Una mayor eficacia en el análisis de TOC en aguas residuales Método 5310B y USEPA Método 415.1

Aplicación 018

Resumen

La determinación del Carbono Orgánico Total (TOC) es muy importante para el control operativo de las plantas depuradoras dado que los compuestos orgánicos que constituyen los contaminantes son un grupo muy Amplio. El parámetro TOC a pesar de su sencillez ha sido durante muchos un análisis problemático. Los laboratorios han buscado siempre una mejora en la productividad y una reducción en sus costes operativos para mantener su reproducibilidad. Esta aplicación demuestra la capacidad para su determinación en aguas superficiales y aguas residuales con una mejora de productividad de >25% siguiendo los métodos normalizados Método 5310B y USEPA Método 415.1.

Introduction

In the evaluation of industrial process waters and wastewaters, of particular interest is organic carbon contamination from either microbial or synthetic derivatives, due to their possible environmental impact. High temperature combustion Total Organic Carbon (TOC) analyzers provide the most efficient way to measure organic carbon in these waters.

TOC users from around the globe requested an instrument from Teledyne Tekmar that meets the following criteria:

- • Economical
- • Easy-to-use software
- • Shorter run times
- • Low maintenance and easy, fast access to combustion tube
- • Longer catalyst life without compromising performance or reliability

The new Lotix TOC Combustion analyzer is designed to accurately measure carbon content in aqueous matrices down to the ppb level. It uses proven high temperature combustion, oxidation of carbon material into carbon dioxide, and detection using a new Non-Dispersive Infrared (NDIR) Detector.

The concentration of organic carbon may fall in the ppb range for drinking water samples or the ppm range for wastewater samples containing suspended organic carbon or those with high concentrations of TOC. Laboratories that are required to analyze for this large range often need to run multiple calibration curves or are forced to dilute the majority of samples, which can add a significant amount of time to daily analysis.

This study evaluates the Lotix and its ability to meet the linearity, accuracy, and reproducibility requirements set forth in TOC wastewater Method 5310B by removing all inorganic carbon with the addition of 20% phosphoric acid and sparging, leaving only the Non-Purgeable Organic Carbon (NPOC) fraction.

Experimental Instrument Conditions

A 1000 ppmC organic carbon stock solution was prepared according to the method by dissolving 2.1254 grams of potassium hydrogen phthalate (KHP) in 1 liter of deionized water. This stock standard was then diluted to create a working calibration curve from 500 ppbC to100 ppmC. Eight points were chosen at final concentrations of 0.5, 1.0, 5.0, 10.0, 25.0, 50.0, and 100.0 ppmC. These standards were then poured into 40 mL vials and placed in the autosampler for analysis.

The primary method parameters used to generate the data in this application note are depicted in Table I.

Table I TOC Method Parameters	
Parameter Value	**Value**
Sample Volume	0.50 mL
Furnace Temperature	680 °C
Acid Volume	0.20 mL
Carrier Gas Delay Time	60 seconds
IC Sparge Time	60 seconds
TOC Loop Fill	11 seconds
TOC Sample Injection	8 seconds

Each calibration level was run in triplicate with the %RSD depicted in Table II along with the linear curve and coefficient of correlation (r^2) in Figure 1.

Figure 1   Calibration curve 500 ppbC-100 ppmC

Table II Calibration Curve 0.5-100 ppmC	
Point (ppm)	**%RSD**
0.0	4.11
0.5	1.68
1.0	0.97
5.0	2.92
10.0	1.85
25.0	3.06
50.0	1.93
100.0	1.37

$$y = 267.86(x) + -36.74$$
$$r^2 = 0.99962$$
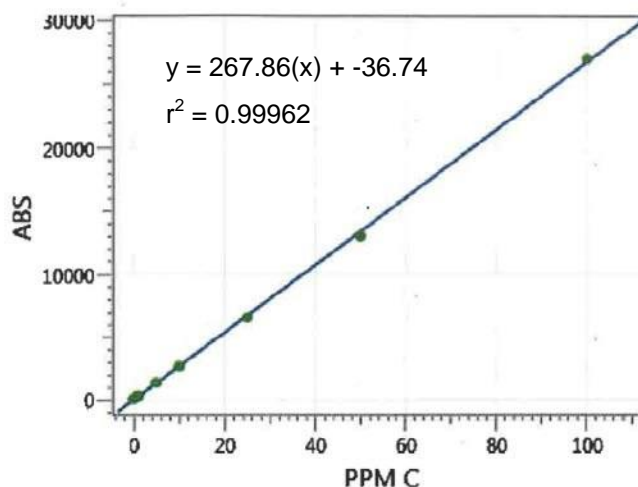
To ensure that the instrument provides reproducible results, the method requires that samples be injected until consecutive measurements are obtained that are reproducible within ±10%. To verify reproducibility and accuracy, consecutive samples at known concentrations were analyzed in triplicate along with check

standards for verification, and can be found in Table III. This information was extracted from the printed PDF report in the software.

