Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory— Determination of Nonpurgeable Suspended Organic Carbon by Wet-Chemical Oxidation and Infrared Spectrometry

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CONTENTS

FIGURES

TABLES

CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
gram	3.53×10^{-2}	ounce
micrometer	3.94×10^{-5}	inch
milligram	3.53×10^{-5}	ounce
milliliter	2.64×10^{-4}	gallon
millimeter	3.94×10^{-2}	inch

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation: °F = 1.8 (°C) + 32.

Abbreviations

g	gram
g/kg	gram per kilogram
µg/L	microgram per liter
µm	micrometer
mg	milligram
mg/L	milligram per liter
mL	milliliter
mm	millimeter
N	normality (equivalents per liter)

Acronyms

CCB	continuing calibration blank
CCV	continuing calibration verification
DOC	dissolved organic carbon
FEB	field equipment blank
LRB	laboratory reagent blank
MDL	method detection limit
NWQL	National Water Quality Laboratory
QA/QC	quality assurance/quality control
SOC	suspended organic carbon
SRM	standard reference material
TOC	total organic carbon
USGS	U.S. Geological Survey

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ABSTRACT

Precision and accuracy results are described for the determination of nonpurgeable suspended organic carbon (SOC) by silver-filter filtration, wet-chemical oxidation, and infrared determination of the resulting carbon dioxide (CO_2) used at the U.S. Geological Survey's National Water Quality Laboratory. An aliquot of raw water is filtered through a 0.45-micrometer silver filter. The trapped organic material is oxidized using phosphoric acid and potassium persulfate in a sealed glass ampule, and the resulting CO_2 is measured by an infrared CO_2 detector. The amount of CO_2 is proportional to the concentration of chemically oxidizable nonpurgeable organic carbon in the sample. The SOC method detection limit for routine analysis is 0.2 milligram per liter. The average percent recovery is 97.1 percent and the average standard deviation is 11 percent.

INTRODUCTION

Organic particulate material in surface and ground water is composed of a variety of volatile and nonvolatile carbon-containing species. These organic compounds include, but are not limited to, carboxylic acids, alkanes, alkenes, aromatic acids, amino acids, biologically derived polymers, humic acid, and oxygenated compounds (Thurman, 1985). These compounds come in several physical forms, including particulates, colloids, and dissolved gas. The form and composition of these compounds determine how they affect biological, biochemical, or chemical processes such as hydrolysis, photolysis, sorption, precipitation, and complexation (Thurman, 1985). Knowing the concentration of the carbon content of a water sample (total organic carbon, TOC; dissolved organic carbon, DOC; and suspended organic carbon, SOC) is one of the factors that allows the environmental scientist to characterize the biological and chemical demand being placed on the water as well as relate the carbon load to the chemical properties of the water sample.

The National Water Quality Laboratory (NWQL) analyzes approximately 4,000 surface- and ground-water samples a year for SOC by wet-chemical oxidation. Since the early 1970's, SOC was determined using the method reported by Wershaw and others (1987). However, Wershaw and others (1987) do not provide precision and accuracy results. Precision and accuracy results are available in the literature (Sugimura and Suzuki, 1988; Aiken, 1992; American Public Health Association, 1992; Kaplan, 1992) for total and dissolved carbon analysis, but there are no precision and accuracy measurements for the silver-filter based, wet-chemical oxidation SOC method described. In addition, after a review in 1995, it was determined that the SOC method developed by the U.S. Geological Survey (USGS) had produced low biased results on the basis of incomplete carbon oxidation.

The possibility of the SOC method by Wershaw and others (1987) giving low biased numbers was first hypothesized during a method review in 1995. Several random samples with varying concentrations of SOC were subjected to silver filter reanalysis. Results of the total measurable SOC found in the reanalysis of the silver filters ranged from 5 to 59 percent of the total SOC measured (see table 1). The results of these

Table 1. Results from the analysis and reanalysis of 27 random environmental samples for suspended organic carbon

[mg/L, milligrams per liter; NA, not applicable]

Initial analysis results (mg/L)	Reanalysis results (mg/L)	Additional recovery upon reanalysis (percent) (reanalysis/initial plus reanalysis) times 100
0.0	0.0	NA
.0	.0	NA
.5	.1	17
.7	.2	22
.8	.1	11
.9	.1	10
.9	.3	25
1.1	.1	8
1.4	.3	18
1.5	.1	6
1.9	.1	5
2.0	2.7	57
2.1	.4	16
2.2	.3	12
3.2	.4	11
3.3	.3	8
3.5	.6	15
3.6	5.2	59
3.7	1.0	21
4.8	.7	13
5.1	6.2	55
5.3	.6	10
5.5	.9	14
5.9	2.2	27
6.5	1.0	13
9.6	1.7	15
11	1.0	8

experiments showing the large recovery in the second analysis are listed in table 1. Several experiments later, it was determined that the use of a sonication bath in combination with the heating step resulted in higher recovery than the method in Wershaw and others (1987) with little or no residual SOC being found after reanalysis.

