STANDARD OPERATING PROCEDURES (SOP)
"DOC/TOC Determinations Using the Tekmar Dohrman Analyzer"

MED-SOP CHA034 DOC-TOC CE 4-2015

Revision 5

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PROCEDURAL SECTION

1.0 SCOPE AND APPLICATION

This method provides procedures for the determination of total organic carbon (TOC), dissolved organic carbon (DOC) in source waters and drinking waters. For TOC and DOC analysis, the sample is acidified and the inorganic carbon (IC) is removed prior to analysis for organic carbon (OC) content using a TOC instrument system. The measurements of TOC and DOC are based on calibration with potassium hydrogen phthalate (KHP) standards. This method is not intended for use in the analysis of treated or untreated industrial wastewater discharges as those wastewater samples may damage or contaminate the instrument system(s).

2.0 SUMMARY OF METHOD

2.1 In both TOC and DOC determinations, organic carbon in the water sample is oxidized to produce carbon dioxide (CO_2), which is then measured by a detection system. There are two different approaches for the oxidation of organic carbon in water samples to carbon dioxide gas: (a) combustion in an oxidizing gas and (b) UV promoted or heat catalyzed chemical oxidation with a persulfate solution. Carbon dioxide, which is released from the oxidized sample, is detected by a conductivity detector or by a nondispersive infrared (NDIR) detector. Instruments using any combination of the above technologies may be used in this method.

2.2 Settleable solids and floating matter may cause plugging of valves, tubing, and the injection needle and/or injection port. The TOC procedure allows the removal of settleable solids and floating matter. The suspended matter is considered part of the sample. The resulting water sample is then considered a close approximation of the original whole water sample for the purpose of TOC measurement.

2.3 The DOC procedure requires that the sample be passed through a 0.45-µm filter prior to analysis to remove particulate OC from the sample.

2.4 The Tekmar Dohrman Phoenix 8000 TOC Analyzer uses sodium persulfate in combination with UV light to oxidize organic material. This TOC technique achieves outstanding analytical accuracy, precision, and long-term calibration stability due to its ability to inject high sample volumes (up to 20 ml) and low

system background. The Non-Dispersive Infra-Red (NDIR) detector that Phoenix 8000 uses is sensitive for very low levels of TOC.

2.5 Definitions

DIW- deionized water
H_3PO_4-phosphoric acid
$Na_2S_2O_8$- sodium persulfate

2.6 Health and Safety Warnings

The proper Personal Protective Equipment should be used when pouring or analyzing samples. Always turn instrument off before repairing or troubleshooting.

2.7 Interferences

The TOC and DOC procedures require that all IC be removed from the sample before the sample is analyzed for organic carbon content. If the IC is not completely removed, **significant error will occur.** The sample, which is then free from IC interference, is injected into a TOC instrument system. The organic carbon is oxidized to CO_2, which is released from the sample, detected, and reported as mg/L or ppm TOC or DOC.

3.0 PERSONNEL QUALIFICATIONS

3.1 This SOP provides the steps necessary for DOC/TOC determination by technicians with basic training in laboratory procedures; however, proper training in the use of the instrument is necessary.

3.1.1 Trained personnel are identified in the instrument logbook located next to instrument.

3.2 The instrument manager should be consulted for all instrument use and procedures.

4.0 APPARATUS AND MATERIALS

4.1 Instrument

4.1.1 Tekmar Dohrman Phoenix 8000 TOC Analyzer: standards, QA standards and blanks (section 4.2).

4.1.2 Various volume Eppendorf pipets and disposable tips.

4.1.3 Gas Supply: 99.999% pure nitrogen (5.0 Ultra High Purity) or hydrocarbon and CO2 free air with TOC content <1ppm. It is recommended when using hydrocarbon and CO2 free air that an ozone trap be used

4.1.4 Gas Pressure: 30 to 35 psi (206.7 to 241.2 kPa)

4.2 Standards and QA/QC

4.2.1 TOC/TC Standards: Prepare the standards from purchased DOC/TOC stock standard, diluting to concentrations which will encompass expected sample concentration ranges. Dilutions should be made using ADIW (see Section 4.3.1). Make fresh weekly or as needed. Examples are listed below.

