Online TOC Analysis Based on Reagent-free Oxidation of Dissolved Organic Matter Using a Mercury Lamp-Pass-Through Photoreactor

Takayuki SATOU, Tetsuya NAKAZATO,† and Hiroaki TAO

Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

The reagent-free mineralization of dissolved organic matter (DOM) in river water was achieved within 1 min using a lamp-pass-through photoreactor containing a narrow reaction tube (2 mm i.d.) passing through a 40 W mercury lamp. The structure efficiently irradiated the sample solution in the tube with vacuum ultraviolet (VUV; 185 nm) light from the lamp, which rapidly decomposed the DOM with hydroxyl radicals generated efficiently from the water and oxygen that are naturally present in the solution. The photoreactor was also applicable to oxidizing reagent-free online total organic carbon (TOC) analysis of DOM in river-water samples using a non-dispersive infrared radiation detector after acidification of the sample using 20 mmol L⁻¹ phosphoric acid. The detection limit for phthalate at the injection of 390 μL was 6.2 μg of carbon L⁻¹. The repeatability, as expressed by the relative standard deviation, was 2.5% for thrice-repeated analyses of a river sample with 1.85 mg of carbon L⁻¹.

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Introduction

Dissolved organic matter (DOM) in river water is a key substance in biogeochemical carbon cycling in aquatic environments. However, excess DOM degrades the water quality, which can threaten human and environmental health. The treatment and control of water resources require rapid online analysis of the total organic carbon (TOC) of the DOM portion of river-water samples. A key to successful analysis is the rapid decomposition of DOM to inorganic carbon during analysis, which is subsequently detected by non-dispersive infrared radiation (NDIR), conductivity, or capacitance measurements. For widespread analysis, it is also important for decomposition to use the smallest amounts of chemicals and facilities by the greatest degree possible, which can reduce both the costs and maintenance.

Typical decomposition methods employed by conventional TOC analyzers are high-temperature catalytic oxidation (HTCO) and photochemical oxidation with ultraviolet irradiation and oxidant reagents (UV/OX). However, the HTCO methods require high temperatures (>600°C) and expensive catalysts that must be renewed at regular intervals because of degradation, whereas the UV/OX method requires oxidants or photocatalysts, such as peroxodisulfate or titanium dioxide. Many of these reagents are hazardous, expensive when employed for analysis, and necessitate frequent maintenance.

Photodecomposition methods using vacuum ultraviolet (VUV) light (e.g., 185 nm light provided by a low-pressure mercury lamp) can achieve the reagent-free decomposition of organic materials using hydroxyl radicals (‘OH) generated from the homolysis of the water molecules in the solution. The radicals can oxidize DOM to carbon-centered radicals, which subsequently add the oxygen molecules dissolved in the solution to mineralize the intermediate products to inorganic carbon. To achieve rapid decomposition within minutes for on-line TOC measurements, the VUV light emitted from the lamp must irradiate a sample solution efficiently in a thin reactor. The sample solution thickness should be less than several millimeters because the high absorption coefficient of water provides a short incident path for 185 nm light. Some VUV flow-through photoreactors employing thin-film reaction chambers have achieved such decomposition, but they require a great deal of chemicals and facilities that are too expensive for analysis. For example, cylindrical thin-film photoreactors that employ mercury lamps use a reactor equipped with many polymer pins and an electric motor to stir the sample solution to promote decomposition. Nitrogen gas is also used to minimize attenuation of the VUV light of the lamp by the atmosphere. The thin-film photoreactors were usually used as a post-column reactor in size-exclusion chromatography combined with NDIR for the characterization of DOM in natural water.

Another VUV light source, a xenon excimer lamp, is useful for DOM decomposition because of its high quantum yield of ‘OH generated from water molecules. However, Xe-excimer lamps require high-frequency and high-voltage power supplies, which increase the costs and raise the necessary safety management levels. In some cases, rapid mineralization of the DOM requires additional oxygen gas because the
thickness of the portion of the solution in which ‘OH and the radicalized intermediates are produced is too low to react with the oxygen that is naturally present in a bulk solution as a result of the extremely strong absorption of 172 nm light.\textsuperscript{15,16,14}

Furthermore, for all VUV photoreactors, the decomposition efficiency of the DOM decreases in the presence of coexisting substances that absorb the VUV light and scavenge ‘OH, such as chloride and carbonate.\textsuperscript{12,19} To minimize that interference, the chromatographic separation of the coexisting substances was applied before decomposition.\textsuperscript{17,20–23}