Silver membrane filters are used for two reasons. First, silver dissolved into the sample at the time of filtration has the potential to act as a preservative (Chambers and others, 1962), minimizing any biologically derived degradation. Second, the silver membrane filters, once rinsed, exhibit less than the detection limit SOC residue.

This report describes the silver-filter based, wet-chemical oxidation method developed by the U.S. Geological Survey (USGS) for determining SOC in surface-, ground-, and drinking-water samples and provides precision and accuracy results. In addition, it provides a detailed description of all aspects of the method from sampling protocol through calibration and reporting of results. The report also describes how to minimize incomplete chemical oxidation. This method supplements other methods of the USGS for determining organic substances in water and fluvial sediments (Wershaw and others, 1987). The method was implemented at NWQL on July 1, 1997.

ANALYTICAL METHOD

Organic Compound and Parameter Code: Carbon, organic, suspended, wet oxidation, O-7132-97 (mg/L as C): 00689

1. Application

This method is used to determine SOC by wet-chemical oxidation in drinking-, surface-, and ground-water samples. The analytical range is from 0.2 to 50 mg/L of SOC, depending on sample volume. The method is not suitable for the determination of volatile organic compounds.

2. Summary of Method

Organic material that can be removed from acidified water samples by filtration through a 0.45-µm silver filter is purged with oxygen to remove inorganic carbon-containing acids and volatile organic compounds, and oxidized with phosphoric acid and potassium persulfate in a sealed glass ampule in an autoclave at 116 to 130°C. The resulting carbon dioxide (CO_2) is measured by infrared spectrometry. The measured amount of CO_2 is directly proportional to the concentration of chemically oxidizable nonpurgeable suspended organic carbon in the sample. The method detection limit for routine analysis is 0.2 mg/L.

3. Interferences

3.1 Water samples containing large concentrations of reducing agents will interfere by decomposing the persulfate oxidant.

3.2 Inorganic forms of carbon that are not fully purged after acidification will produce positive interference.

3.3 All purgeable organic compounds are lost during preparation of samples.

3.4 Biological activity may result in negative bias. A 14-day holding time has been arbitrarily adopted as the sample holding time.

4. Apparatus and Instrumentation

4.1 Instrumentation and support equipment

4.1.1 OI analytical carbon analyzer model 524, with Horiba nondispersive infrared detector or equivalent.

4.1.2 OI analytical ampule purging and sealing module or equivalent.

4.1.3 Labtronics DP-1000 software loaded onto IBM compatible computer or equivalent.

4.1.4 All American pressure steam sterilizer or equivalent.

4.1.5 Solution 2000 water purification unit or equivalent.

4.1.6 Mettler model ME 5.5 sonicator or equivalent.

4.1.7 HAAKE model E-12 circulating heater or equivalent.

4.1.8 Linear Instruments, Inc. strip chart recorder, model 0585-0000 or equivalent.

4.2 Sample containers

4.2.1 Glass ampules, 10 mL, preburned at 525°C.

CAUTION—Handle burned ampules with care to prevent breakage.

4.2.2 Silver filters, 47-mm diameter, 0.45-µm pore size, Poretics Corporation or equivalent.

4.3 Sample and standard preparation

4.3.1 Adjustable (1 to 10 mL) pipet dispensers.

4.3.2 Class A volumetric flasks and pipets.

4.3.3 Analytical balance accurate to 0.1 mg.

5. Safety Issues

5.1 Wear safety glasses, gloves, and protective clothing throughout the analytical procedure.

5.2 Potassium persulfate is a strong oxidizer. Contact with combustible or flammable materials can cause fire or explosion.

5.3 Safety personnel will dispose of all waste products in accordance with laboratory safety policy.

6. Reagents

6.1 *Water*—All references to water shall be understood to mean ASTM Type II reagent water (American Society for Testing and Materials, 1995). This reagent is provided from the Solution 2000 Water Purification Unit.

6.2 *Potassium biphthalate*—reagent grade, granular.

