

## TOC Analysis of Hot Spring Water and Bathtub Water

In Japan, water quality standards and inspection methods are provided for inlet hot water (unrecycled hot water supplied directly to the bath), original water (water used for hot water and temperature adjustment), and bathtub water used in public bathhouses. Until recently, the organic content of these types of water had been evaluated by potassium permanganate consumption, but under a recent revision of Guidelines for Management of Sanitation, Etc. in Public Bathhouses, evaluation by total organic carbon (TOC) was added (as of Sept. 19, 2019, Ministry of Health, Labour and Welfare Notification EF 0919, No. 8 of the Director-General of the Department of Environmental Health and Food Safety). As a result of this revision, it is now possible to measure the organic content by either TOC or potassium permanganate consumption.

The potassium permanganate consumption test requires much manual work, including preparation of the reagent, boiling, and titration, which occupy the analyst's time. In contrast, TOC is an instrumental analysis technique, and stable results can be obtained regardless of the analyst. If a sampler is used, continuous analysis of multiple samples is also possible, and the work efficiency of the laboratory can be improved by running the sampler at night.

Moreover, when hot spring water (geothermal water) is used in inlet hot water or bathtub water, the water sometimes contain chlorides, sulfates, and alkali salts originating from the hot spring. Although the measured values obtained in the potassium permanganate consumption test may be affected in some cases if the sample contains oxidizable substances other than organic compounds, TOC measurements are not affected by coexistent substances.

This article introduces an example of evaluation of the organic content in hot spring water used as bathhouse water and water containing bath additives using a Shimadzu combustion-type TOC analyzer.

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### ■ Analysis Method

Using commercially-available concentrated-type hot spring water and bathing agents, measurement samples were prepared by dissolving each of the products in pure water to the use concentration indicated on the package.

Measurement samples were also prepared by adding potassium hydrogen phthalate to those samples so as to obtain 5 mgC/L (carbon concentration in mg/L) and 10 mgC/L as TOC, and TOC measurements were conducted.

The instrument was calibrated with 0 mgC/L and 20 mgC/L aqueous solutions of potassium hydrogen phthalate, and a 2-point calibration curve was prepared.



**Table 1 Hot Spring Water and Bathing Agents Used**

Bathing agent		Features
Concentrated hot spring water A	Liquid	Weakly alkaline high tonicity spring
Concentrated hot spring water B	Liquid	Alkaline simple spring
Concentrated hot spring water C	Liquid	Acid-aluminum-sulfate-chloride spring
Concentrated hot spring water D	Liquid	Simple radioactive spring (low tonicity high neutrality spring)
Medicinal bathing agent E	Powder	White turbid agent
Medicinal bathing agent F	Powder	Light green transparent

**Table 2 Guidelines for Water Quality Standards, Etc. in Public Bathhouses (Excerpt)**

Article 3 The water quality standard and inspection methods for inlet hot water, original water, hot water for washing and rinsing, and water for washing and rinsing shall be as provided in the following.
1. Water quality standard
d. Organic compounds (amount of total organic carbon (TOC)) shall be 3 mg/L or less, or potassium permanganate consumption shall be 10 mg/L or less.
Article 4 The water quality standard and inspection methods for bathtub water shall be as provided in the following.
1. Water quality standard
b. Organic compounds (amount of total organic carbon (TOC)) shall be 8 mg/L or less, or potassium permanganate consumption shall be 25 mg/L or less.

**Table 3 Measurement Conditions**

Analyzer	: Shimadzu TOC-L <sub>CPH</sub> combustion-type total organic carbon analyzer
Measurement item	: TOC (=NPOC; TOC using acidification and sparging)
Catalyst	: TOC standard catalyst
Calibration curve	: 2-point calibration curve prepared using 0 mgC/L and 20 mgC/L potassium hydrogen phthalate aqueous solutions
Injection amount	: 50 µL
Samples	: Hot spring water or bathing agent dissolved in pure water Solutions prepared by adding 5 mgC/L and 10 mgC/L of potassium hydrogen phthalate to the above samples

### ■ Analysis Results

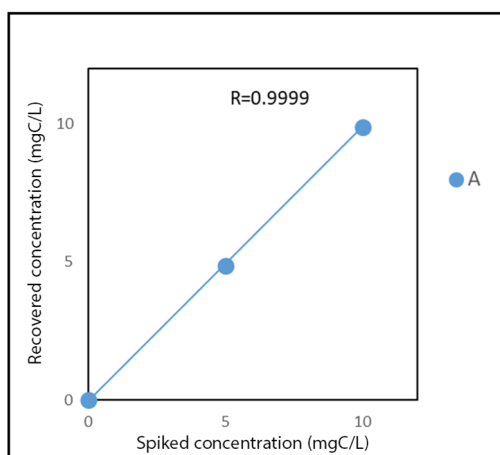
Table 4 shows the results of measurement of aqueous solutions of the concentrated hot spring water or medicinal bathing agents and solutions prepared by spiking those samples with an organic compound. Fig. 1 and Fig. 2 show the correlation diagram for the spiked concentration and recovered concentration. The recovery rate for both samples was substantially 100%. The correlation coefficient R for the spiked concentration and recovered concentration was 0.9999 or higher, showing an excellent correlation.

### ■ Conclusion

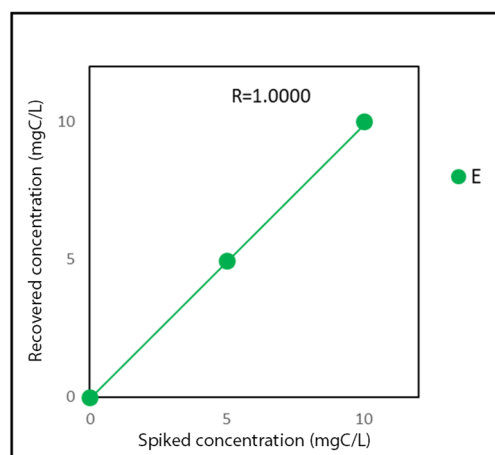
Evaluation of the organic concentration levels of hot spring water and bathhouse water was possible by using a Shimadzu combustion-type TOC analyzers, which is capable of accurate measurement of organic compounds unaffected by other ingredients in hot spring water and bathing agents.

**Table 4 Results of Measurement of Aqueous Solutions of Hot Spring Water and Bathing Agents**

Sample		Hot spring water A	Hot spring water B	Hot spring water C	Hot spring water D	Bathing agent E	Bathing agent F
Spiked concentration	Not spiked	0.197	0.028	0.037	0.067	0.288	1.50
	5 mgC/L (recovery rate)	5.07 (97.5%)	5.06 (100.6%)	4.99 (99.0%)	4.952 (97.6%)	5.26 (99.4%)	6.60 (102%)
	10 mgC/L (recovery rate)	10.1 (99.0%)	10.0 (99.7%)	9.89 (98.5%)	10.0 (99.0%)	10.3 (100%)	11.6 (101%)
Correlation coefficient R for above 3 points		0.9999 (see Fig. 1)	1.0000	1.0000	0.9999	1.0000 (see Fig. 2)	1.0000



**Fig. 1 Correlation Diagram of Spiked Concentration and Recovered Concentration (Hot Spring Water A)**



**Fig. 2 Correlation Diagram of Spiked Concentration and Recovered Concentration (Bathing Agent E)**



**Fig. 3 Shimadzu TOC-L Total Organic Carbon Analyzer**