In this paper, we propose a reagent-free and rapid decomposition method for DOM in river water using a VUV mercury lamp-pass-through (LPT) photoreactor. Its most distinguishing feature is its narrow synthetic quartz reaction tube, which passes directly through a low-pressure mercury lamp. The reactor effectively irradiated a sample solution with VUV light emitted at 185 nm without the need for purging with nitrogen gas. It efficiently decomposed DOM without stirring equipment or the addition of oxygen. We previously used a VUV reactor with a similar structure as a post column reactor in liquid chromatography combined with inductively coupled plasma mass spectrometry.\textsuperscript{24} The reactor enabled a reagent-free and rapid decomposition of refractory organoarsenic species, such as arsenobetaine, but the interfering substances for decomposition were separated using chromatography. This study examined a reagent-free decomposition of DOM in river water without the separation. We also investigated the mechanism underlying rapid decomposition. Finally, we examined the system’s applicability to online TOC analysis of river water under conditions that reduce the need for chemicals and facilities.

**Experimental**

**Reagents**

Analytical-grade ethanol, acetic acid, malonic acid, glucose, sodium carbonate, sodium nitrate, sodium chloride, and acetanilide were obtained (Wako Pure Chemical Industries Ltd., Osaka, Japan). Ultrapure-grade phosphoric acid was acquired from Merck and Co. Inc. (NJ). Two reference humic substances, Nordic Aquatic Humic Acid (NAHA, 1R105H) and Nordic Aquatic Fulvic Acid (NAFA, 1R105F) and Nordic Aquatic Humic Acid (NAHA, 1R105H), were obtained from the International Humic Substances Society (MN). Ultrapure water (Milli-Q TOC; Millipore Corp., MA) was used throughout the study.

**River-water samples**

River-water samples (HiR1 – 4) were collected at four points from upstream to downstream portions of the Hinuma River in Ibaraki Prefecture, Japan. Specifically, sample points HiR1 and HiR4 were located, respectively, near a hilltop reservoir and near an urban area. The samples, after collection in polypropylene bottles that had been washed with 5% HNO\textsubscript{3} and VUV reactor with a nitrogen gas. It efficiently decomposed DOM without stirring (Milli-Q TOC; Millipore Corp., MA) was used throughout the study. Specifically, sample points HiR1 and HiR4 were located, respectively, near a hilltop reservoir and near an urban area. The samples, after collection in polypropylene bottles that had been washed with 5% HNO\textsubscript{3} and ultrapure water, were filtered immediately using a cellulose acetate membrane (0.45 μm, CA45A047A; Advantec Toyo Kaisha Ltd., Tokyo, Japan), after which they were stored at 4°C in the dark until use for decomposition experiments, which were conducted within two weeks. The inorganic anions in the river waters were determined using an ion chromatograph (IC-20; Dionex Corp., CA).

**LPT photoreactors**

A schematic diagram of the LPT reactor is shown in Fig. 1(a). The reactor consisted of a synthetic quartz reaction tube (o.d. 4 mm, i.d. 2 mm) passed through a low-pressure mercury lamp. All reactors were fabricated in our laboratory.\textsuperscript{24} Two lamps with respective output powers of 6 and 40 W were used in the present study. The respective lengths of the 6 and 40 W lamps were 150 and 250 mm. The surface of the lamps was covered with aluminum foil during use to protect the operator from VUV irradiation. In the case of the 40 W reactors, the outer surfaces of the lamps were cooled at 10°C using a Peltier device to prevent the sample solution from boiling. A peristaltic pump was used to introduce the sample solution. The VUV irradiation time was changed by varying the pump flow rate, pump tube diameter, and by repeated introduction of a sample that had been irradiated once.

**Online TOC analysis using an LPT photoreactor**

Figure 1(b) presents a schematic diagram of an online TOC analyzer combined with an LPT reactor with a 40 W lamp and the NDIR detection component of a commercial HTCO-type TOC analyzer (TOC-V; Shimadzu Corp., Kyoto, Japan). The sample solution was only acidified with phosphoric acid, but not air-purged to positively remove inorganic carbon (IC) that originally exists in the solution. The final concentration of the acid was set at 20 mmol L\textsuperscript{-1}. Then, 390 μL of a sample was introduced into the LPT reactor using a peristaltic pump at 0.78 ml min\textsuperscript{-1} with a three-way switching valve. A carrier solution of 20 mmol L\textsuperscript{-1} phosphoric acid was applied between introductions of the samples after switching the valve. The DOM in the sample was then decomposed, and was converted immediately to CO\textsubscript{2} gas, which was detected by the NDIR detector through a glass gas-liquid separator with flowing carrier gas of air at 150 mL min\textsuperscript{-1}.