6.3 *Sodium benzoate*—reagent grade, granular.

6.4 *Phosphoric acid solution (85 percent H_3PO_4)*—14.7 *N*/85 percent phosphoric acid.

CAUTION—Heat is produced when concentrated phosphoric acid is mixed with water. Wear safety glasses, gloves, and protective clothing.

6.5 *Potassium persulfate*—reagent grade, granular.

CAUTION—Potassium persulfate is a strong oxidizer. Contact with combustible or flammable materials can cause fire or explosion.

6.6 *Anhydrone* (magnesium perchlorate).

CAUTION—Use a dust mask when preparing anhydrone tubes.

7. Standards

7.1 *Suspended organic carbon standard stock solution (1,000 mg/L).* Prepare a 1,000 mg/L SOC standard stock solution by dissolving 4.254 g of potassium biphthalate (dried at 120°C for 2 hours, then desiccator cooled) in reagent water and dilute to 2,000 mL (1 mL equals 1 mg carbon).

7.2 *Suspended organic carbon working standard solutions.* Make a series of dilutions from the stock to prepare the 12 standards (1, 2, 3, 4, 5, 7.5, 10, 15, 20, 30, 40, and 50 mg/L) needed for the analysis.

The zero milligram-per-liter standard is carbon-free reagent water.

7.3 *Continuing calibration verification (CCV) solution.* Prepare a 1,000 mg/L organic carbon spike stock solution by dissolving 0.343 g of sodium benzoate (dried at 105°C for 1 hour, then desiccator cooled) in reagent water and dilute to 200 mL. Then dilute this stock to produce a 5-mg/L solution.

8. Sample Collection

The sampling procedure for SOC is outlined in Shelton (1994) and Ward and Harr (1990). However, the following procedural changes have been identified through this investigation and should be included when sampling for SOC.

8.1 Collect water sample using appropriate procedure (Shelton, 1994, p. 21–23).

8.2 Place a 0.45-µm silver-metal-membrane filter into a clean filter unit (fig. 1) between the supporting screen and the Teflon retaining ring using clean, organic-free tweezers.

8.3 Precondition the silver filter by forcing approximately 100 mL of organic-free water through the unit. Discard this 100-mL wash.

8.4 Agitate the water sample (Shelton, 1994) to re-suspend any sediment. Process the sample through the silver filter. Use a prebaked, clean graduated cylinder to measure the water processed through the filter. Do not place the water sample into the graduated cylinder first and then pour it into the filtering apparatus; doing so will bias the SOC results low because SOC will adhere to the sides of the graduated cylinder and will not be transferred quantitatively to the filtering apparatus.

8.5 Open the top of the filtering apparatus and rinse any sediments or suspended solids off the inside of the apparatus with a small amount of organic-free water. This step transfers any particulate material that may have adhered to the sampler walls to the silver filter.

8.6 Reseal unit and force all water out of the filtering apparatus.

8.7 Release pressure on system, open the bottom end of the filtering apparatus, and carefully remove the silver filter using organic-free tweezers. Fold the filter in half with the sediment on the inside. Place the folded filter into a clean plastic petri dish.

8.8 Write the volume of water filtered through the silver filter on the petri dish. Tape the petri dish closed to prevent it opening in transit and place in sealable plastic bag.

8.9 Place sealed bag in a cooler and transport the sample to laboratory. Keep the sample at or less than 4°C.

8.10 Analyze samples within 14 days of sampling. The 14-day holding time was chosen on the basis of previous sampling recommendations, the absence of any added preservation agent, and the lack of holding-time-study data in the scientific literature.

9. Instrument Performance

Evaluate the infrared spectrometer each day using the SOC working solutions and throughout the analytical sequence by using blanks and CCVs. The infrared spectrometer performance is normally evaluated by peak shape and by the variation in response (peak area) to the different concentrations of CO_2. Abnormal peak shape or inconsistent peak areas require immediate attention, which may include recalibration or maintenance, or both. The performance criteria for the calibration curve are discussed in section 10.

10. Calibration

The response of the infrared spectrometer to carbon dioxide is not linear over the SOC calibration concentration range. A third-order polynomial least-squares curve-fitting algorithm, therefore, is used to evaluate the calibration results obtained from analyzing the SOC working standard solutions from section 7.2. The correlation coefficient (r) of the calibration plot must be greater than or equal to 0.9975 for sample analysis. A typical calibration curve for SOC working standard solutions, in the concentration range from 0 to 50 mg/L, is shown in figure 2.

