration changes. Section 9: CCV limits changed.

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02/04/2013 MDL changed from 0.40 mg C/L to 0.50 mg C/L. PQL changed from 0.8 mg C/L to 1.0 mg C/L.

07/22/2015 Section 6: Title changed to Sample Preparation and Analysis. Section 7: Title changed to Data Archival. Section 10: Title changed to Safety/Waste Management. Section 11: Title changed to References.

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