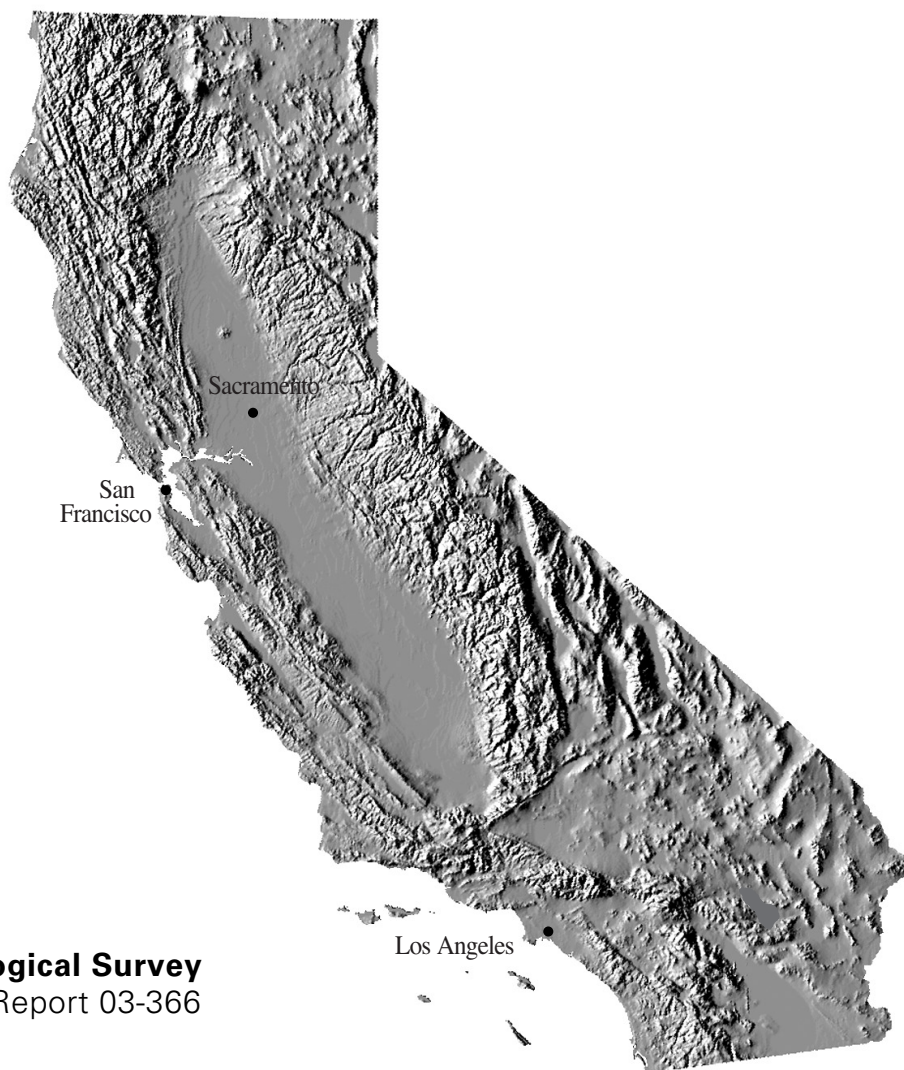


Method of Analysis by the U.S. Geological Survey California District Sacramento Laboratory—Determination of Dissolved Organic Carbon in Water by High Temperature Catalytic Oxidation, Method Validation, and Quality-Control Practices



**U.S. Geological Survey**  
Open-File Report 03-366

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*By Susan M. Bird, Miranda S. Fram, and Kathryn L. Crepeau*

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U.S. GEOLOGICAL SURVEY

Open-File Report 03-366

8006-51

Sacramento, California  
2003

**U.S. DEPARTMENT OF THE INTERIOR**

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**U.S. GEOLOGICAL SURVEY**

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# CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

## CONVERSION FACTORS

	<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
	gram (g)	0.03527	ounce, avoirdupois
	millimeter (mm)	0.03937	inch

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

## ABBREVIATIONS

mg/L	milligram per liter
µm	micrometer
µS/cm	microsiemens per centimeter
mm	millimeter
mL	milliliter
mS/m	millisiemens per meter
psi	pounds per square inch
µL	microliter
mL/min	milliliter per minute
CO <sub>2</sub>	carbon dioxide
CO	carbon monoxide
NaHCO <sub>3</sub>	sodium bicarbonate
NaCl	sodium chloride
HCl	hydrochloric acid
ppm	parts per million

## ACRONYMS

CV	coefficient of variation
DIC	dissolved inorganic carbon
d	duplicate
Dil	dilution
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
GR#	LIMS number
HC	hydrocarbon
KHP	potassium hydrogen phthalate, C <sub>8</sub> H <sub>5</sub> KO <sub>4</sub>
LIMS	laboratory information management system

LRL	laboratory reporting level
LT-MDL	long-term method detection limit
MDL	method detection limit
N	normal
NPOC	non-purgable organic carbon
NWIS	U.S. Geological Survey National Water Information System database
OWQRL	U.S. Geological Survey Ocala Water-Quality and Research Laboratory
SD	standard deviation
THMFP	trihalomethane formation potential
TOC	total organic carbon
USGS	U.S. Geological Survey



# **Method of Analysis by the U.S. Geological Survey California District Sacramento Laboratory— Determination of Dissolved Organic Carbon in Water by High Temperature Catalytic Oxidation, Method Validation, and Quality-Control Practices**

By Susan M. Bird, Miranda S. Fram, and Kathryn L. Crepeau

## **ABSTRACT**

An analytical method has been developed for the determination of dissolved organic carbon concentration in water samples. This method includes the results of the tests used to validate the method and the quality-control practices used for dissolved organic carbon analysis. Prior to analysis, water samples are filtered to remove suspended particulate matter. A Shimadzu TOC-5000A Total Organic Carbon Analyzer in the nonpurgeable organic carbon mode is used to analyze the samples by high temperature catalytic oxidation. The analysis usually is completed within 48 hours of sample collection. The laboratory reporting level is 0.22 milligrams per liter.