11. Procedure

Warm up the infrared spectrometer for at least 30 minutes.

11.1 Standards preparation

11.1.1 First, burn ampules at 525°C in a muffle furnace, then label with standard concentration and Julian date. The standard solutions need to be instrumentally verified, so prepare and analyze three ampules of each standard concentration.

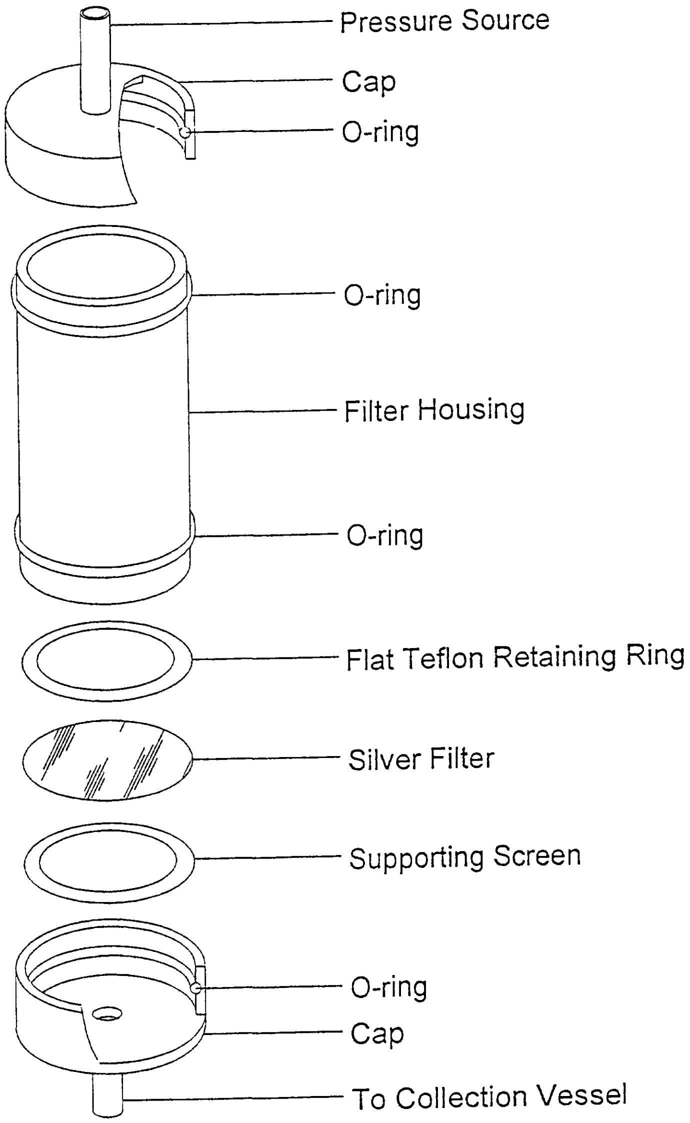

Figure 1. Suspended-organic-carbon sampling apparatus.

11.1.2 Fill each ampule with 0.2 g of potassium persulfate using a calibrated scoop.

11.1.3 Then add 0.5 mL of 85 percent phosphoric acid to each ampule.

11.1.4 Now pipet 10.0 mL of standard into the ampules.

11.1.5 Place the ampules onto the purging and sealing unit (eight ampules at a time). Purge the ampules for 10 minutes and then seal.

11.1.6 Place sealed ampules upside down in autoclave racks. Follow safety instructions for operating the autoclave. Autoclave the samples for 8 hours.

