

Application News

No. TOC-004

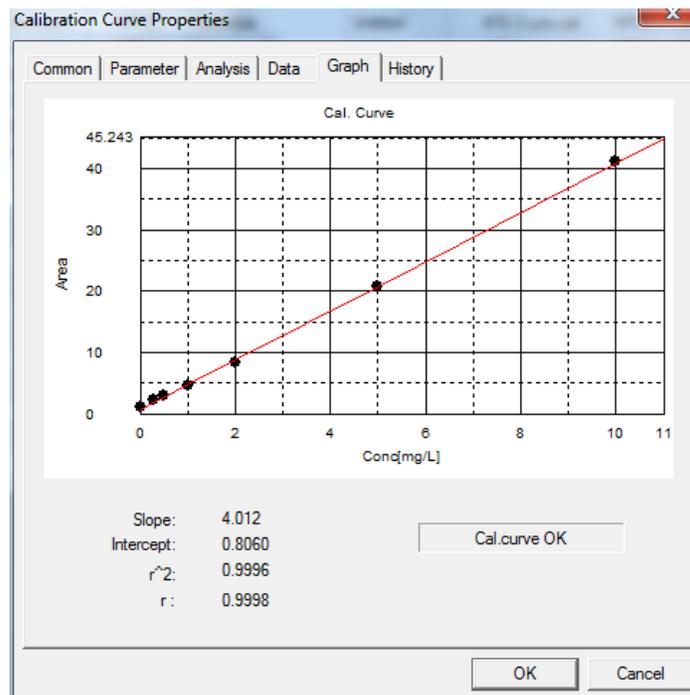
Total Organic Carbon Analysis

EPA Method 415.3 - Determination of TOC in Source Water and Drinking Water

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Method 415.3 states that the measurement of Total Organic Carbon (TOC) and DOC must use a TOC instrument that oxidizes organic carbon in the water to create carbon dioxide gas, which is then measurable. The instruments are required to use one of two basic oxidation methods – either through combustion with an oxidizing gas, or through chemical oxidation with persulfate promoted by either UV or heat catalyzing – coupled with a non-dispersive infrared (NDIR) detector or a conductivity detector. The ability of the Shimadzu TOC-L to meet the requirements set forth in method 415.3 was assessed.

For the combustion instrument, a TOC-L CPH was set up using a normal-sensitivity catalyst. The instrument was calibrated according to the method. Standards were prepared from KHP and a curve was created from 0 – 10 ppm carbon, with points at 0, 0.3, 0.5, 1, 2, 5, and 10 ppm. The coefficient of determination (r^2) was 0.9998 for the 7 point calibration curve to ensure linearity. The method only requires 4 points and a blank so the user need not include as many points as used in this application note.



Quality Control

The method requires that laboratories using the method have a quality control program in place:

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. QC requirements for TOC include: the initial demonstration of laboratory capability (IDC) followed by regular analyses of continuing calibration checks (CCC), independent quality control samples (QCS), laboratory reagent blanks (LRB), field duplicates (FD), and laboratory fortified matrix samples (LFM). For this method, a TOC laboratory fortified blank (LFB) is the same as a CCC (Sect. 10.3) and no LFB is required. QC requirements for DOC include: the IDC followed by regular analyses of CCCs, QCSs, filter blanks (FB), LFB, FDs, and LFMs. See

Appendix A for a complete table of acronyms at the end of this application note.

The first of these requirements is the Initial Demonstration of Laboratory Capability (IDC). It is actually a series of tests including blanks, calibration, inorganic carbon removal sparging efficiency, initial demonstration of accuracy, initial demonstration of precision, and a detection limit study. The TOC-L exceeded all IDC requirements.

