SHIMADZU
Excellence in Science

Application News

No. AD-0134

Glass Containers / TOC-VWP

Alternative Method for Determination of Total Organic Carbon in Certified Pre-Cleaned Glass Containers

❑ Introduction

Measurement of Total Organic Carbon (TOC) in ultra-pure water is required in pharmaceutical [1], electronics and semiconductor [2] industries. Typically, the water sample is collected into clean glass containers and analysed directly to minimise contamination. The USP 643 procedure mentions that containers must have been scrupulously cleaned of organic residues as this could result in higher TOC values. Hence, it is critical to ensure that these glass sampling containers have low organic residues. Organic carbon residues in glass containers can be checked by gas chromatography - mass spectrometry following EPA Drinking Water Method 524.2 [3]. Organic residues can also be measured by a TOC analyzer. However, there are no international standard methods to evaluate TOC in glass containers. Here, we describe a method to measure TOC content in glass containers using Shimadzu TOC-VWP TOC analyzer. The TOC-VWP, with a detection limit of 0.5 ppb [4] uses the wet-oxidation method which combines ultra-violet (UV) irradiation, persulfate reagents and heating at 80°C.

❑ Experimental

Potassium hydrogen phthalate ($C_8H_5O_4K$) used to prepare Total Carbon (TC) standard solutions was from Kanto Chemical Co Ltd, Japan. The sodium persulfate ($Na_2S_2O_8$) and 85 % phosphoric acid (H_3PO_4) were purchased from Sigma Aldrich, USA. Type E-1 ultra-pure water with resistivity of 18 MΩ using the Milli-Q system from Millipore, Germany was used. The 1000 ppm TC standard solution, UV oxidant and acid reagents were prepared as described in the TOC-VWP User's Manual [4]. The TOC analysis conditions are shown in Table 1.

Table 1: TOC Instrument and analytical conditions

Instrument	:	TOC-VWP
Detector	:	Non-Dispersive Infrared (NDIR)
Method	:	Non-Purgeable Organic Carbon (NPOC)
UV Oxidant	:	1.5 mL
Acid	:	1 %
Sparging Time	:	5 minutes
No of Wash	:	1
Injection Volume	:	3 mL

The pre-cleaned 40 mL glass containers, purchased from Altus Science, United Kingdom were certified to have less than 10 ppb TOC. Two used 40 mL glass containers by the Shimadzu ASI-L auto sampler were also analysed (Figure 1). These used glass containers which have been used to store TC standard solutions, were cleaned by rinsing with ultrapure water several times.

Figure 1: Glass containers tested in this study

The Certificate of Analysis from Altus Science mentions that the "TOC result represent blank subtracted concentration". Hence, before each glass container was measured, blank measurement was performed to correct for instrument blank. Just before analysis, the glass containers were filled completely to the top with ultra-pure water to minimise headspace. During measurement, the sampling tube of the TOC instrument was placed in the ultra-pure water for direct sampling.

❑ Results and Discussion

The NPOC calibration curve established has a coefficient of linear regression (R^2) of more than 0.999 (Figure 2) and good reproducibility as the percentage coefficient of variation (% CV) was less than 3 % (Table 2).

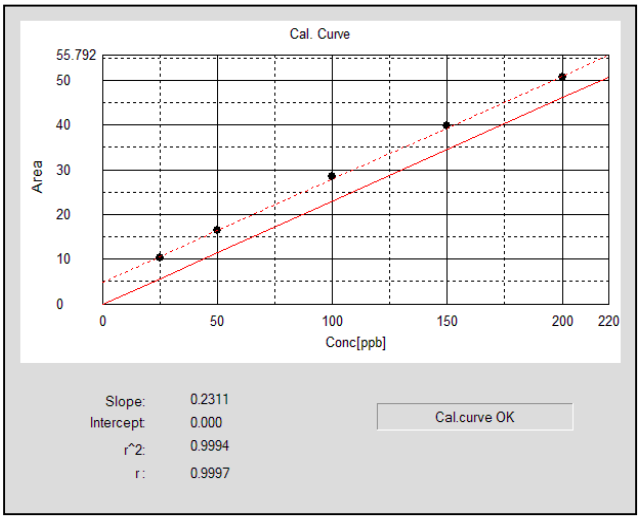

Figure 2: Non-Purgeable Organic Carbon (NPOC) calibration Curve

Table 2: Repeatability of Non-Purgeable Organic Carbon (NPOC)

Standard Concentration	Average Area (3 injections)	% CV
25 ppb	10.30	1.17 %
50 ppb	16.54	0.81 %
100 ppb	28.49	0.44 %
150 ppb	39.89	2.19 %
200 ppb	50.72	0.22 %

The limit of detection (LOD) of the method is calculated by dividing the slope of calibration curve by the area which is equal to 3.3 times the standard deviation (SD) of 10 repetition measurements of the blank solution (ultra-pure water) [5]. The LOD of 1.53 ppb obtained (Table 3) is higher than the reported LOD of 0.5 ppb. This is because the injection volume of 3 mL used in this experiment is less than that of 20.4 mL used to obtain LOD of 0.5 ppb.

Table 3: Calculation of LOD of the TOC method

SD of blank solution (10 repetitions)	0.1072
Slope of NPOC calibration curve	0.2311
LOD	1.53 ppb

Since LOD obtained is less than 2 ppb, the TOC-VWP can be used to measure TOC in glass containers used to collect ultra-pure water. The TOC results of the glass two containers are shown in Table 4.

Table 4: TOC results of glass containers tested

(1) Certified glass containers					
No	Instrument blank (A)		Glass container (B)		Actual Conc. (B - A) (ppb)
	Conc. (ppb)	% CV	Conc. (ppb)	% CV	
1	20.87	0.44	25.75	3.01	4.88
2	15.49	0.26	22.24	2.09	6.75
(2) Used glass containers					
No	Instrument Blank (A)		Glass container (B)		Actual Conc. (B - A) (ppb)
	Conc. (ppb)	% CV	Conc. (ppb)	% CV	
1	17.14	0.32	36.91	2.44	19.77
2	14.87	0.16	37.92	1.48	23.05

The TOC contents of pre-cleaned glass containers were less than 10 ppb, which were as obtained by Altus Science. The TOC of used glass containers was higher than the pre-cleaned glass containers as these containers were only cleaned by rinsing with ultra-pure water. Hence, by analyzing TOC in ultra-pure water collected in glass containers, the total carbon residue in glass containers can be monitored and quantified.

❑ Conclusions

Carbon residues in glass containers can be measured by analyzing TOC in ultra-pure water collected in glass containers directly. The TOC-VWP can be used to determine whether the glass containers are cleaned effectively as it has a LOD of less than 2 ppb.

❑ References

1. United States Pharmacopoeia <643>. TOC.
2. ASTM D5127-13. Standard Guide for Ultra-Pure Water Used in the electronics and Semiconductor Industries.
3. EPA Method 524.2. Measurement of Purgeable Organic Compounds in Water by Capillary Column GC-MS.
4. Shimadzu TOC-VWP User's Manual (2013).
5. TOC-LCPH - TOC Detection Limit Test Standard Operating Procedures (ZEHV-0225).

SHIMADZU
Excellence in Science

SHIMADZU (Asia Pacific) Pte. Ltd
79 Science Park Drive, #02-01/08 Cintech IV, Singapore 118264
www.shimadzu.com.sg
Tel: +65-6778 6280 Fax: +65-6778 2050