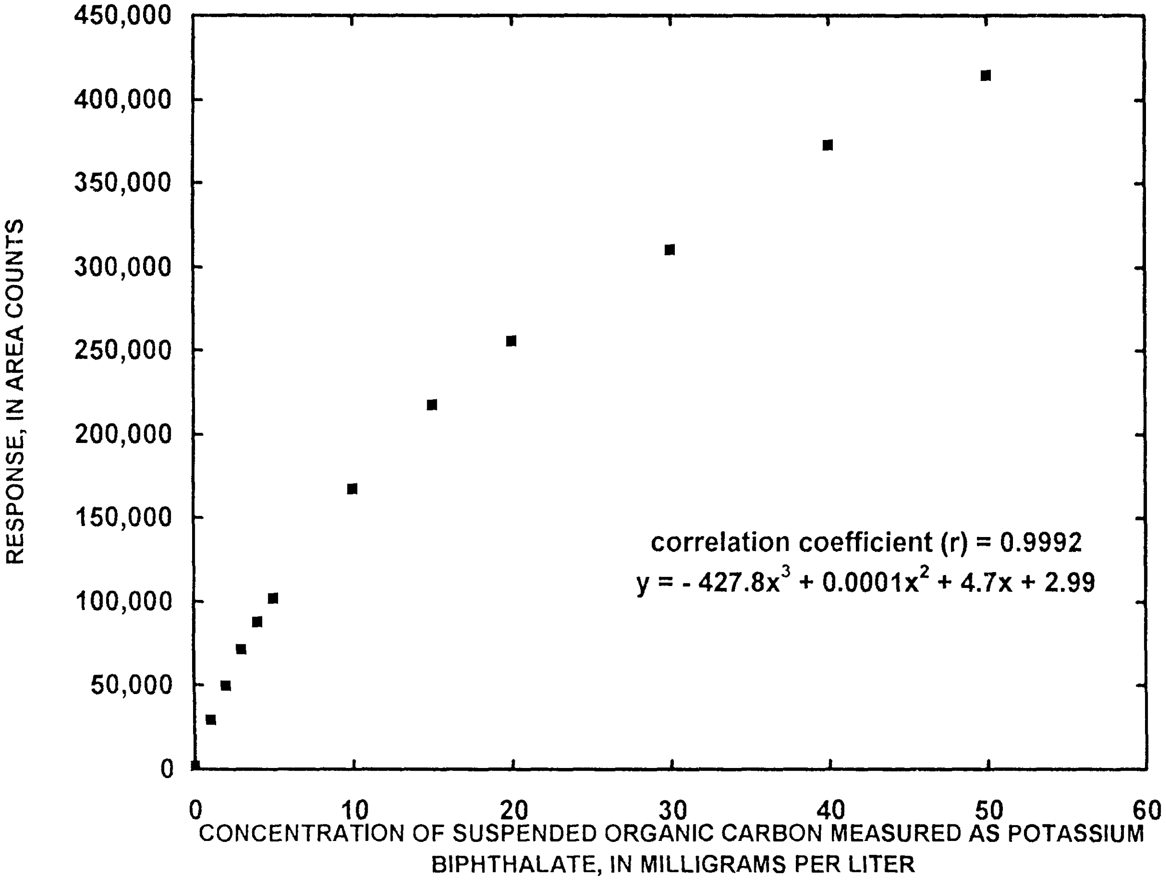

Figure 2. Typical calibration curve for the determination of nonpurgeable suspended organic carbon in environmental water samples using wet-chemical oxidation and infrared spectrometry.

This process converts the organic carbon to CO_2 with the assistance of high temperature and pressure and a strong oxidizer.

11.2 Sample preparation

11.2.1 Individually cut the silver filters into strips and place them into a labeled ampule with cleaned and burned tweezers.

11.2.2 Then add 0.5 mL of 85 percent phosphoric acid to each ampule.

11.2.3 Next add 8.0 mL of reagent water to each ampule. Cover each ampule with a small piece of aluminum foil.

11.2.4 Place the rack of ampules in a sonicating water bath at 80°C for 4 hours. With the help of a self-delivering water system, the water bath can be unattended for the duration. After 4 hours, remove the rack from the bath and place in a small pan in the sink. Run cold water over the ampules. This step is important because the addition of potassium persulfate to hot water will begin to oxidize the carbon in the ampule before it is sealed.

11.2.5 When the ampules have cooled to room temperature, remove the aluminum foil tops from each. Add 0.2 g of potassium persulfate followed by 2 mL of reagent water.

11.2.6 The ampules are now ready to be purged, sealed, and then autoclaved following the procedure in 11.1.6.

11.3 Sample analysis

11.3.1 Arrange the standards, spikes, blanks, and samples in sequential order in a 70°C heated water bath. Place a collar, followed by a rubber seal, onto the first standard ampule. Load standard into front of instrument by using the screw device to tighten the seal. With some pressure and twisting, bring the crusher down onto the top of the ampule until it is opened, enabling the purge rod to be lowered. This process allows the CO_2 to escape into the tubing leading to the instrument detector. The gas released travels through a pair of tubes filled with anhydrone to eliminate the presence of any water.

11.3.2 Immediately after the purge rod is lowered, read the ensuing peak. The screen will display the peak, elapsed time, and the percent of full scale for 130 seconds, then will stop. Remove the sample from the instrument as soon as the peak reaches baseline prior to completion of the timer. Then remove the ampule and broken glass for insertion of the next standard to be analyzed. When the timer stops, crush the next ampule and start data collection.

