

TOC Recovery Studies Comparing Combustion/NDIR with UV-Persulfate/Membrane Conductometric Methods for Municipal Raw and Finished Drinking Water Monitoring

Objective

Numerous studies have been conducted to compare the performance of various TOC methodologies on a wide range of raw source water and finished drinking water samples. The methodologies studied are those that are approved for TOC monitoring under the USEPA's Disinfectants and Disinfection Byproducts Rule (D/DBPR).

The results of these studies demonstrate that UV-Persulfate oxidation combined with membrane conductometric detection produces results comparable to combustion oxidation combined with NDIR detection. The studies discussed and summarized in this application note include:

1. USEPA study referenced in USEPA Method 415.3 for TOC and SUVA
2. City of Fort Collins study
3. Central Kagaku Corporation study

1. USEPA study referenced in USEPA Method 415.3 for TOC and SUVA

The USEPA method for TOC measurement was developed for use with D/DBPR compliance monitoring. A copy of the method can be reviewed at http://www.epa.gov/nrlcwww/m_415_3Rev1_1.pdf.

Section 17 of this method lists the results of testing accomplished on the various TOC measuring methodologies covered by the method, including UV-Persulfate/Membrane Conductometric and Combustion/ NDIR. Testing was performed on real-world samples collected from sites around the United States. **Table 1** summarizes the TOC recoveries for three instruments compared in the study.

Table 1. TOC Recoveries for Instruments Compared in the USEPA Study

Source Water	Sievers UV-Persulfate/Membrane Conductometric			Catalyzed High-Temp Combustion / NDIR			High-Temp Combustion/ NDIR		
	%RSD	Mean (ppm)	%Recov.	%RSD	Mean (ppm)	%Recov.	%RSD	Mean (ppm)	%Recov.
Boulder Creek	0.33	12.1	103	2.86	11	100	6.02	11.0	97
Shingobee River	0.18	13.0	98	2.19	13	97	0.84	12.1	97
Bolten Well	0.44	11.4	100	1.70	11	100	1.02	10.8	98
Ohio River	0.57	13.2	102	1.79	13	100	1.19	12.1	98
Muddy Creek	0.00	14.6	103	2.02	14	96	3.40	13.1	98
Great Miami River	0.33	13.8	102	1.66	14	101	0.78	12.3	96
Saint Leon Well	0.52	11.1	104	7.64	10	100	n/a	10.0	97
Average	0.34	12.7	101.7	2.84	12.3	99.1	2.21	11.6	97.3



Table 2. City of Fort Collins Comparison Study Results

Instrument	Conc Range	Humic Acid	Isopropanol	Maltose	Potassium Acid Phthalate	Sodium Acetate	Sodium Salicylate	Tanic Acid
OI	~7mg/L	82.1	97.9	98.1	108.3	108.4	106.6	106.8
OI	~7mg/L	80.0	93.5	91.7	97.1	103.5	99.9	100.9
	Avg %R	81.1	95.7	94.9	102.7	105.9	103.2	103.8
Sievers	~0.7	121.4	109.3	102.5	113.1	104.2	109.5	106.4
Sievers	~7mg/L	108.3	103.8	93.9	101.0	98.4	102.0	118.5
Sievers	~7mg/L	107.0	111.8	96.7	104.1	102.3	103.7	107.2
Sievers	~7mg/L	105.4	88.8	94.5	102.4	99.8	101.1	108.1
	Avg %R	110.5	103.4	96.9	105.1	101.2	104.1	110.0
Shimadzu	~0.7	51.2	99.9	103.6	103.9	112.8	109.2	97.6
Shimadzu	~7mg/L	64.0	80.6	84.9	100.3	87.9	89.7	90.6
Shimadzu	~7mg/L	64.6	88.7	90.8	95.8	95.7	95.9	94.4
Shimadzu	~7mg/L	54.6	63.0	83.0	87.2	88.6	87.0	88.4
WQL TOC	~7mg/L	77.4	90.3	93.0	101.5	100.8	100.3	98.6
	Avg %R	62.4	84.5	91.1	97.7	97.1	96.4	93.9

2. City of Fort Collins

The City of Fort Collins, Colorado conducted a comparison study between three instruments manufactured by Sievers¹ (UV-Persulfate/ Membrane Conductometric), Shimadzu (Combustion/NDIR) and OI (Combustion/NDIR). This study differs from the EPA study in that this study evaluated seven known compounds considered to be common to drinking water sources and that would present a significant analytical challenge to the instruments. The same concentration standard solutions were prepared on several different days, and then run on each instrument. **Table 2** and **Figures 1** and **2** summarize the results of the comparison.

In general, the results show good comparison between the different TOC methodologies. For Humic Acid, one of the Combustion/NDIR methods yielded significantly lower than expected recoveries. Other studies have suggested that this effect—not limited to Humic Acid—is a result of significant loss of Dissolved Organic Carbon (DOC) during the sparging step, which is conducted to remove background inorganic carbon.²