4.2.1.1 0.0 ppm = ADIW
0.5 ppm Std. 0.25 mL 1000 ppm TOC Stock => 500 mL ADIW
1.0. ppm Std. 0.50 mL 1000 ppm TOC Stock => 500 mL ADIW
2.0 ppm Std. 1.00 mL 1000 ppm TOC Stock => 500 mL ADIW
5.0 ppm Std. 2.5 mL 1000 ppm TOC Stock => 500 mL ADIW
10.0 ppm Std. 5.0 mL 1000 ppm TOC Stock => 500 mL ADIW
20.0 ppm Std. 10.0 mL 1000 ppm TOC Stock => 500 mL ADIW
40.0 ppm Std. 8.0 mL 1000 ppm TOC Stock => 200 mL ADIW
80.0 ppm Std. 4.0 mL 1000 ppm TOC Stock => 50 mL ADIW
160.0 ppm Std. 8.0 mL 1000 ppm TOC Stock => 50 mL ADIW

4.2.2 Matrix spikes and Blank spikes:
Dilute 0.125 mL of 2000 ppm TOC Stock => 25mL sample or DIW to yield 10 ppm theoretical increase

4.2.3 Quality Assurance Sample: ERA 516: **0.25 mL** Stock => **200mL** ADIW ~ **12.35 ppm Organic Carbon.** Make fresh weekly.

4.2.4 **1000 ppm Inorganic Carbon** (IC) Stock Solution: Dissolve 8.833 g (Na2CO3) => 1 L DIW. Make fresh as needed.

4.2.5 **20 ppm IC Standard.** 2.0 mL 1000 ppm IC Stock => 100 mL DIW. Make fresh weekly or as needed.

4.3 Reagents:

4.3.1 **21% H_3PO_4**: 150 mL DIW + 50 mL 85% H_3PO_4.

4.3.2 **0.2% H_3PO_4** ("Acidified DIW", ADIW): 16 mL 1:1 H3PO4 => 4 L DIW.

4.3.3 **0.5 M K_2SO_4**

4.3.4 **Potassium Hydrogen Phthalate** (dried and stored in vacuum desiccator)

4.4 Analysis Procedures:

NOTE: Before opening the software make sure that the acid reservoir tube on instrument has been removed and placed into an empty test tube. When opening the software, all values are set to Default and the instrument will empty the syringe into the acid reservoir and it will contaminate it.

4.4.1 Refer to the separate "Tekmar Dohrman Operating Procedure for current instrument set up, located next to instrument.

4.4.2 Water samples are collected, preserved with H_3PO_4 and stored at 4 deg C until analysis. Samples should be analyzed within 28 days. Samples are either analyzed unfiltered for TOC, or filtered through 0.45uM membrane for DOC following the same procedures and calibration.

5.0 DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION

5.1 Every sample run will be automatically saved in the Tekmar Dohrman Phoenix 8000 software program. A backup copy of the data should be printed or transferred via flash drive to L: or M: drive.

5.2 Concentrations are reported as a ppm and are determined from standard curves run at the beginning and end of each run.

6.0 QUALITY CONTROL AND QUALITY ASSURANCE

6.1 Duplicate field samples should be collected on 10% of total number of samples

6.2 Replicate lab samples should be analyzed on at least 10% of total number of samples analyzed. Replicate samples should agree within 25% of each determination.

6.3 Matrix and blank water spikes should be run on 10 -20% of total samples analyzed. Recoveries of matrix spikes should be within 25% of nominal.

6.4 Parameters based on current instrument

6.4.1 **Analytical Limit of Detection**: 2 ppb

6.4.2 **Maximum Measurable Concentration**: 10,000 ppm (sample volume and dilution dependent)

6.4.3 **Precision*:** = 2% RSD or CV, +/- 1ppb or +/- 0.02 ug C, whichever is greater over seven replicates.

6.4.4 **Sample Size**: 500uL to 20 mL

6.4.5 **Analysis Time**: 4 to 8 minutes, typical

7.0 REFERENCES

7.1 EPA Method 415.1. Total Organic Carbon. Official Name: Organic Carbon, Total (Combustion or Oxidation).

7.2 EPA Method 415.3. Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water.

7.3 Standard Method 5310C. Persulfate-ultraviolet or heated-persulfate oxidation method.

7.4 EP 2.2.44. European Pharmacopoeia Method 2.2.44: Total Organic Carbon (TOC) Analysis for Pharmaceutical Water using the Phoenix 8000 UV Persulfate TOC Analyzer.

7.5 ASTM D4779 and D 4839. Standard Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection (Withdrawn 2002). ASTM D4839 - 03(2011) Standard Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection.

7.6 Annual Book of ASTM Standards, 1976. Part 31, "Water", Standard D 2574-79. pp. 469.

7.7 Standard Methods for the Examination of Water and Wastewater, 14th Edition, Method 505. pp 53.