## **INTRODUCTION**

Accurate, precise, and timely measurements of dissolved organic carbon (DOC) concentrations are essential for studies of the roles of natural organic matter in environmental, ecological, and geochemical processes. The capability to analyze DOC was established at the U.S. Geological Survey (USGS)

California District research laboratory in Sacramento to provide analytical support for research projects concerning natural organic matter in the Sacramento-San Joaquin Delta in central California.

Research projects in the California District range from water-quality investigations to subsidence mitigation studies. Oxidation of peat islands in agricultural production is a primary cause of land subsidence in the Delta (Miller and others, 2000). The subsidence mitigation research projects involve construction of wetland systems on Twitchell Island in the Delta and detailed investigation of carbon cycling and soil accretion in these wetlands. DOC is an important component of the carbon mass balance in the wetlands.

The Delta is the source of drinking water for more than 22 million Californians as well as the primary source of the organic carbon that feeds the base of the food web in the San Francisco Bay Estuary. DOC enters the Delta channels mainly from wetlands, agricultural lands, and urban runoff. The quantity (concentration and load) and quality (compositional characteristics) of the DOC in the Delta is critically important to the drinking water and ecological functions of the water. Water-quality research projects on DOC include chemical characterization and quantification of loads from different sources and land-use practices. Chemical characterization has focused on disinfection by-product formation potentials, optical

properties, microbial utilization, and stable isotopic values. DOC reacts with disinfectants added during the drinking water-treatment process to produce an array of potentially carcinogenic disinfection by-products, including trihalomethanes and haloacetic acids. Analyses of disinfection by-product formation potentials and optical properties require DOC concentrations and must be performed as rapidly as possible after sample collection because the concentrations may change as the DOC in the samples ages (K.L. Crepeau, U.S. Geological Survey, written commun., 2003; E. Kalve, U.S. Geological Survey, written commun., 2003). Standard procedures for sample preservation are not used in this method because they may change the quality (not the quantity) of the DOC.

DOC analyses must be made with great care because there are many potential pitfalls, including contaminated blank water, insufficient removal of inorganic carbon, inefficient oxidation of all the organic carbon, and treatment of difficult samples (Hedges and others, 1993; Urbansky, 2001; Aiken and others, 2002). A method was not developed for total organic carbon (TOC) because of the known problems with analysis of particulates by instrumentation used for DOC analyses (Aiken and others, 2002).

## **METHOD OF ANALYSIS OF DISSOLVED ORGANIC CARBON IN WATER (PARAMETER CODE 00681) BY HIGH TEMPERATURE CATALYTIC OXIDATION (U.S. GEOLOGICAL SURVEY METHOD NUMBER 0-2201-04)**

### **Scope and Application**

The analytical method used by the USGS California District research laboratory in Sacramento is suitable for the analysis of filtered water samples containing at least 0.2 milligrams per liter (mg/L) of DOC. The calibration range for the method is 0 to 50 mg/L. Water samples with DOC concentrations greater than 50 mg/L are diluted and reanalyzed.

### **Summary of Method**

Water samples are collected and filtered to remove suspended particulate material. A number of different collection and filtration methods are used, depending on the source and size of the water sample. Filtered water samples are stored at 4°C either with no added preservative or with concentrated hydrochloric acid (HCl) added to pH of 2 until analysis if stored for more than 3 weeks. All samples are logged into the laboratory's information management system (LIMS; Labworks, Analytical Automation Specialists, Inc.) and assigned a unique laboratory identification number. Analysis of the sample generally is performed within 48 hours of arrival at the lab.

DOC analyses are made using a Shimadzu Total Organic Carbon Analyzer (Shimadzu TOC-5000A) with a Shimadzu Autosampler (Shimadzu ASI-5000A). Inorganic carbon is removed from the samples by automated acidification with HCl to a pH of approximately 2 and purging of the resulting carbon dioxide (CO<sub>2</sub>) with high purity air. High purity air is a composite air made of pure nitrogen and pure oxygen. The air does not contain more than 1 part per million (ppm) each of carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), and hydrocarbon (HC), respectively (Shimadzu Corporation, 1997). Organic carbon is oxidized to CO<sub>2</sub> by high-temperature catalytic oxidation and the CO<sub>2</sub> is measured by a nondispersive infrared detector. Detector response is linear and calibrated (for each run) with standards containing known concentrations of potassium hydrogen phthalate (KHP).

### **Equipment and Materials**

The equipment and materials used for analysis of DOC are listed in [table 1](#). DOC analysis procedure is performed in a laboratory that contains no organic solvents to eliminate vapor-phase contamination of the water. Organic-free water is produced onsite with a recirculating Picotech water system (Hydro Service and Supplies, Inc.). Inlet water for the Picotech system is deionized and produced onsite with an Ionics Ultra Pure water system. Scheduled routine maintenance and replacement of cartridges is done on the Picotech and Ionics Ultra Pure water systems.

Table 1. Laboratory equipment and reagents used for analysis of dissolved organic carbon

#### Equipment

- Shimadzu TOC-5000A TOC Analyzer
- Shimadzu ASI-5000A Autosampler
- Clean, amber glass bottles with Teflon-lined lids from the U.S. Geological Survey Ocala Water-Quality Laboratory in Ocala, Florida
- Computer with Shimadzu Total Organic Carbon Control software (version 1.05.01)
- Clean autosampler vials, 45- and 6-milliliter sizes (Shimadzu Corporation)
- Clean, class A volumetric flasks
- Analytical balance, certified accuracy of 0.050 gram  $\pm$  0.0001
- 250 microliter syringe (Hamilton Company)
- Motorized microliter pipettes (Rainin Instrument Company, Inc.) with disposable tips

#### Reagents

- Ultra-high purity dry, carbon-free air (Airgas)
- Hydrochloric acid, concentrated, American Chemical Society grade, certified organic carbon content less than 0.5 percent
- Potassium hydrogen phthalate, minimum 99.95-percent purity
- Ultra-pure, organic carbon-free, deionized water (Picosystem Plus, Hydro Service and Supplies, Inc.)
- Sodium hydroxide, certified American Chemical Society grade

The organic-free water is tested frequently by direct analysis of DOC (see section in this report on Quality-Control Practices, instrument blanks) and by analysis of trihalomethane formation potential (THMFP). THMFP is determined by chlorinating the water sample and then measuring the amount of trihalomethane produced after a 7-day incubation period. The organic-free water generally has a THMFP of 1 to 2 micrograms per liter (K.L. Crepeau, U.S. Geological Survey, written commun., 2003). Most reported specific THMFP values for natural DOC in water samples are between 1 and 15 carbon atoms per 1,000 carbon atoms in the DOC (Oliver and Thurman, 1983; Reckhow and others, 1990; and Fram and others, 1999). Assuming that the contaminant is natural DOC, a THMFP of 1 to 2  $\mu\text{g/L}$  translates into a DOC concentration of less than 0.005 mg/L in the organic-free water.