11.3.3 Plot the working standard solution absorbance readings as a function of the known working standard solution concentrations. Use a third-order polynomial least-squares curve-fitting algorithm to evaluate the calibration plot. The correlation coefficient of the calibration plot must be greater than or equal to 0.9975 for the analysis to continue. If the correlation coefficient is greater than or equal to 0.9975, then perform steps 11.2 to 11.3 on environmental samples requiring SOC determination.

12. Calculations

Determine the milligrams per liter of SOC by matching the CO_2 measured to the corresponding SOC concentration using the calibration line produced by plotting the peak area of each standard in relation to milligrams per liter of each SOC standard. Apply appropriate dilution factors to every sample that has been diluted.

13. Reporting of Results

Report SOC concentrations as follows: less than 10 mg/L, two significant figures; 10 mg/L and greater, two significant figures; less than (<) the reporting limit of 0.2 mg/L, <0.2 mg/L. Suspended organic carbon samples flagged with an "R" are samples that had CO_2 peak areas greater than the highest standard. These concentrations are recorded as "greater than" (>).

14. Precision and Bias

14.1 The precision was calculated using carbon-free water as the sample matrix. The precision for the presented method, based on 59 replicates, ranged from 83.6 to 122 percent recovery, with standard deviations of the recovery ranging from 5 to 24 percent. The SOC (mean theoretical) concentration in these analyses ranged from 0.59 to 6.61 mg/L.

14.2 Bias was estimated from the reanalysis of the silver filter. The method described by Wershaw and others (1987, p. 16–17) ranged from 5 to 59 percent low bias (see table 1). The method described in this report has demonstrated a low bias of 3.4 ± 2.7 percent. The lower range of bias and smaller variability for the described method is based on the more complete oxidation of the SOC in the method with the aid of the sonication apparatus.

METHOD PERFORMANCE

Choice of Sediments

Five sediment samples were selected and analyzed for organic carbon. The first sample was a marine sediment purchased from the Marine Research Council of Canada, Marine Analytical Standards Program. This sediment is distributed as a Standard Reference Material (SRM). The second sediment was obtained from the U.S. Geological Survey, Geologic Division, and also is distributed as an SRM. The remaining three sediment samples were from the U.S. Geological Survey, Water Resources Division. They were river-bed sediments sent to the laboratory for analysis of total carbon, inorganic carbon, and organic carbon by difference. The sediments were from Miller Creek (Iowa), Uncompahgre River (Colorado), and Indian Creek (Minnesota).

These samples initially were analyzed for organic carbon by two different methods. The first method involved oxidizing the total carbon in a furnace at 1,500°C and measuring the resultant carbon dioxide with a thermal resistance detector (USGS method O-5101-83, Wershaw and others, 1987, p. 17–19). The inorganic carbon was measured with a manometric technique (USGS method O-5102-83, Wershaw and others, 1987, p. 19–22) and subtracted from the total carbon to obtain the organic carbon. In the second method, the sediments were analyzed for

TOC by a persulfate oxidation technique that measured the resultant carbon dioxide with an infrared detector (USGS method O-3100-83, Wershaw and others, 1987, p. 15–16). The results for organic carbon using the two methods are listed in table 2.

Method Performance

The persulfate oxidation results were used to calculate the theoretical concentrations to determine the recovery of SOC in the spiked samples. The results were comparable in that the persulfate oxidation step was used in the SOC analysis as well as the TOC analysis. From 8 to 10 replicates at two concentrations were analyzed for the geologic sediment and marine sediment samples. Three to four replicates at two concentrations were analyzed for each of the river-bed sediments. The theoretical organic carbon concentrations ranged from 0.52 to 7.55 mg/L.

Each sediment sample was weighed on an analytical balance using a metal foil weighing boat. The sediment then was transferred to a 200-mL beaker. The beaker was swirled for 3 minutes to mix the sediment and water. The spiked sample then was extracted using the procedure in section 8 and analyzed using the method described in section 11. The percent recoveries, means, and standard deviations were calculated by comparing the theoretical concentration (calculated using the data in table 2) and the measurements found using the method described.

The recovery, mean, and standard deviation for each of the five sediments and the average for all sample matrixes analyzed by the SOC techniques are listed in table 3. The mean recovery of the SOC in the marine sediment was slightly lower than the other sediments, probably because of the nature of the organic material found in marine sediment (more labile, possibly more volatile, and higher content of dissolvable organic carbon than in nonmarine samples). However, the marine sediment and the higher sediment results are included for completeness, representing the worst-case scenarios, and were used in all subsequent calculations.

