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Application News

No. O79

Total Organic Carbon Analysis

TOC Measurement Using Pre-Cleaned Vials

Analysis of samples with low total organic carbon (TOC) concentrations, such ultrapure water and cleaning solutions, is conducted in many industrial fields, including drug and semiconductor manufacturing, and regular control of TOC values is necessary in order to confirm that water quality and equipment cleanliness satisfy the prescribed standards.

When sampling water, even assuming the sample is clean, contamination may proceed due to organic compounds or carbon dioxide dissolving into the sample from the atmosphere or substances in contact with the water after sampling. As a result, the measured value will be higher than the actual value, and reanalysis may be required. Thus, countermeasures to prevent sample contamination are of the utmost importance when handling test materials with low TOC concentrations.

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Fig. 1 "CQ Vial™ for TOC Analyzer" Pre-Cleaned Vials with QC Certificate of Analysis

Impurities of Sample Containers

In TOC measurements, the results may be affected not only by the ultrapure water, reagents used, and the surrounding environment, but also by contamination from the sample container and glassware. These problems occur unexpectedly, and in many cases, they cannot be reproduced and no clear cause can be determined. For this reason, the United States Pharmacopeia (USP) <643> stipulates "use glassware and sample containers that have been scrupulously cleaned of organic residues." USP <1051> describes several cleaning methods, such as use of hot nitric acid or a chromic acid-sulfuric acid mixture. As safer alternatives, USP <1051> also mentions cleansing agents such as trisodium phosphate and synthetic detergents, but notes that prolonged rinsing is necessary.

When establishing a cleaning method, it is important to demonstrate that its procedure is appropriate and effective, but this requires much time and labor. In addition, it is also necessary to verify a method for storing glassware so as to avoid TOC contamination after cleaning.

Pre-Cleaned Vial with QC Certificate of Analysis

The following introduces "CQ Vial™ for TOC," a pre-cleaned vial with a QC certificate of analysis that supports reliable and high sensitivity measurement of TOC.

CQ vials are pre-cleaned and can be used as-is after opening, reducing the time and trouble involved in vial cleaning, drying, and storage work, and also reduces the quality risks due to human error and differences in the skill level of personnel.

Table 1 Specification of Pre-Cleaned Vials

Product name	CQ vial for TOC
Part No.	227-34039-01
Content	40 mL vial × 72, QC Certificate of Analysis
Applicable equipment	Autosamplers for TOC analyzers (Devices using 40 mL vial)

Fig. 2 Appearance of CQ Vials and QC Certificate of Analysis

CQ vials are manufactured and cleaned in accordance with a strict procedure. After manufacture and cleaning, a dustproof cap is placed on each vial, and the vials are packed in a box made of dust-free plastic material. A lot number is assigned to the product, which is shipped with a QC Certificate of Analysis declaring that elution into the vials does not exceed 10 µgC/L (i.e., carbon concentration of 10 µg/L).

After opening at the intended place of use, the CQ vials can be filled with the sample without cleaning or other treatment. Cleaning before use is not necessary. If CQ vials are used, error can be reduced along the entire workflow and quality can be improved, not only with ultrapure water and unknown samples, but also with standard solutions for calibration use and control samples. This article introduces the data obtained when ultrapure water was measured using CQ vials and reusable vials which were cleaned after use.

Measurement Method

Calibration Curve

The TOC analyzer was calibrated by using standard solutions of potassium hydrogen phthalate with concentrations of 20, 100, and 200 µgC/L (= ppb). Fig. 3 shows the calibration curve. In order to eliminate the effect of carbon impurities in the ultrapure water used in preparing the standard solutions, the calibration curve was shifted in parallel so as to pass through the origin of the graph.