To ensure that all inorganic carbon was removed from the samples prior to analysis, an inorganic carbon removal sparging efficiency test was performed. An IC standard was prepared (IC Test Mixture) by first preparing 4 separate solutions as shown in Table 1:

FLASK (1 L)	SALT	WEIGHT(g)
A	magnesium sulfate heptahydrate, MgSO ₄ C•7H ₂ O	2.565
B	ammonium chloride, NH ₄ Cl	0.594
	calcium chloride dihydrate, CaCl ₂ C•2H ₂ O	2.050
	calcium nitrate tetrahydrate, Ca(NO ₃) ₂ C•4H ₂ O	0.248
	potassium chloride, KCl	0.283
C	sodium chloride, NaCl	0.281
	sodium bicarbonate, NaHCO ₃	2.806
D	sodium phosphate dibasic heptahydrate, Na ₂ HPO ₄ C•7H ₂ O	0.705
	sodium-meta silicate nonahydrate, Na ₂ SiO ₃ C•9H ₂ O	1.862

Table 1

The IC Test Mixture was prepared by adding 10 mls of each of the above solutions to a 40 ml vial, and adding 40 uL of HCl. This yielded an IC concentration of 102.5 ppm. The content of this mixture was chosen to simulate waters likely to be found in waste treatment plants. The mixture was analyzed several times with different sparge

times to determine the IC removal efficiency. The TOC-L has the ability to add acid and sparge samples automatically within the instrument using the non-purgeable organic carbon (NPOC) function. The IC test mixture was analyzed using 3% HCl addition and the results are shown in Table 2.

IC Removal Sparge Efficiency Study						
Sparging time (min.)	0	2	3	5	10	20
Concentration (mg/L)	102.50	0.52	0.30	0.23	0.23	0.22
Blank	0.22	0.22	0.22	0.22	0.22	0.22
Net Concentration	102.28	0.30	0.08	0.01	0.01	0.00

Table 2

As shown in Table 2, a sparge time of 5 minutes with 3% HCl is sufficient to remove all IC present in the samples. (The blank value during the above study was 0.22 mg/L). It should be noted that after 2 minutes the concentration dropped to 0.30 ppm, which is below the required method concentration of 0.35 ppm.

Next, the Organic Carbon Detection Limit (OCDL) was determined. The test was conducted over 3 days, analyzing 7 replicates of a low concentration standard (LFB) each day. A concentration of 0.25 ppm carbon was used for the study. The OCDL calculated from the results of the 3-day study was 0.0697 mg/L, as shown in Table 3.

OCDL			
	Day 1	Day 2	Day 3
0.25 ppm	0.2696	0.3012	0.3192
	0.2658	0.3158	0.2796
	0.2686	0.3399	0.2612
	0.2753	0.2917	0.304
	0.2809	0.2943	0.2881
	0.2363	0.3101	0.3038
	0.3371	0.2957	0.2829
Mean	0.2762	0.307	0.2913
Std. Dev.	0.03037	0.01696	0.01923
SD x3.14	0.0954	0.05325	0.06038
OCDL	0.0697		

Table 3

The 3-day OCDL study was also performed with the high-sensitivity catalyst. The

calculated OCDL was 0.0175 ppm, as shown in Table 4.

OCDL High Sensitivity			
	Day 1	Day 2	Day 3
0.10 ppm	0.09182	0.06853	0.0731
	0.0832	0.0744	0.06592
	0.07673	0.07545	0.07772
	0.08101	0.06562	0.07061
	0.07015	0.06811	0.06318
	0.07214	0.06905	0.06644
	0.8182	0.07175	0.06123
Mean	0.07955	0.07042	0.06831
Std. Dev.	0.00733	0.00358	0.00581
SD x 3.14	0.02302	0.01124	0.01824
OCDL	0.0175		

Table 4

The minimum reporting level (MRL) is established as 2 times the mean LRB measurement. In the case of this study:

$$\begin{aligned} \text{MRL} &= \text{Mean LRB} \times 2 \\ &= 0.145 \times 2 = 0.29 \text{ ppm} \end{aligned}$$

Samples of drinking water and source water were collected from various locations, and analyzed for TOC per the method. All QC requirements outlined in the method were met. The results are shown in Table 5 (drinking water) and Table 6 (source water).

