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Application News

No.O54

Total Organic Carbon Analysis

Measurement of TOC in Perfluorochemical (PFOS) Solution

Perfluorooctane sulfonate (PFOS) is a man-made organic straight-chain compound consisting of an 8-carbon chain with fluorine atoms bonded to each carbon, and a sulfonic acid terminal group (Fig. 1). It is a surfactant that easily dissolves in both oil and water, and is used, among other things, as a stain repellent, fabric protector, and in fire-fighting foam. PFOS is an extremely stable compound with strong carbon - fluorine bonds, and reports of its accumulation in wildlife and the environment have attracted international attention and concern, leading to the designation of PFOS as a persistent organic pollutant (POP).
The persistent nature of PFOS prevents oxidative decomposition using wet chemical oxidation TOC analyzers, however, the Shimadzu high-temperature catalytic combustion TOC analyzer quantitatively recovers PFOS with high sensitivity and accuracy. Here, we demonstrate measurement of PFOS using the TOC-L$_{CPH}$ high-temperature catalytic combustion and the TOC-V$_{WS}$ wet chemical oxidation total organic carbon analyzers.

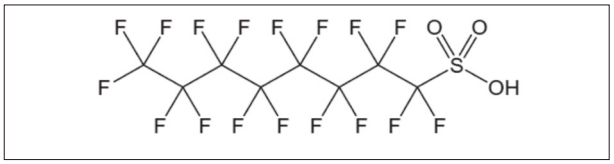


Fig. 1 Structure of PFOS

(1) Analysis of PFOS Using TOC-L$_{CPH}$ High-Temperature Catalytic Combustion TOC Analyzer

Measurement Method

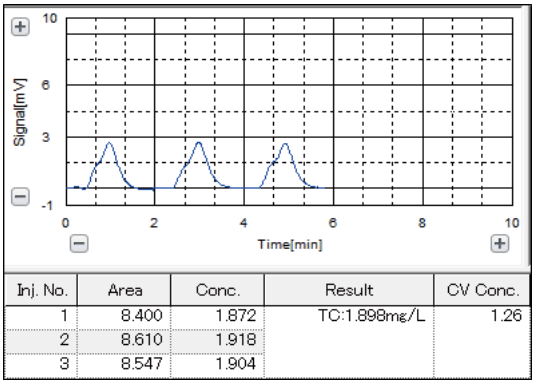
PFOS was dissolved in purified water, and aqueous solutions were prepared at 10 mg/L and 5 mg/L. The TOC concentrations in these solutions were 1.921 mgC/L (carbon concentration) and 0.961 mgC/L, respectively. Because PFOS solutions are prone to foaming, TOC measurement was conducted using the TC-IC method.

Measurement Conditions

Analyzer	:TOC-L$_{CPH}$ Combustion Total Organic Carbon Analyzer
Catalyst	:Standard catalyst
Measurement items	:TOC (= TOC by TC-IC)
Calibration curves	:TC: 2-point calibration curve using 0 – 3 mgC/L potassium hydrogen phthalate solution IC: 2-point calibration curve using 0 – 3 mgC/L sodium carbonate / sodium hydrogen carbonate aqueous solution
Sample	:PFOS; 1, 1, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 8-Heptadecafluoro-1-octanesulfonic acid (Manufactured by Wako Pure Chemical Industries, Ltd.)

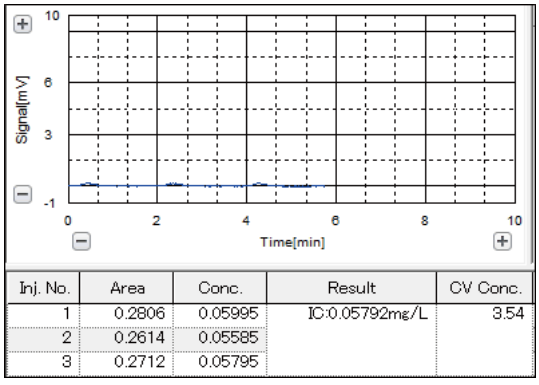
Measurement Results

The measurement results are shown Table 1 and the measurement data sheets obtained are shown in Fig. 2. These results demonstrate that using the high-temperature catalytic combustion TOC analyzer allows accurate analysis of PFOS solutions with high detection rates.



