METHOD #: 415.2 (Issued December 1982)

TITLE: Organic Carbon, Total (Low Level) (UV Promoted, Persulfate Oxidation)

ANALYTE: CAS # Total Organic Carbon TOC
C 7440-44-0

INSTRUMENTATION: Carbon Analyzer

1.0 Scope and Application

1.1 This method covers the determination of total organic carbon in drinking water and other waters subject to the limitations in 1.3 and 5.1 .

1.2 This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method.

1.3 This method is applicable only to the carbonaceous matter which is either soluble or has a particle size of 0.2 mm or less.

1.4 The applicable range is from approximately 50 μg/L to 10 mg/L. Higher concentrations may be determined by sample dilution.

2.0 Summary of Method

A sample is combined with 1 mL of acidified persulfate reagent and placed in a sparger. The sample is purged with helium which transfers inorganic CO_2 and purgeable organics to a CO_2 scrubber. The CO_2 is removed with at least 99.9% efficiency with a 2.5-minute purge. The purgeable organics proceed through a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is measured by a flame ionization detector. The detector signal is integrated and displayed as the concentration of purgeable organic carbon.

The sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeables are converted to CO_2 and transferred to a second sparger where a helium purge transfers the CO_2 to the reduction system and into the detector. The signal is integrated, added to the purgeable organic carbon value, and displayed as the concentration of total organic carbon:

3.0 Definitions

3.1 Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO_2 scrubber. The definition is instrument- condition dependent.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the purgeable organic carbon from the sample containing acidified persulfate reagent and which is converted to CO_2 under the instrument conditions.

3.4 The system blank is the value obtained in 8.2 for an irradiated, recirculated reagent distilled water sample.

4.0 Sample Handling and Preservation

4.1 Sampling and storage of samples must be done in glass bottles.
Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.

5.0 Interferences

5.1 If a sample is homogenized to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results.

6.0 Apparatus

6.1 Apparatus for blending or homogenizing samples: A household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

6.2 Apparatus for Total Organic Carbon: The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator. This method is based on the Dohrmann Envirotech DC-54 Carbon Analyzer. Other instruments having similar performance characteristics may be used.

6.3 Sampling Devices: Any apparatus that will reliably transfer 10 mL of sample to the sparger. A 50 mL glass syringe is recommended when analyzing samples with easily purgeable organics so as to minimize losses.

7.0 Reagents

7.1 Reagent Distilled Water: Distilled water used in preparation of standards and for dilution of samples should be ultra-pure to reduce the magnitude of the blank. Carbon dioxide-free, double distilled water is recommended. The water should be distilled from permanganate or be obtained from a system involving distillation and carbon treatment. The reagent distilled water value must be compared to a system blank determined on a recirculated distilled water

sample. The total organic carbon value of the reagent distilled water should be less than 60 μg/L. Purgeable organic carbon values of the reagent distilled water should be less than 4 μg/L.

7.2 Potassium hydrogen phthalate, stock solution, 500 mg carbon/liter: Dissolve 1.063 g of potassium hydrogen phthalate (Primary Standard Grade) in reagent distilled water (7.1) and dilute to 1 liter.

7.3 Potassium hydrogen phthalate (2 mg/L): Pipet 4 mL of potassium hydrogen phthalate stock solution (7.2) into a one liter volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.4 Potassium hydrogen phthalate (5 mg/L): Pipet 1 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.5 Potassium hydrogen phthalate (10 mg/L): Pipet 2 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.6 Acidified Persulfate Reagent: Place 100 mL of reagent distilled water (7.1) in a container. Add 5 g of potassium persulfate. Add 5 g (3 mL) of concentrated (85%) phosphoric acid.

7.7 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 mL volumetric flask. Dissolve with reagent distilled water (7.1) and dilute to the mark.

7.8 Carbonate-bicarbonate, standard solution 50 mg/L: Place 5 mL of the carbonate-bicarbonate stock solution in a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

8.0 Procedure

8.1 Allow at least 30 minutes warm-up time. Leave instrument console on continuously when in daily use, except for the ultraviolet light source, which should be turned off when not in use for more than a few hours.