Vials and other glassware items used for DOC analysis are cleaned rigorously. Glassware is washed with dilute Liqui-Nox soap and rinsed with copious amounts of organic-free water. Openings are covered with aluminum foil and then the glassware is baked for 4 hours at 450°C in a muffle furnace. Baked glassware is stored in closed drawers or cabinets until use. Glass-fiber filters are baked under the same conditions. Samples are stored in baked, amber glass bottles with

Teflon-lined caps supplied by the USGS Ocala Water-Quality Laboratory (OWQRL). These bottles, made of virgin glass, were baked at 500°C for 1.5 hours and, thus, are used without further cleaning. The bottles can be reused if necessary and will go through the cleaning process mentioned above.

#### Sample Collection, Filtration, and Storage

The specific methods used for sample collection and filtration varies with the field setting and the volume of the sample being collected. However, all methods used have several important features in common: only clean glass, steel, or Teflon comes in contact with the sample; no organic solvents are used to clean the sampling and filtration apparatuses; and samples are filtered in the field or in the laboratory within 24 hours of collection. Many samples are filtered in 47-mm diameter Teflon filtration towers (Savillex). The samples drip through 0.3 or 0.7-micron pore size baked glass fiber filters by gravity. A stack of baked glass fiber filters consisting of 2.7-, 1.6-, and 0.3-micron pore size filters is often used to slow clogging of the 0.3-micron pore size final filter. The filtration methods described in the USGS National Field Manual section 5.2.2.C (Radtke and others, 2002) also are commonly used.

Filtered samples are stored at 4°C until analysis. If samples are to be stored for longer than 3 weeks, they are preserved by addition of reagent-grade, concentrated HCl. Sufficient HCl is added to lower the pH of the sample to 2. Although acidification does not change the DOC concentration, it can change the DOC quality (E. Kalve, U.S. Geological Survey, written commun., 2003).

## Standards

Solutions of potassium hydrogen phthalate (KHP, C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>) are used as analytical standards. The 1,000-milligrams per liter DOC stock solution is prepared by weighing 1.0625 grams of KHP with an analytical balance and dissolving it in organic-free water in a 500-milliliter volumetric flask. This stock solution can be stored in a baked amber glass bottle for as long as 2 months at 4°C (Shimadzu Corporation, 1997). Calibration standard solutions are prepared from the stock solutions using volumetric glassware and pipettes with concentrations ranging from 0.5 to 50.0 mg/L DOC. These solutions can be stored for as long as 1 week at 4°C.

Standard curves are constructed using four appropriate standard concentrations per curve. Samples with DOC concentrations less than 2 mg/L are analyzed with a standard curve comprising 0-, 0.5-, 1.0-, and 2.0-milligrams per liter calibration standards. Samples with DOC concentrations between 2 and 10 mg/L are analyzed with a standard curve comprising 0-, 2.5-, 5.0-, and 10-milligrams per liter calibration standards, and samples with DOC concentrations between 10 and 50 mg/L are analyzed with a standard curve comprising 0-, 10.0-, and 20.0-, and 50-milligrams per liter calibration standards.

## Carbon Analyzer Performance

The procedures for operating the Shimadzu TOC-5000A and ASI-5000 are adapted from the Shimadzu operation manual (Shimadzu Corporation, 1997) and Standard Method 5310B (American Public Health Association and others, 1995). The operational parameters for the Shimadzu TOC-5000A are as follows:

Gas: Ultra high purity dry CO<sub>2</sub>-free air, 80 pounds per square inch (psi)

Carrier gas flow rate: 150 milliliters per minute (mL/min)

Purge gas flow rate: 50 mL/min (adjust such that samples do not bubble out of the vials during purging)

Combustion temperature: 680°C

Combustion tube packing (from base): two sheets platinum net, 5-millimeter quartz wool (regular sensitivity only), 110-millimeter catalyst

Analysis mode: non-purgeable organic carbon (NPOC)

Rinses: two with water and two with sample

Injection size: 100 microliters (μL) for high sensitivity and 53 or 55 μL for regular sensitivity

Injection number: three, maximum five

The Shimadzu TOC-5000A can be configured with a regular or high sensitivity combustion catalyst. The regular sensitivity catalyst consists of platinum-coated alumina beads (Shimadzu part number: 017-42801-01) and is used for analysis of samples with DOC concentrations greater than 2 mg/L. The catalyst accumulates salts from the samples with usage and some of the beads crack. The catalyst can be removed for rinsing with water to remove salts and sieving to remove broken beads. The high sensitivity catalyst consists of platinum-coated quartz wool (Shimadzu part number: 630-00996-00) and is used for analysis of samples with DOC concentrations less than 2 mg/L. It is discarded after the quality-control numbers show that its performance has deteriorated (see Quality-Control Practices section in this report).

Before any standards or samples are analyzed, organic-free water is analyzed until the reported peak area reaches an acceptably low and stable value. Peak areas of 1,000-area counts for a 100-microliter injection of organic-free water in high sensitivity mode, and 2,250 area counts for a 53-microliter injection in regular sensitivity mode are acceptable. It can take more than 100 injections to reach an acceptably low peak area value. Failure of the peak area to reach an acceptably low and stable value indicates that replacement of the combustion catalyst is needed.