Complete SOC Oxidation

The determination that there was significant SOC after the reanalysis was the reason for improving this method. To compare the efficiency of the new method to the method described by Wershaw and others (1987), silver filters using sonication and no sonication steps were reanalyzed. Samples were analyzed using one of the methods. The silver filters were then removed from the glass ampules and placed in clean, new ampules. The silver filters then were subjected to

Table 2. Total organic carbon content using thermal combustion and persulfate oxidation methods

[g/kg, grams per kilogram; DI, determined in-house]

Sediment source	Organic carbon by thermal combustion (g/kg)	Organic carbon by persulfate oxidation (g/kg)	Number of replicates	Reference or most probable value (g/kg)
Marine	21.0 ± 0.2	17.8 ± 1.0	7	21.3
Geologic Division	25.9 ± 1.3	27.8 ± 3.1	7	28.3
Miller Creek, Iowa	4.8 ± 0.4	3.8 ± 0.2	4	DI
Uncompahgre River, Colo.	3.8 ± 0.2	3.4 ± 0.2	4	DI
Indian Creek, Minn.	3.1 ± 0.2	3.1 ± 0.2	4	DI

Table 3. Mean recovery and standard deviation data for suspended organic carbon using five environmental matrices

[mg/L, milligrams per liter; conc., concentrations]

Sediment source	Number of replicates	Mean theoretical conc. (mg/L)	Range of theoretical conc. (mg/L)	Mean analyzed conc. (mg/L)	Mean recovery (percent)	Recovery standard deviation (percent)
Marine	8	0.59	0.52 - 0.72	0.50	84.8	11
Marine	9	6.31	5.2 - 7.55	5.51	87.3	6.3
Geologic Division	10	.73	0.60 - 0.89	.61	83.6	24
Geologic Division	9	6.61	5.46 - 7.51	5.96	91.2	6.7
Miller Creek, Iowa	3	1.53	1.46 - 1.59	1.46	95.4	8.0
Miller Creek, Iowa	4	.72	0.66 - 0.79	.88	122	15
Uncompahgre River, Colo.	4	1.68	1.63 - 1.71	1.78	106	5.0
Uncompahgre River, Colo.	4	.85	0.81 - 0.88	.88	104	10
Indian Creek, Minn.	4	1.86	1.83 - 1.88	1.73	93.0	7.2
Indian Creek, Minn.	4	.89	0.88 - 0.93	.94	106	11
	Total = 59			Average	97.1	11

another complete analysis using the corresponding SOC method. The new method significantly reduces the amount of SOC on the silver filter, as listed in table 4, and improves precision. The no-sonication-step samples were the environmental samples listed in table 1. The with-sonication-step results used the marine sediment concentrations and the lower spiked geologic sample concentrations, which are listed in table 3.

With or Without Sonication Method Comparison

Ten SOC samples were collected in duplicate and analyzed by both methods. The samples were either duplicates split from the same sample container or replicates taken from the river at the same time. The rivers were in New Jersey, Colorado, and Washington State. The results of analyzing these samples using the original method and the new method with the added sonication step are listed in table 5. Table 5 also lists the difference between the concentrations as a percentage.

The new method provides a higher recovery (on average) than the old method. Coupled with the lower SOC results found upon reanalysis in table 4, these results demonstrate that the sonication step improves recovery, reduces bias, and provides more accurate data compared to analysis without sonication.

Analysis of Potential Error

There are two major sources of potential error in this analysis. The first is residual SOC material trapped on the silver filter prior to processing environmental samples. This source of SOC can cause a positive bias in the environmental results. The second source of potential error is the retention of SOC from the environmental water sample on the sample collection device. Suspended sediment will adhere to the walls and the O-ring of the filter device, providing a negative bias if the adhering sediment is not rinsed onto the filter.

Considerable organic carbon may be present in the unused silver filters. This carbon can produce a positive bias for SOC and DOC if the filter is not prerinsed properly. Thirty-six blank filters were analyzed using the method without prerinsing to determine the residual SOC found on these silver filters. The average SOC concentration was 1.2 mg/L with a standard deviation of 0.36 mg/L. This average SOC concentration is six times the method detection limit and can cause high biased results if the silver filter is not prerinsed.