**Evaluation of the decomposition efficiency of the DOM**

The decomposition efficiency of the DOM in a sample solution placed in the photoreactors was defined as the removal rate of organic carbon (OC) from the sample solution, which included the parent and organic intermediate compounds. The values of the OC removal (%) were calculated using the

![Fig. 1 Schematic diagrams of the LPT photoreactor (a) and an online TOC analyzer using the photoreactor (b). Symbols: R, reaction tube; L, low-pressure mercury lamp; S, sample solution; RS, reacted sample solution; C, cooler; P, pump; V, voltage power supply; PS, phosphoric acid solution; SV, 3-way switching valve; GLS, gas-liquid separator; H, halogen scrubber; M, membrane filter; D, NDIR detector.](image-url)
following equation: \( \frac{\text{TOC concentration after irradiation}}{\text{initial TOC concentration}} \times 100 \). The concentrations of TOC were measured using an HTCO-type TOC analyzer with a non-purgeable organic carbon (NPOC) method applied to remove a large amount of IC by acidification with hydrochloric acid and air-bubbling before TOC measurements. Another TOC measurement method subtracting the concentration of IC from that of the total carbon (TC) was not applied because the TC-IC method disabled an accurate measurement of a small amount of TOC in the presence of a large amount of IC at high removal rates of the OC, especially above 90%. The TOC in the river samples given in Tables 2 and 3 was determined by the TC-IC method. The amounts of IC and TC were measured, respectively, by acidification of the sample with phosphoric acid and air-bubbling and by no-acidification.

**Confirmation of the OH radicals generated from water using LPT photoreactors**

The generation of •OH from water molecules by the LPT photoreactors was confirmed, as described previously using benzene as a chemical probe.25 An aqueous solution of benzene was introduced into the LPT photoreactors and collected after irradiation using a method similar to the procedure described in the previous section. The phenol produced by the irradiation was determined by liquid chromatography combined with fluorescence detection (LC-FL). The LC-FL system was equipped with a C18 column (2.1 mm i.d., 150 mm length, Symmetry, Waters Corp.), a column oven (40°C, CTO-40S; Shimadzu Corp., Japan) and a fluorescence detector (excitation and emission wavelengths, 270 and 298 nm, respectively, RF-530; Shimadzu Corp.). The mobile phase was CH3CN:H2O = 60:40 (v/v). The flow rate was 0.2 ml min\(^{-1}\). The sample injection volume was 20 μL.

**Results and Discussion**

**Decomposition of organic substances in pure water by LPT photoreactors**

Six compounds were used as model compounds of DOM in river water for evaluating the LPT photoreactor efficiency. The initial concentration of each substance was set at 2.0 mg of carbon (C) L\(^{-1}\), which is comparable to a typical concentration of TOC in river-water samples from major rivers in Japan. Figure 2 shows the decomposition of the reference material, Nordic Aquatic Fulvic Acid (NAFA), using the 6 W LPT reactor with no reagent. Although fulvic acid is well known as a refractory substance in river-water samples, it decomposed rapidly within only 1 min. Increasing the lamp output to 40 W reduced this time by half. Ethanol, acetic acid, malonic acid, glucose, and Nordic Aquatic Humic Acid (NAHA) were also decomposed during this period. The decomposition of ethanol is shown in Fig. S1 (Supporting Information). Even when the concentration of the TOC of NAFA increased to 10 mg of C L\(^{-1}\), the decomposition was completed within 3 min (Fig. 2). It is noteworthy that rapid decomposition required no additional chemicals or facilities, such as nitrogen, oxygen, and stirring equipment, all of which are required for conventional VUV photoreactors, as described in the Introduction section.

To ascertain the decomposition mechanism, the generation of •OH from water and the effects of oxygen that is naturally present in the sample solution were confirmed. The generation of •OH was confirmed using benzene as a chemical probe. It can react with •OH to produce phenol during a short irradiation period when no OH-radicalization of the phenol or the successive

![Fig. 2](image_url) Reagent-free decomposition of NAFA using LPT photoreactors. Solid and open symbols, respectively, denote 40 and 6 W lamps used for the reactors. The initial concentrations of NAFA were, respectively, 2 (circles), 5 (triangles), and 10 (squares) mg of C L\(^{-1}\).