Samples, standards, and blanks are acidified with HCl and purged for 3 minutes with high purity air before analysis. This procedure removes dissolved inorganic carbon from the sample. Purging is automated with the Shimadzu ASI-5000A and acid addition may be done manually or by the autosampler. A subset of samples are pretested to determine the

amount of acid required to reduce sample pH to less than 2.5. Amounts generally range from 15 to 40  $\mu\text{L}$  of 0.5–2.0 N HCl for 5 milliliters of sample.

Initial calibration curves are generated before any samples are analyzed. The computer software generates a linear regression equation for detector response (peak area) over the concentration range of the calibration curve. The detector response for each standard is the mean of three injections from the same vial. The computer software calculates the coefficient of variation (CV) and standard deviation (SD) of the three injections using the following equations:

$$\bar{C} = \frac{\sum_{i=1}^n C_i}{n} \quad (1)$$

$$SD = \sqrt{\frac{\sum_{i=1}^n (C_i - \bar{C})^2}{n - 1}} \quad (2)$$

$$CV = \frac{SD}{\bar{C}} \times 100\% \quad (3)$$

where

---

$C_i$  = DOC concentration in the  $i^{\text{th}}$  injection

$n$  = number of injections

$\bar{C}$  = average DOC concentration.

---

If the CV is greater than 2 percent and the SD is greater than 200 area counts, as many as two additional injections can be made and the combination of three injections that yields the lowest coefficient of variation and standard deviation is chosen. If the correlation coefficient of the regression is greater than 0.999 and the CV of each standard is 2 percent or less or the SD is 200 area counts or less, the calibration is accepted. For regular sensitivity runs, two separate standard curves

are generated—the first with calibration standards of 0, 2.5, 5.0, and 10.0 mg/L and the second with calibration standards of 0, 10.0, 20.0, and 50.0 mg/L. If the samples are known to be less than 10 mg/L, then only the calibration standards of 0, 2.5, 5.0, and 10.0 mg/L are generated. Both standard curves encompass the same range in peak area counts because the instrument automatically adjusts the gain for the detector response such that the response for the 0–50 mg/L standard curve is one-fifth of the response of the 0–10-milligram per liter standard curve. The computer software selects injection volumes such that the highest concentration calibration standard in each standard curve yields a peak area of approximately 36,000 counts.

When a sample is analyzed, the first injection is compared to the first standard curve. If the peak area exceeds the range of the first standard curve, the computer software automatically adjusts the injection volume to match that of the second standard curve for the remaining injections. The measured peak areas then are compared to the second standard curve.

In addition to the standard curve, an analytical sample run includes analysis of standards as calibration verification samples, duplicates, and blanks. A typical sample run documentation sheet is shown in [figure 1](#).

## Data Processing and Archiving

The computer software calculates the mean DOC concentration, SD, and CV for each sample in the analytical run. The instrument operator transfers the mean DOC results to an Excel spreadsheet and scrutinizes the results after each run. Acceptance criteria for results of analyses of standards run as unknowns, duplicates, and blanks are discussed in the section “Quality-Control Practices” of this report. If quality-control criteria are not met, the samples are rerun. The Excel spreadsheets for each analytical run are stored electronically on a local computer and are backed up weekly on the USGS California District’s computer back-up system. The spreadsheets also are printed and stored by the instrument operator.

**DOC Run Sheet**

Standards	mean area
blank	1589
2.5 ppm	11042
5 ppm	19649
10 ppm	38251

Run Date:	8-19-02
Analyst:	SB
Sensitivity:	regular
Max. samples: 44	

r2 = .999799  
 d = duplicate  
 v = verification samples

Circled #'s have a standard deviation > 200 and a CV > 2%. For rerun.

#	Samples	GR#	Dil	DOC	ppm	%
					Final DOC	
1	blank				0.037	
2	2.5 v				2.517	100.7
3	5 v				4.986	99.7
4	10 v				10.08	100.8
5	blank				0.019	
6	blank				0.018	
7	Tw-0503				3.751	
8	Tw-0504				3.736	
9	Tw-0501				3.461	
10	Tw-0502				1.654	
11	Tw-0503 d				3.720	99.2
12	Tw-0504 d				3.651	97.7
13	blank				0.161	
14	2.5 v				2.557	102.3
15	5 v				4.976	99.5
16	10 v				10.04	100.4
17	blank				0.058	
18	Tw-0503				3.719	
19	Tw-0504				3.615	
20	Tw-0501				3.393	
21	Tw-0502				1.683	
22	Tw-0503 d				3.558	95.7
23	Tw-0504 d				3.539	97.9
24	blank				0.032	
25	2.5 v				2.517	100.7
26	5 v				4.942	98.8
27	10 v				9.936	99.4
28	blank				0.062	
29	blank				-0.010	
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						

#	Samples	GR#	Dil	DOC	ppm	%
					Final DOC	
40						
41						
42						
43						
44						
45						
46						
47						
48						
49						
50						
51						
52						
53						
54						
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78						

Figure 1. Typical sample run documentation sheet.

(DOC, dissolved organic carbon; ppm, parts per million; SB, Susan Bird; r2, coefficient of determination of the slope of the standard curve; d, duplicate; #, number; GR#, Laboratory Information Management System number; dil, dilution; %, percent; CV, coefficient of variation; >, greater than; Max., maximum; v, verification samples)

After quality-control criteria are met satisfactorily, the instrument operator transfers the final DOC concentrations to the laboratory information management system (LIMS) into the appropriate location. Because all samples are logged into the LIMS and assigned a unique identification number, DOC data are archived easily. The LIMS entries are checked by the instrument operator and by the chief or designate of the research project for which the samples were analyzed, and then flagged as “verified”. The entire LIMS database is mirrored daily to a second hard-drive and backed up weekly on the USGS California District’s external, secure data back-up system. Procedures are being developed to export DOC concentrations from the LIMS database to the USGS National Water Information System (NWIS) database.