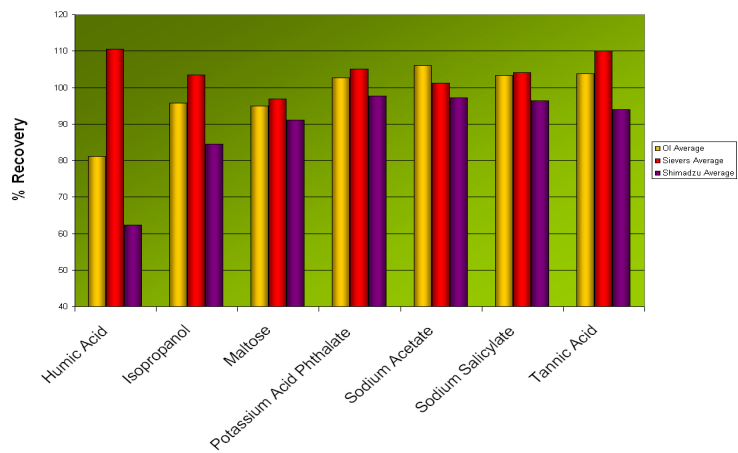


Figure 1. Average % Recovery of Spiked Compounds in City of Fort Collins Study

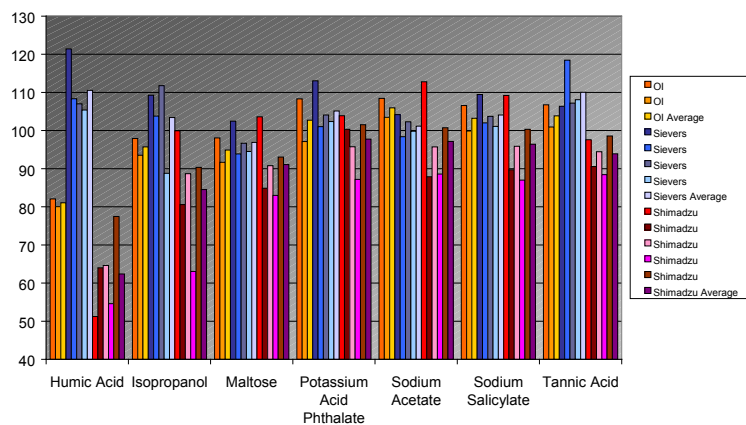


Figure 2. City of Fort Collins Study Results



3. Central Kagaku Corporation Study

In preparation of TOC regulations in Japan, Central Kagaku Corporation (distributor at the time for Hach Company and Sievers Instruments) conducted a study comparing the UV-Persulfate method to the Combustion/NDIR method on real-world raw water samples.

Three pretreatment techniques were utilized on split samples:

- Filtration with a 0.45-micron filter to measure DOC
- Filtration through a 100-micron filter followed by filtration through a 50-micron filter
- Homogenization, per the Japanese regulation which specified homogenization for samples containing particulates

The study evaluated performance of a Sievers TOC Analyzer and a Shimadzu TOC analyzer. The results are summarized in **Figures 3–5**. Turbidity and suspended solids are graphed with the TOC data.

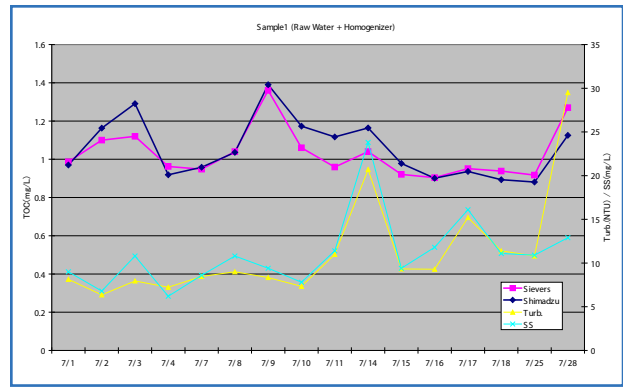


Figure 3. Sample 1 (Raw Water + Homogenizer) from the Central Kagaku Study

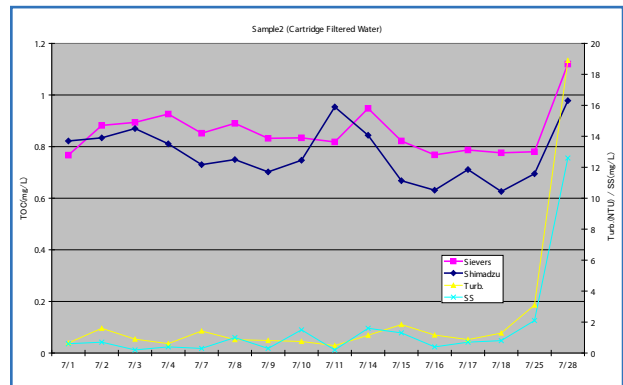


Figure 4. Sample 2 (Cartridge filtered water) from the Central Kagaku Study

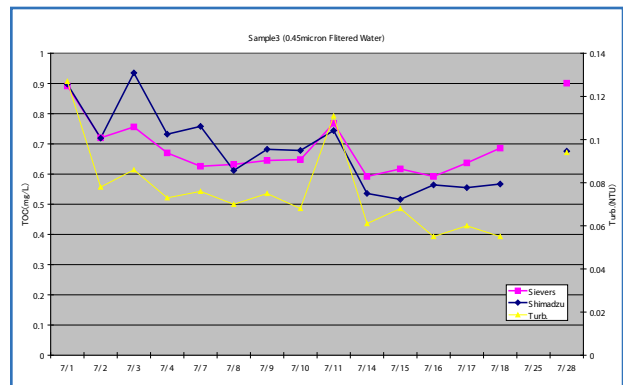


Figure 5. Sample 3 (0.45 micron filtered water) from the Central Kagaku Study

¹ Sievers Instruments is now GE Analytical Instruments

² Kaplan, Louis A. "Comparison of Three TOC Methodologies," AWWA

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