Table 4. Reanalysis results of silver filters with and without sonication step

[SOC, suspended organic carbon; mg/L, milligrams per liter]

Method with and without sonication	SOC found on reanalysis (percent)	Standard deviation of SOC found on reanalysis (percent)	SOC initial concentration range (mg/L)	Number of samples
No sonication	19	15	0 - 11	27
Sonication	3.4	2.7	0.59 - 6.31	27

Table 5. Suspended-organic-carbon concentrations for environmental samples using the method described with and without sonication step

[SOC, suspended organic carbon; mg/L, milligrams per liter]

Sediment collection location	SOC results without sonication step (mg/L)	SOC results with sonication step (mg/L)	Percent difference [(with/without)-1] times 100
Ralston Creek, Colo.	2.0	2.8	40
Ralston Creek, Colo.	.52	.51	-2
Ramapo River, N.J.	1.6	1.5	-6
Ramapo River, N.J.	1.2	1.4	17
Columbia River, Wash.	.80	1.2	50
Columbia River, Wash.	1.1	1.1	0
Columbia River, Wash.	1.0	1.3	30
Columbia River, Wash.	.80	1.0	25
Columbia River, Wash.	.80	1.0	25
Columbia River, Wash.	.80	1.0	25

Errors associated with using the sampling apparatus in figure 1 were quantified to determine the average error as a percentage caused by SOC particulates being retained on the sampling apparatus. The errors caused by particulate retention on the Teflon ring (the Teflon retaining ring used to hold the silver filter in place, which occupies about 24 percent of the surface area of the silver filter) and retention on the side-walls of the sample device housing are listed in table 6. Individually, the errors are small, but collectively, the errors can be as much as 19 percent.

The SOC error associated with the retention of organic material on the inside walls of the sampling apparatus was quantified by rinsing the inside walls of the sampling apparatus with organic-free water and collecting the water and sediment into another ampule. This second ampule was analyzed for TOC and the results reported as a percentage of the known suspended organic content placed in the initial sample.

Table 6. Errors associated with Teflon-retaining ring and sampler walls

Sampler component	Mean percent recovery	Standard deviation of mean percent recovery	Number of samples
Teflon retaining ring	6.5	4.2	36
Sampler walls	4.1	3.8	36

Table 7. Method detection limit summary for suspended organic carbon

[mg/L, milligrams per liter; MDL, method detection limit]

Reporting MDL (mg/L)	Calculated MDL (mg/L)	Standard deviation (mg/L)	*T*-value	Number of replicates (*n*)
0.2	0.21	0.08	2.602	16

Method Detection Limit

A method detection limit (MDL) was calculated for SOC using the protocol set forth by the U.S. Environmental Protection Agency (1992):

$$\text{MDL} = S \times T_{(n-1,\ 1-alpha = 0.99)} \qquad (1)$$

where S = standard deviation of replicate analyses, in micrograms per liter;

$T_{(n-1, 1-alpha = 0.99)}$ = T-value for the 99 percent confidence level with $n-1$ degrees of freedom; and

n = number of replicate analyses.

The MDL was calculated using the determination of SOC in 16 replicates of reagent water spiked between 0.5 to 0.8 mg/L of SOC. The data were produced on two nonconsecutive days. The MDL data are listed in table 7. Note that the calculated concentration for the MDL is 0.21 mg/L (208 µg/L) but has been rounded to 0.2 mg/L for use by NWQL.

QUALITY ASSURANCE

Field filtered SOC samples are formed into sets of 10 environmental samples with a blank and spike for a total set number of 12. In addition, the following QA/QC samples are analyzed with each set of environmental samples:

1. *Continuing calibration verification.* The use of a continuing calibration verification (CCV) directly following the working standards allows the concentration and preparation of the standard curve to be verified. The use of the CCVs every 10 samples verifies that the instrument is performing within the expected accuracy ranges throughout the analytical sequence. The percent recovery from the analysis of the first CCV must be maintained in a control chart to monitor long-term trends. The acceptance criterion for a CCV is ±15 percent from the known SOC concentration.
2. *Continuing calibration blank.* Use continuing calibration blanks (CCBs) every 10 samples to verify that the glassware and reagents have not been contaminated. Contamination can come from the

glassware, reagents, and poor technique. Blanks are SOC-free deionized-water samples. The acceptance criteria for a blank is <0.2 mg/L SOC.

3. *Field equipment blank.* A sample of carbon-free water is processed exactly as for environmental samples using all appropriate field-sampling equipment and techniques. This process includes bottles, compositing, splitting, and filtering. The field equipment blank (FEB) is processed at the start of sampling and then approximately every 15 to 20 samples. The FEB monitors for contamination or carryover, or both, between environmental samples.

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