## Difficult Samples

Many of the research projects require analysis of soil pore water extracts or ground-water samples. These water types can be difficult to analyze because they may flocculate under laboratory or analysis conditions. For example, samples collected from piezometers installed in the deep ground-water system beneath the peat layer on Twitchell Island often contain high concentrations of dissolved iron. Upon exposure to the atmosphere, the iron precipitates – and DOC can be sorbed to the iron precipitate. Samples collected from piezometers installed in the peat soil or aqueous extracts of the peat soils produced in the laboratory often contain very high concentrations of DOC and sometimes flocculate when acidified. The fraction of DOC that precipitates at a pH of 2 is defined as the humic acid fraction (Thurman, 1985). Flocculation of DOC and formation of precipitates may interfere with DOC analysis because particles may not be sampled reliably by the narrow-bore needle, syringe, and tubing in the carbon analyzer and because particles may not be efficiently oxidized to CO<sub>2</sub> during combustion of the sample (Aiken and others, 2002).

Three strategies are used to minimize the flocculation of DOC from peat soil water samples. First, samples that flocculate can be diluted with organic-free water using volumetric pipettes and reanalyzed.

Second, samples that flocculate are acidified with the minimum amount of acid necessary to assure removal of dissolved inorganic carbon (DIC). A test was done to determine the pH value required to assure removal of DIC. The sample pH value required to assure removal of DIC was determined using a sample (that was known to flocculate) containing 3.6 mg/L DOC and 30 mg/L DIC [added as sodium bicarbonate (NaHCO<sub>3</sub>)]. The sample was acidified to pH values ranging from 8.3 to 1.9. The DOC concentration decreased as pH decreased from 8.3 to about 2.7 and then remained roughly constant as pH decreased further ([fig. 2](#)). The results indicated that acidification to pH < 2.7 is necessary for removal of DIC ([fig. 2](#)). For samples that flocculate, acidification to lower pH values increases the amount of flocculation. (The standard procedure for samples that do not flocculate involves acidification to a pH of 2 because adding excess acid insures against incomplete removal of DIC from the occasional sample with a very high concentration of DIC.) The analyst must test the sample to ensure that the correct amount of acid is added to reach a pH of less than or equal to 2.7.

Third, samples that flocculate are analyzed as soon as possible after acidification. Flocculation generally occurs during a period of hours. The Shimadzu ASI-5000A acidifies all of the samples prior to beginning analysis of the first sample. Thus, samples placed near the beginning of the run will be analyzed sooner after acidification. Alternatively, samples can be acidified manually just prior to analysis. In most cases, these three strategies are sufficient to permit analysis of samples that have a tendency to flocculate.

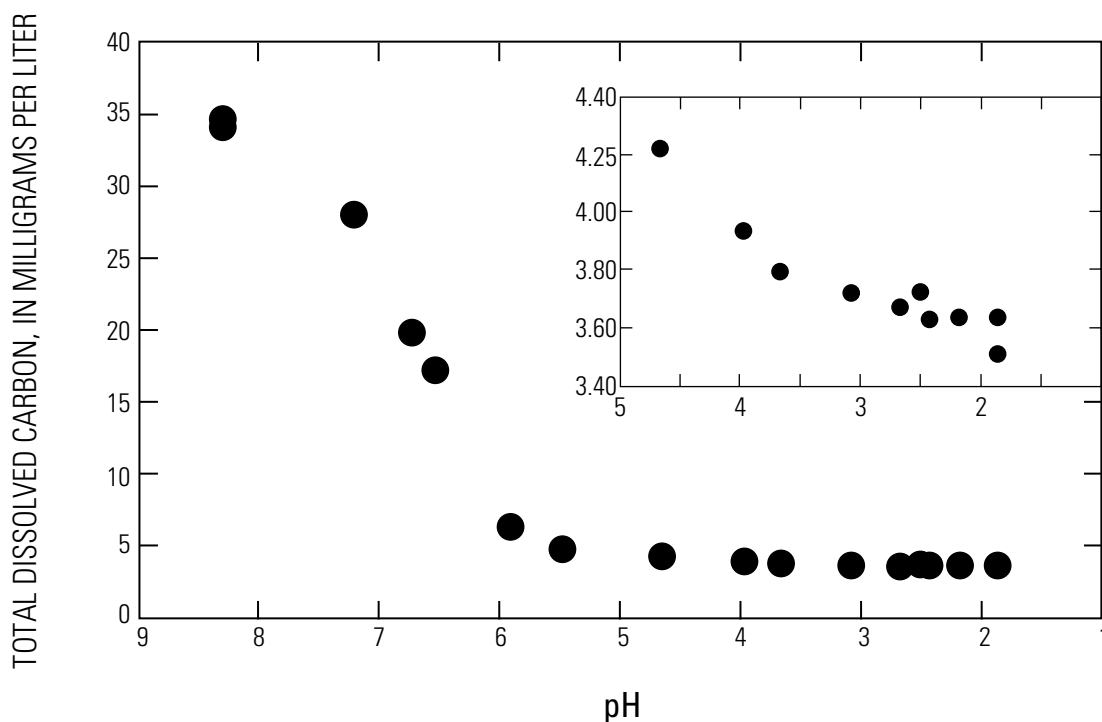


Figure 2. Variation in measured total dissolved carbon concentration as a function of pH for a sample containing 3.6 milligrams per liter (mg/L) dissolved organic carbon and 30 mg/L dissolved inorganic carbon. Inset shows data at low pH with an expanded scale on the total dissolved carbon axis.

## METHOD VALIDATION

Several tests were done to validate the analytical method. Precision was assessed by replicate analyses of several samples that represent the types of samples collected during research projects as well as by replicate analyses of standards analyzed as calibration verification samples (fig. 2). Overall method performance was evaluated by analyzing test samples similar to those used by Aiken and others (2002). The method detection limit (MDL) and laboratory reporting level (LRL) were determined from replicate analyses of calibration verification standards and instrument blanks.