Drinking Water			
Sample	Result (mg/L)	QC result	QC requirement
QCS (5ppm)	4.92	98.4% Rec.	20% TV (+/-)
CCC Low(0.3ppm)	0.25	83.3% Rec.	50% TV (+/-)
Colesville	1.72		
Severna Park	0.50		
Columbia	1.51		
Columbia-FD	1.59	5.16% RPD	< 20% RPD
Columbia-LFM (+5 ppm)	6.23	94.4% Rec.	30% TV (+/-)
CCC-Mid (5ppm)	5.08	101.6% Rec.	20% TV (+/-)

Table 5

Equation 1: Recovery of QCS and CCC:

$$\% \text{ Recovery} = (\text{measured value}/\text{true value}) * 100$$

$$\% \text{ Recovery of QCS} = (4.92 \text{ ppm}/5.00 \text{ ppm}) * 100 = 98.4\%$$

Equation 2: Relative percent difference (RPD) for duplicate measurements (FD) of sample 1 (FD1) and duplicate sample 2 (FD2):

$$\text{RPD} = (|FD1 - FD2|)/((FD1+FD2)/2)*100$$

$$\text{RPD} = (|1.51 \text{ ppm} - 1.59\text{ppm}|)/((1.51 \text{ ppm} + 1.59 \text{ ppm})/2)*100 = 5.16\%$$

Equation 3: Percent spike recovery (% REC) for LFM using the equation:

$$\% \text{ Recovery} = (A-B)/C * 100$$

$$\% \text{ Recovery} = ((6.23 \text{ ppm} - 1.51 \text{ ppm})/5 \text{ ppm}) * 100 = 94.4\%$$

where,

- A = measured concentration in the fortified sample
- B = measured concentration in the unfortified sample,
- and
- C = fortification concentration.

Source Water			
Sample	Result (mg/L)	QC result	QC requirement
CCC-Low(0.3 ppm)	0.32	106.7 Rec.	20% TV (+/-)
Centennial Lake	6.44		
Centennial - FD	6.24	3.15% RPD	<20% RPD
Lake Kittamaqundi	7.76		
Middle Patuxent River	2.41		
Middle Patuxent-LFM(+5 ppm)	7.2	95.8% Rec.	30% TV (+/-)
CCC-Mid (5 ppm)	5.07	101.4% Rec.	20% TV (+/-)

Table 6

Conclusion

Shimadzu's TOC-LCPH exceeds all of the requirements outlined in method 415.3 for analyzing source water and drinking water. For low-level analyses, the H model with normal and high-sensitivity catalysts yielded detection limits of 0.070 and 0.017 ppm, respectively, due to different default injection volumes of 50 and 81 microliters. Detection limits can be improved with larger injection volumes. The injection volumes of 300 uL and 2000 uL can be selected for the regular and high-sensitivity catalysts, respectively.

The instrument's time-saving functions include the ability to run a calibration curve from a single high standard solution. The instrument will automatically perform dilutions to the desired concentrations of the calibration points. The TOC-LCPH also has the ability to auto-dilute over-range samples, keeping them in the range of the calibration curve. In addition, all measurements were performed with sparging in the syringe. Adding the optional external sparge function can improve sample throughput as samples are sparged in the vials on the autosampler.

Appendix A: Table of Acronyms

Acronym Term	
CB	calibration blank
CCC	continuing calibration check
DOC	dissolved organic carbon
FB	filter blank
FD	field duplicate
FRB	field reagent blank
IC	inorganic carbon
IDC	initial demonstration of capability
KHP	potassium hydrogen phthalate
LFB	laboratory fortified blank
LFM	laboratory fortified matrix
LRB	laboratory reagent blank
LRW	laboratory reagent water
MRL	minimum reporting level
MSDS	material safety data sheet
OC-CAL	organic carbon calibration standard
OC-PDS	organic carbon primary dilution standard
OCDL	organic carbon detection limit
QCS	quality control sample
SCS	spectrophotometer check solution
SDWA	Safe Drinking Water Act
SOP	standard operating procedure
TC	total carbon
TOC	total organic carbon

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