Table III Reproducibility and Accuracy					
Pos	Sample Type	ID	ppmC	Std Dev	%RSD
1	Sample	DI Water			
2	Blank	Blank			
3	Sample	1ppm	0.979	0.010	1.064
4	Sample	1ppm	0.978	0.007	0.739
5	Sample	1ppm	0.969	0.032	3.350
6	Sample	1ppm	0.956	0.031	3.196
7	Sample	1ppm	0.958	0.035	3.656
8	Check Standard	5.0 ppm	4.951 Passed	0.076	1.540
9	Sample	5ppm	4.810	0.042	0.874
10	Sample	5ppm	4.909	0.008	0.163
11	Sample	5ppm	4.784	0.068	1.418
12	Sample	5ppm	4.838	0.093	1.924
13	Sample	5ppm	4.818	0.015	0.308
14	Check Standard	10.0 ppm	9.732 Passed	0.134	1.378
15	Sample	10ppm	9.555	0.212	2.222
16	Sample	10ppm	9.488	0.070	0.743
17	Sample	10ppm	9.609	0.152	1.587
18	Sample	10ppm	9.465	0.118	1.251
19	Sample	10ppm	9.605	0.020	0.209
20	Check Standard	25.0 ppm	23.846 Passed	0.320	12.66
21	Sample	25ppm	23.951	0.509	2.125
22	Sample	25ppm	23.597	0.057	0.240
23	Sample	25ppm	24.067	0.457	1.900
24	Sample	25ppm	24.224	0.463	1.909
25	Sample	25ppm	23.936	0.278	1.161
26	Check Standard	50.0 ppm	47.862 Passed	0.924	1.930
27	Sample	100ppm	94.966	0.234	0.247
28	Sample	100ppm	95.003	1.367	1.439
29	Sample	100ppm	96.336	1.947	2.021
30	Check Standard	100.0 ppm	94.653 Passed	0.961	1.016

The ability to calibrate an instrument across a wide calibration range can improve overall efficiency in a laboratory by eliminating the need for bracketing calibration curves and minimizing the number of samples requiring dilution. A 1000 ppmC organic carbon stock solution was prepared and used to make a 0.0-1000 ppmC calibration curve. Each calibration level was run in triplicate with the %RSD depicted in Table IV along with linear curve and coefficient of correlation (r^2) in Figure 2.

Table IV Calibration Curve 0-1000ppmC	
Point (ppm)	**%RSD**
0.0	3.31
1.0	1.18
10.0	1.01
25.0	1.31
50.0	3.15
100.0	2.63
250.0	1.28
500.0	1.42
1000.0	0.74

Figure 2 TOC Calibration from 0-1000 ppmC using a single 0.5 mL injection volume
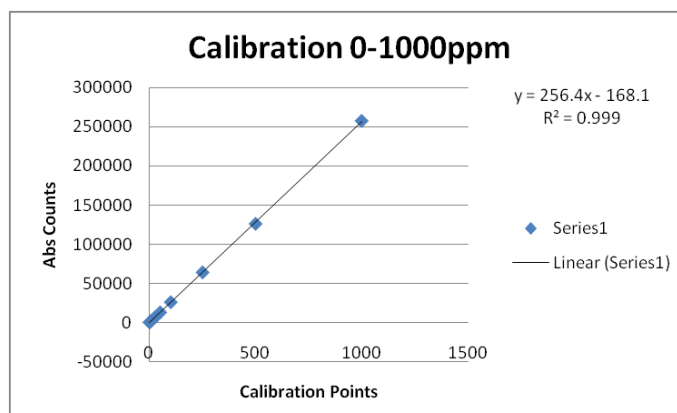
Also during this study, though not required by method 5310B, the Minimum Detection Limits (MDLs) were determined for the TOC method. In order to test the MDL, a smaller calibration curve ranging from 0.5 ppmC-10.0 ppmC was used with an r^2 value of 0.99982. The MDL was determined by analyzing seven replicates at 0.50 ppmC and the following equation was used to obtain a value for the MDL: MDL= (Standard Deviation)*(Student's t value for 99% confidence level)

T value for 7 replicates = 3.14

A demonstration of precision is also required in Method 5310B. According to the method, for a single operator, the following equation must be used to determine the maximum difference between two

consecutive samples. If the samples fall within the determined range, then the instrument is considered precise.

$$S_o = 0.027x + 0.29$$

S_o is the single operator precision and x is the TOC concentration

The concentration for the wastewater reproducibility was 0.50 ppmC. Table V shows the results for the reproducibility study, the MDL study, and S_o value.

Table V TOC MDL	
Repetition	**ppmC**
1	0.446
2	0.444
3	0.445
4	0.432
5	0.443
6	0.472
7	0.480
Average	0.452
Std Dev	0.01738
%RSD	3.85%
MDL	**0.054**
S_o	0.302

Conclusion

The Teledyne Tekmar Lotix TOC analyzer is an instrument aimed at increasing sample throughput, while maintaining reproducibility. The Lotix is ideal for accurately analyzing samples from 0-1000 ppm using a single calibration curve. The necessity to have several methods attached to several calibration curves is resolved by the ability to simply have one calibration curve and one method that can continuously analyze samples with reproducibly and precision. In addition to only needing one calibration curve, the ability to reach low %RSD and standard deviations is a reality. The newest Teledyne Teklink™ software presents the ability to add replicates to maintain the desired %RSD or standard deviation with ease.

The new software enables users to set up a calibration curve in < 1 minute. An 8-point curve from 500 ppbC to 100 ppmC takes just under 2 hours from start to finish (including initial DI Water samples) which equates to 13-15 minutes per triplicate, depending on concentration level.

Tekmar's new flow-through Non-Dispersive Infrared Detector (NDIR) is highly sensitive and can reproducibly quantitate into the low ppb range with a single 0.5 mL injection volume.

References

1. American Public Health Association (APHA) 2005. Standard Methods of Water and Wastewater. 21st ed. American Public Health Association, American Water Works Association, Water Environment Federation publication. APHA, Washington D.C.
2. American Society For Testing and Materials, 1994. Standard Test Method for Total Organic Carbon in Water by High Temperature Oxidation