### Precision

Analytical precision is expressed in terms of the coefficient of variation of replicate analyses of a water sample (eq. 3). Three standard solutions and five representative water samples were analyzed 10–12 times (table 2). The 1.0-milligram per liter DOC standard and sample Twa-0450 were analyzed using the high sensitivity combustion catalyst; whereas, the 5.0- and 20.0-milligram per liter DOC standards and

samples Swa-0439, Twa-0160, and Cfa-Y0056 were analyzed with the regular sensitivity catalyst. Swa-0439 was a surface-water sample with a specific conductance of 900 microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ ) at 25°C. Twa-0450 was 201  $\mu\text{S}/\text{cm}$ . Twa-0160 was 368  $\mu\text{S}/\text{cm}$ . Cfa-Y0056 was a column eluate obtained during fractionation of DOC in a surface water sample by XAD-4 resin column chromatography. The standard solutions yielded estimates of method precision ranging from 0.7 to 1.6 percent; whereas, the water samples yielded estimates ranging from 0.3 to 2.9 percent (table 2). The lower precision estimated from replicate analyses of natural water samples may reflect slight heterogeneities present in natural water samples. Estimates of method precision were similar for the high sensitivity and regular sensitivity catalysts (table 2). Based on these results, the reported precision for DOC analyses is estimated conservatively as 3 percent for DOC concentrations between 1 and 25 mg/L and 10 percent for DOC concentrations less than 1 mg/L. For comparison, the USGS National Water-Quality Laboratory determined method precision ranging from 8.4 percent at a DOC concentration of 0.3 mg/L to 1.3 percent at a DOC concentration of 17.9 mg/L (Brenton and Arnett, 1993).



**Table 2.** Analytical precision for dissolved organic carbon analyses of standard solutions and representative water samples

[mg/L, milligram per liter; H, high sensitivity catalyst; R, regular sensitivity catalyst; NA, not applicable]

Sample	Catalyst	Number of replicates	Mean concentration (mg/L)	Range of concentrations (mg/L)	Standard deviation of replicates (mg/L)	Coefficient of variation of replicates (percent)
Instrument blanks	H	336	0.021	-0.125–0.147	0.047	NA
0.33-milligram per liter standard	H	11	0.340	0.292–0.403	0.033	9.8
1.0-milligram per liter standard	H	11	1.000	0.982–1.022	0.014	1.4
Twa-0450	H	11	1.680	1.618–1.747	0.045	2.7
5.0-milligram per liter standard	R	10	5.053	4.976–5.218	0.080	1.6
Swa-0439	R	12	5.256	4.997–5.578	0.155	2.9
20.0-milligram per liter standard	R	10	20.23	20.10–20.56	0.13	0.7
Twa-0160	R	10	19.91	19.11–20.68	0.56	2.8
Cfa-Y0056	R	10	22.39	22.23–22.47	0.08	0.3
Tw-0653 (diluted sample)	R	11	18.56	17.79–19.06	0.37	2.0

A precision of 3 percent indicates that for DOC concentrations less than 10 mg/L, the digit in the hundredths place is significant, and the digit in the tenths place is significant for DOC concentrations greater than 10 mg/L (American Society for Testing and Materials, 1993). DOC concentrations are reported with one digit beyond the last significant digit.

### Method Detection Limit and Laboratory Reporting Level

The U.S. Environmental Protection Agency (EPA) defined the method detection limit (MDL) as the minimum concentration that can be measured and reported as greater than zero at the 99-percent confidence level (U.S. Environmental Protection Agency, 1997). Two estimates were made of the MDL for the DOC analytical method. The first estimate was calculated according to the procedure specified by the U.S. Environmental Protection Agency (1997).

The MDL was calculated using the formula:

$$MDL = SD \times t_{(n-1, \alpha=0.01)} \quad (4)$$

where

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*MDL* = method detection limit,  
*SD* = standard deviation of replicate analyses at the lowest concentration (in milligrams per liter),

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*n* = number of replicate analyses, and  
 $t_{(n-1, \alpha=0.01)}$  = Student's *t*-test value for the 99-percent (1- $\alpha$ ) confidence level with *n* - 1 degrees of freedom. (Student's *t*-test addresses the problems associated with inference based on small samples).

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The MDL is determined from replicate analyses of a standard with a concentration of no greater than five times the MDL. Eleven replicate analyses of a standard with a DOC concentration of 0.33 mg/L yielded an MDL of 0.08 mg/L DOC (table 2).

The second estimate of the MDL was based on the procedure for determining the long-term MDL (LT-MDL) specified in Oblinger Childress and others (1999). The LT-MDL is calculated using the same formula as the MDL (eq. 4), but the replicate analyses of the low-concentration spike sample are made during an extended period of time, typically 6–12 months. Both procedures assume that the SD of replicate analyses is constant at low concentrations and, thus, the SD of replicate analyses of a low-concentration spike sample equals the SD of replicate analyses of a hypothetical sample containing a concentration of zero. We used the measured DOC concentration in replicate analyses of instrument blanks to estimate the LT-MDL. The high sensitivity catalyst was used to analyze 336 blanks in 38 separate runs between May 2002 and May 2003 (table 2). These analyses yielded an estimate of the LT-MDL of 0.11 mg/L, which is similar to the MDL estimated using the first procedure.

The laboratory reporting level (LRL) is defined as the minimum concentration that can be measured and reported as greater than the MDL at the 99-percent confidence level and is equal to twice the MDL (Oblinger Childress and others, 1999). The LRL for the DOC method is estimated to be 0.22 mg/L. Concentrations between the MDL and the LRL are reported, but are considered only semi-quantitative.

## Method Performance Evaluation

Overall method performance was evaluated by analyzing test samples similar to those used by Aiken and others (2002) in an interlaboratory comparison study designed to assess the relative accuracy of determination of DOC and TOC by different laboratories, instruments, and analysts. A set of standards was prepared and sent to 31 laboratories for analysis of TOC and DOC. To evaluate the performance of the DOC analysis method used in the USGS California District Laboratory, a set of standards similar to the set used by Aiken and others (2002) was prepared and analyzed. Because the method is not applicable to TOC, only DOC standards were prepared. Standards were prepared from reagent-grade KHP, technical-grade caffeine, and five different fulvic acid isolates. The organic carbon contents of the fulvic acid isolates were determined by elemental analysis, and the KHP and caffeine were assumed to have stoichiometric compositions. Solutions of each standard were prepared using clean volumetric glassware and organic-free water. The DOC concentration range for the dissolved standards was 3 to 5 mg/L. KHP is oxidized easily and, thus, easy to analyze. Caffeine was chosen because it is more difficult to oxidize than is KHP and, therefore, may be more difficult to analyze. Fulvic acid is naturally occurring DOC and constitutes

a large proportion of the DOC in most water samples. Fulvic acid contains refractory organic material and, thus, may be more difficult to oxidize than KHP.