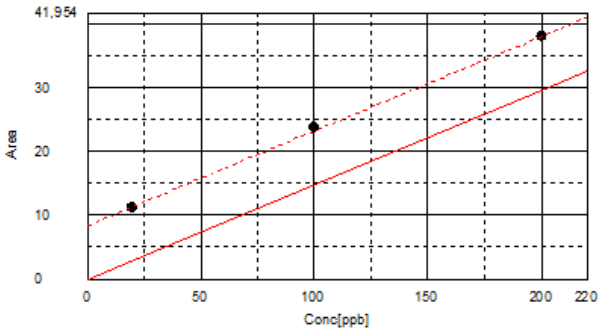

Fig. 3 3-Point Calibration Curve for 20,100,200 µgC/L (= ppb)

Measurement Conditions

Table 2 shows the measurement conditions.

Table 2 Measurement Conditions

Analyzer	: TOC-V_{WP} wet oxidation type TOC analyzer
Measurement item	: NPOC (Non-purgeable organic carbon) (=TOC by acidification and sparging treatment)
Measurement method	: UV oxidation decomposition – NDIR method
Oxidizer	: 1.5 mL
Injection volume	: 3,000 µL
Sparge time	: 3 min

The detection limit (DL) of this measurement method was calculated by the following formula from the standard deviation σ of the values of 5 measurements of blank water (ultrapure water) and the slope S of the calibration curve.

$$DL = \frac{3.3 \times \sigma}{S} \Rightarrow DL = \frac{3.3 \times 0.09794}{0.1491} = 2.168\ \mu gC/L^{*1}$$

*1 A lower detection limit is obtained when the injection volume is increased.

Measurement Results

As blank water, ultrapure water was sampled in a large glass container (B). A portion of the blank water was transferred from the glass container to a vial (V), which was then sealed with a cap with a septum (Fig. 4). NPOC (non-purgeable organic carbon) measurements of both samples were carried out with a TOC-V_{WP} analyzer. Next, the pure water initially from the glass container was measured, and then was measured from the vials.

The TOC value due to elution from the vial was obtained by subtracting the measured value (B) of the blank water from the measured value (V) of the vial. This procedure was repeated 3 times with CQ vials and 3 times with reusable vials (vials cleaned with a cleaning machine in the laboratory), for a total of 6 repetitions. The vials were not prewashed with the sample. Table 3 shows the measurement results.

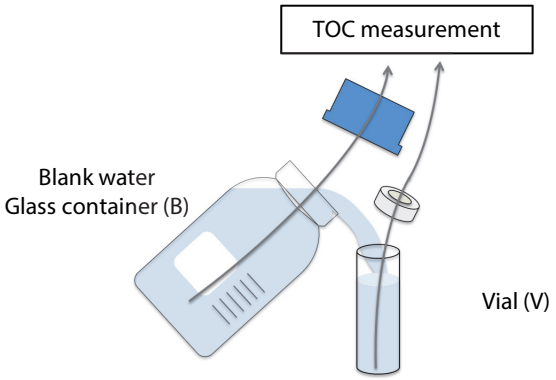

Fig. 4 Sample Measurement Procedure

Table 3 Measurement Results

Sample name	Blank (B) [µgC/L]	Vial (V) [µgC/L]	Elution (V–B) [µgC/L]
CQ vial 1	28.68	35.29	6.61
CQ vial 2	27.05	35.38	8.33
CQ vial 3	25.86	32.23	6.37
Reusable vial 1	25.23	134.2	108.97
Reusable vial 2	27.25	94.43	67.18
Reusable vial 3	26.69	133.0	106.31

When the CQ vials were used, V–B, that is, the TOC value due to contamination from the vial, was not more than 10 µgC/L in all cases. However, with the reusable vials, V–B was 60 to 110 µgC/L. Thus, it can be understood that the TOC value of the samples increased due to elution of impurities adhering to the interior of the vial when the reusable vials are used.

Conclusion

If CQ vials are used, elution of impurities from the interior of the vial to the sample can be suppressed as much as possible, and more reliable and high sensitivity measurement is possible.

In addition, the work of cleaning, drying, and storing the vials is not necessary, which not only saves time and space, but can also reduce the quality risks associated with human error and variations in the skill level of personnel.

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