8.2 Adjust all gas flows, temperatures and cycle times to manufacturer's specifications. Perform the "System Cleanup and Calibration" procedure in the manufacturer's specifications each day. Recirculate a sample of irradiated distilled water until two consecutive readings within 10% of each other are obtained. Record the last value for the system blank. This value is a function of the total instrument operation and should not vary significantly from previous runs. Reasons for significant changes in the value should be identified.

8.3 Check the effectiveness of the CO_2 scrubber by analyzing the carbonate-bicarbonate standard solution(7.8). Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of the solution. Transfer 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle. No response, or a very minor reading, should be obtained from this solution.

8.4 Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of reagent distilled water (7.1) blank, standards 7.3, 7.4, and 7.5 and the samples.

8.5 Calibrate the analyzer as follows:

8.5.1 Run the reagent distilled water (7.1) and 5.0 mg/L standard (7.4): Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle.

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and

start the analysis cycle
Record the meter reading (see 9.1) of the final carbon value for each of the reagent distilled water (7.1) and the standard (7.4).
If the meter reading is more than 25% above or below the calculated value of standard 7.4, reanalyze the standard and set the calibration within 25% (8.5.4), reanalyze the system blank, and then begin 8.5.1 again. If the meter reading (see 9.1) is within 25% of the calculated value, continue to next step. The calculated value is defined in 8.5.2.

8.5.2 Calculate the factor for the deviation of the instrument reading (see 9.1) for the standard (7.4) from the calculated value by:

$$\frac{\text{standard reading} - \text{calculated value}}{\text{calculated value}} = \text{FACTOR}$$

where the calculated value is that value obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water (7.1) with which it has been diluted.

8.5.3 Calculate the adjusted reading by:
calculated value + (RDW - (FACTOR X RDW)) = ADJUSTED READING. where RDW = mean reagent distilled water (7.1) value.

8.5.4 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 8.5.3.

8.6 Analyze the standards 7.3 and 7.5 in order to check the linearity of the instrument at least once each day:
Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle
Ignore the meter reading for the first cycle
Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle
Record the meter reading (see 9.1) of the final carbon value for each of the standards 7.3 and 7.5.
The range of concentration used for calibrating the instrument and checking the linearity of the instrument should be ascertained from a knowledge of the range of concentrations expected from the samples.
Standards for lower ranges can be prepared by diluting standards 7.2, 7.3, and 7.4.

8.7 Analyze the samples. Transfer 10 mL of sample with reagent to the first sparger and start the analysis cycle.
Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle
Ignore the meter reading for the first cycle
Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle
Record the meter reading (see 9.1) of the final carbon value for each of the samples.

9.0 Calculations

9.1 The values are read off the final digital readout in μg/L. The system blank reading obtained in 8.2 must be subtracted from all reagent distilled water,

standard and sample readings.

10.0 Precision and Accuracy

10.1 In a single laboratory (MERL), using raw river water, centrifuged river water, drinking water. and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from ten replicates were ±0.13, ±0.03, ±0.02, and ±0.02 mg/L, respectively.

10.2 In a single laboratory (MERL), using potassium hydrogen phthalate in distilled water at concentrations of 5.0 and 1.0 mg/L total organic carbon, recoveries were 80% and 91%, respectively.

Bibliography

1. Proposed Standard Method for Purgeable and Nonpurgeable Organic Carbon in Water (UV-promoted, persulfate oxidation method). ASTM Committee D-19, Task Group 19.06.02.03 (Chairman R. J. Joyce), January 1978.
2. Operating Instruction Dohrmann Envirotech, 3420 Scott Boulevard, Santa Clara, California 95050.
3. Takahashi, Y., "Ultra Low Level TOC Analysis of Potable Waters." Presented at Water Quality Technology Conference. AWWA, Dec. 5-8, 1976.