The effect of sample matrix on analytical accuracy was examined by amending solutions with DIC or sodium chloride (NaCl). Each standard was divided into three aliquots. One aliquot was amended with reagent-grade sodium bicarbonate ( $\text{NaHCO}_3$ ) to yield a solution with a DIC concentration of 30 mg/L. A second aliquot was amended with reagent-grade NaCl to yield a solution with a specific conductance of 630  $\mu\text{S}/\text{cm}$  at 25°C (a chloride concentration of 182 mg/L). The standards were prepared and labeled by a laboratory chemist and submitted to the DOC instrument operator with no information other than a LIMS number.

Analytical results for the standard solutions are compared to the calculated DOC concentrations in figure 3. No systematic differences were seen between DOC concentrations in sample aliquots with the three different matrices (no additions, added DIC, and added NaCl). This indicates that the analytical method is successful in analyzing DOC in the presence of moderate amounts of potential interferences from DIC and chloride. For KHP, caffeine, and three of the fulvic acid samples (FA3–5) the measured concentrations were within  $\pm 3$  percent of the calculated concentration (fig. 3). A relative accuracy of  $\pm 3$  percent for analysis of DOC concentrations is significantly better than the  $\pm 20$  percent required for EPA-certified laboratories and better-than-average relative accuracies reported in Aiken and others (2002) interlaboratory comparison. The other two fulvic acid samples had measured DOC concentrations that were 14 to 22 percent lower than the calculated concentrations (fig. 3). The poor accuracy for these two samples may be due to incomplete dissolution of the fulvic acid solids during preparation of the samples.

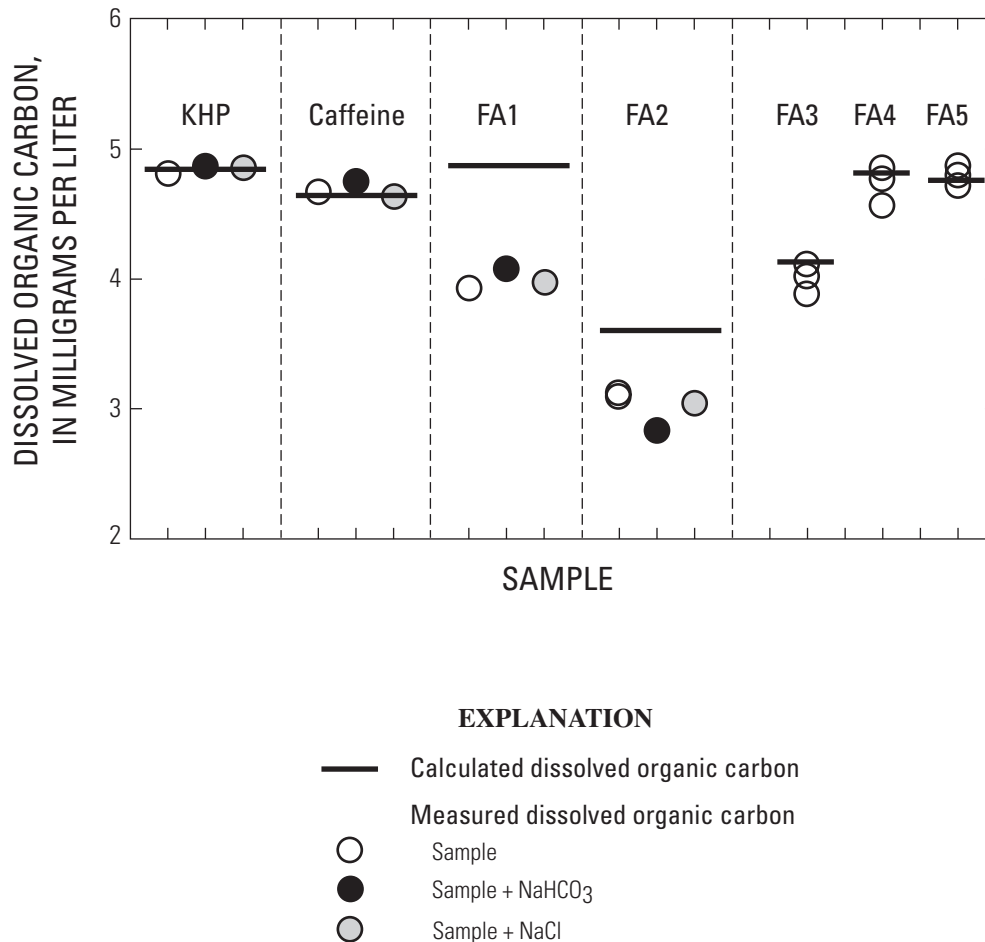


Figure 3. Measured and calculated dissolved organic carbon (DOC) concentrations in samples of potassium hydrogen phthalate (KHP), caffeine, and five natural fulvic acid (FA) isolates. (NaHCO<sub>3</sub>, sodium bicarbonate; NaCl, sodium chloride)

## QUALITY-CONTROL PRACTICES

Several different types of quality-control samples are analyzed regularly. These include field blanks, instrument blanks, duplicate field samples, duplicate analysis samples, and standards analyzed as unknown samples. Acceptance criteria for results of analyses of quality-control samples and corrective actions prescribed in response to unacceptable quality-control results have been established in this study.

### Blank Samples

Field blanks are samples of organic-free water filtered under the same conditions as the environmental samples. The purpose of a field blank is to verify that there is negligible contamination of samples with DOC

during the entire sample collection and filtration protocol. For sample collection and filtration protocols that involve filtration at the collection site, the field blank is collected from a carboy of organic-free water that is brought to the collection site. Field blanks are collected at the inception of a new sample collection and filtration protocol, when a protocol is modified, at the beginning of a new research project, and at intervals of approximately 6 months for ongoing research projects. Field blanks are entered into the LIMS and analyzed as samples. Because field blanks contain low concentrations of DOC, they are analyzed using the high sensitivity combustion catalyst. A measured DOC concentration in a field blank above the MDL necessitates a thorough examination of each step of the collection and filtration protocol to determine the source of the contaminant and eliminate it. Such occurrences are rare for established protocols.