Inj. No.	Area	Conc.	Result	CV Conc.
1	8.400	1.872	TC:1.898mg/L	1.26
2	8.610	1.918		
3	8.547	1.904		

10 mg/L PFOS aqueous solution TC Measurement Data



Inj. No.	Area	Conc.	Result	CV Conc.
1	0.2806	0.05995	IC:0.05792mg/L	3.54
2	0.2614	0.05585		
3	0.2712	0.05795		

10 mg/L PFOS aqueous solution IC Measurement Data

Fig. 2 Data Obtained Using TOC-L$_{CPH}$ Combustion TOC Analyzer

Table 1 Results Using TOC-L$_{CPH}$ Combustion TOC Analyzer

Sample Name	TOC Theoretical Value (mgC/L)	TC Measurement Value (mgC/L)	IC Measurement Value (mgC/L)	TOC (= TC-IC) Measurement Value (mgC/L)
10 mg/L PFOS aqueous solution	1.921	1.898	0.058	1.840
5 mg/L PFOS aqueous solution	0.961	0.959	0.038	0.921

(2) Analysis of PFOS Using TOC-Vws Wet Chemical Oxidation TOC Analyzer

Measurement Method

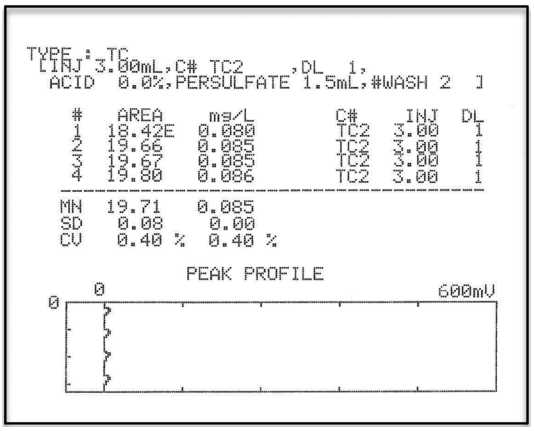
As in item (1), PFOS solutions of 10 mg/L and 5 mg/L were prepared, and TOC measurement was conducted by the TC-IC method.

Measurement Conditions

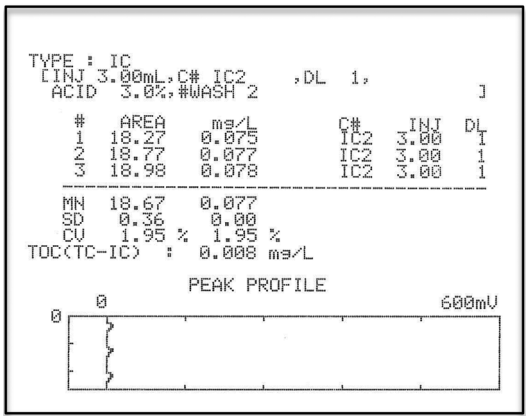
Analyzer	:TOC-Vws Wet Oxidation Total Organic Carbon Analyzer
Measurement items	:TOC (= TOC by TC-IC)
Calibration curves	:TC: 2-point calibration curve using 0 - 3 mgC/L potassium hydrogen phthalate solution IC: 2-point calibration curve using 0 - 3 mgC/L sodium carbonate / sodium hydrogen carbonate aqueous solution
Sample	:PFOS; 1, 1, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 8-Heptadecafluoro-1-octanesulfonic acid (Manufactured by Wako Pure Chemical Industries, Ltd.)

Results

The measurement results are shown in Table 2, and the measurement data sheets are shown in Fig. 3. Using wet chemical oxidation, PFOS was barely detected. The wet chemical oxidation TOC analyzer uses an acid persulfate reagent, ultraviolet radiation and heating for oxidizing the sample. In comparison to the 680 °C high-temperature catalytic combustion TOC analyzer, the near absence of detection using the wet-chemical UV oxidation is due to the weaker oxidizing power of wet chemical oxidation TOC analyzers. For measurement of organic compounds like PFOS that are not easily oxidized, it is clear that combustion TOC analyzers are more suitable regardless of the organic substance.



10 mg/L PFOS aqueous solution TC Measurement Data



10 mg/L PFOS aqueous solution IC Measurement Data

Fig. 3 Data by TOC-Vws Wet Chemical Oxidation TOC Analyzer

Table 2 Results by Wet Chemical Oxidation TOC-Vws

Sample Name	TOC Theoretical Value (mgC/L)	TC Measurement Value (mgC/L)	IC Measurement Value (mgC/L)	TOC (= TC- IC) Measurement Value (mgC/L)
10 mg/L PFOS Aqueous Solution	1.921	0.085	0.077	0.008
5 mg/L PFOS Aqueous Solution	0.961	0.079	0.064	0.014

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