Instrument blanks are samples of organic-free water that are put directly into the autosampler vials. Instrument blanks serve several purposes. Blanks placed directly after samples or standards with high DOC concentrations are used to assess the amount of carry-over between samples. Blanks analyzed at intervals during the run (fig. 1) are used to track the drift of the detector baseline. Baseline drift of greater than 0.05 mg/L correlates with unacceptable results for the calibration verification samples. Baseline drift is minimized by running a sufficient number of blank injections before the calibration curve is generated.

## Duplicate Samples

A minimum of 10 percent of samples are collected in duplicate for research projects involving collection of water samples at field sites. Research projects involving generation of water samples in the laboratory have sample duplication rates ranging from 10 to 100 percent, depending on the design of the project. Duplicate samples are entered into the LIMS and analyzed as distinct samples. The purpose of collecting duplicate water samples from field sites is to verify that the sample-collection and filtration protocols, the laboratory sample handling procedures, and the analytical methods all are reproducible. Duplicate samples also are used to test the reproducibility of laboratory experiments.

Instrument duplicates are aliquots of one sample that are placed in separate autosampler vials. Two samples from every set of 10 samples are selected randomly to be analyzed in duplicate. The duplicate vials are placed at the end of the set of 10 samples (fig. 1). The reproducibility of instrument duplicates ( $R_{dup}$ ) is reported as the percent relative agreement between the two analyses and is calculated as follows:

$$R_{dup} = 100 + \left( \frac{C_1 - C_2}{(C_1 + C_2)/2} \right) \times 100 \quad (5)$$

where  $C_1$  and  $C_2$  are the DOC concentrations from first and second analyses, respectively.

$R_{dup}$  values between 97 and 103 percent are acceptable.  $R_{dup}$  values between 95 and 97 percent or between 103 and 105 percent are in the cautionary range.  $R_{dup}$  values less than 95 percent or greater than 105 percent are unacceptable. If  $R_{dup}$  values for both

instrument duplicates analyzed in a set of 10 samples are unacceptable, then the entire set of samples must be reanalyzed. If only one  $R_{dup}$  value is unacceptable, then that sample is reanalyzed and the remaining samples in the set also may be reanalyzed if the calibration verification samples for that set of samples are also unacceptable.

## Calibration Verification

Calibration verification samples are aliquots of the calibration standards that are analyzed as unknown samples. A full complement of calibration verification samples are analyzed at the beginning and end of each run, and two additional calibration verification samples are analyzed between each set of 10 environmental samples (fig. 1). The degree to which the measured concentrations reproduce the known concentrations of the standards ( $R_{std}$ ) is reported as the percent relative agreement and is calculated as follows:

$$R_{std} = \frac{C}{C_{std}} \times 100 \quad (6)$$

where  $C$  and  $C_{std}$  are the measured and known concentrations, respectively.

The acceptance criteria for  $R_{std}$  values are the same as the criteria for  $R_{dup}$  values.

## Standard Deviation and Coefficient of Variation

The DOC concentration for each sample represents the mean value obtained for three injections of sample from the same vial. The computer software calculates the average, SD, and CV for the peak areas obtained for the first three injections (eq. 1–3). If SD is greater than 200 area counts and CV is greater than 2 percent, the instrument will analyze as many as two additional injections of sample from the same vial. The computer software then selects the three injections that yield the lowest SD and CV. The software reports the peak areas and DOC concentrations for all of the individual injections and the average DOC concentration, SD, and CV for the three selected injections. The analyst examines these data. Samples with SD greater than 200 area counts and CV greater than 2 percent are reanalyzed.

Table 3. Maintenance program for the Shimadzu TOC-5000A Total Organic Carbon Analyzer

<b>Parts replaced on a regular schedule</b>	
<b>Part</b>	<b>Replacement interval</b>
Carbon dioxide scrubber	Biannually
Halogen scrubber	Annually
Catalyst	As needed
Combustion tube	As needed
Syringe tip	As needed
Humidifier solution	Monthly
<b>Items checked prior to each run</b>	
Injection and purge needles	
Water level in humidifier container	
Water level in rinse water container	
Operation of syringe	
Remove any air bubbles in syringe	
Syringe pump zero point detection (checked approximately monthly)	
Gas flow rates	
Temperature and stability of combustion furnace	

### Maintenance and Corrective Actions

Production of consistently precise and accurate DOC analyses requires adherence to a maintenance program for the carbon analyzer. The Shimadzu TOC-5000A contains a number of parts that are replaced on a regular schedule ([table 3](#)). The regular sensitivity combustion catalyst is cleaned after approximately four analytical runs. Cleaning consists of rinsing with organic-free water to remove accumulated salts and sieving to remove cracked alumina beads. The regular sensitivity catalyst is replaced if cleaning does not improve the instrument's performance. The high

sensitivity catalyst is replaced when the instrument's performance deteriorates. Deteriorating catalyst performance is identified first by inability to reach a low (1,500 area counts of 100  $\mu\text{L}$  injection on high sensitivity catalyst and 2,500 area counts of 53  $\mu\text{L}$  injection on a regular sensitivity catalyst) and stable peak area after repeated injections of organic-free water or high standard deviations (>200 area counts) and high coefficient of variations (>2 percent) for multiple sample injections from a single vial.

## SUMMARY

This report describes the method for routine analysis of dissolved organic carbon concentration in water samples. The Shimadzu TOC-5000A Total Organic Carbon Analyzer uses high temperature catalytic oxidation to oxidize the organic carbon to CO<sub>2</sub>. A nondispersive infrared detector measures the CO<sub>2</sub>. Keeping the instrument clean and maintained by replacing parts and solutions when needed is necessary for ensuring accurate DOC results. The method is validated by testing the precision of several types of samples, assessing the relative accuracy, and determining the laboratory reporting level (the laboratory reporting level is 0.22 mg/L). Quality-control samples such as instrument blanks, duplicate analysis samples, and calibration verification samples are used to determine the acceptability of the analytical results.

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