![Fig. 3](image_url) Production of phenol from benzene in aqueous solutions using LPT reactors (a) and the influence of the DO in the sample solution on the reagent-free decomposition of NAFA (b). Solid and open symbols, respectively, denote 40 and 6 W lamps used for the reactors. Triangles and squares, respectively, show N\(_2\)-purged and not purged. The initial concentrations of benzene and NAFA were, respectively, 1.28 × 10\(^{-3}\) mol L\(^{-1}\) and 2 mg of C L\(^{-1}\).
products occurs. The relation between the amount of phenol produced and the irradiation time was linear under the experimental conditions. Therefore, the production rate, \( R_{\text{phenol}} \) (mol L\(^{-1}\) s\(^{-1}\)), was calculated based on this linear relation. The generation rate of \( \cdot OH \), \( R_{\text{OH}} \) (mol L\(^{-1}\) s\(^{-1}\)), was estimated using an equation proposed in a previous study: \( R_{\text{OH}} = R_{\text{phenol}} Y_{\text{phenol}} \). The \( Y_{\text{phenol}} \) value was the yield of phenol formed per benzene oxidized by \( \cdot OH \): 0.75.\(^{26} \) Irradiation using the LPT photoreactor to treat benzene in an aqueous solution produced phenol, which was detected by LC-FL (Fig. S2, Supporting Information). The amount of phenol showed a proportional relation to the irradiation time for a few seconds (Fig. 3(a)): the respective correlation coefficients for 40 and 6 W photoreactors were 0.9999 and 0.9990. The results show that the value of \( R_{\text{OH}} \) for a 40 W photoreactor was 7.9 \( \mu \)mol L\(^{-1}\) s\(^{-1}\), which was greater than that for a 6 W photoreactor (3.8 \( \mu \)mol L\(^{-1}\) s\(^{-1}\)). The increase in the amount of \( \cdot OH \) likely contributed to the higher decomposition efficiency obtained using a 40 W LPT reactor.

The influence of naturally present oxygen in the sample solution was evaluated. As shown in Fig. 3(b), the OC removal rate for NAFA in the presence of the dissolved oxygen (DO) at around 8 mg L\(^{-1}\) was higher than that after purging with \( \mathrm{N}_2 \) gas. These findings indicate that DO plays an important role in DOM mineralization, especially the intermediates of the DOM, which are initially radicalized by the \( \cdot OH \).\(^{15,16} \) The results also show that the mineralization was sufficiently rapid under natural DO conditions, except for anoxic water samples. Therefore, additional oxygen gas was not used for subsequent experiments.

We estimated that the decomposition induced by the LPT reactor was based on both the \( \cdot OH \) generated from water and DO in a sample solution, similar to that induced by other reagent-free VUV photoreactors. However, the rapidity of the decomposition was probably derived from the reactor geometry: a narrow reaction tube passes through the lamp. The VUV light of the lamp was irradiated efficiently without light attenuation. The thickness of the sample solution treated using the omnidirectional irradiation was 1 mm, which was equal to the tube interior radius. That small thickness enabled an efficient generation of \( \cdot OH \) throughout the solution, because the 185 nm light was able to pass through the sample solution, but the intensity decreased to only ca. 70% of that of the original as a result of the absorption by water.\(^{14} \) These circumstances enabled efficient mineralization of the DOM by the DO in the entire solution via the production of carbon-centered radicals and peroxy radicals and DOM with the \( \cdot OH \) in the entire solution.

Reagent-free decomposition of DOM in river-water samples

To apply the LPT reactor to actual river samples, we examined the influence of the sample solution pH and some substances, such as carbonate, chloride and nitrate, which are typically present in rivers and absorb VUV light and/or scavenge the \( \cdot OH \).\(^{12,19,27} \) To accomplish this under severe conditions, refractory NAFA was used as a model compound of DOM in river water. A 40 W LPT photoreactor with an irradiation time of 1 min was also used because the reactor generated \( \cdot OH \) more efficiently. Table 1 presents the results. The sample pH was adjusted from 2 to 8 by adding 10 mmol L\(^{-1}\) phosphate buffer. The removal rates of OC were greater than 90% at every level of the pH, indicating pH independence. In the case of carbonate, a sample solution of sodium carbonate was alkalized to pH 8 by adding 10 mmol L\(^{-1}\) phosphate buffer. No decrease in the removal rates was observed when the concentration of carbonate reached 20 mg L\(^{-1}\), which was comparable to that of river-water. Nitrate and chloride each hardly decreased the rates under the respective conditions of the concentrations in river water.

### Table 1 Effects of sample solution pH and influence of carbonate, chloride, and nitrate on the decomposition of NAFA using a 40 W LPT photoreactor

<table>
<thead>
<tr>
<th>Sample solution pH</th>
<th>OC removal rate, %</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>ca. 100</td>
</tr>
<tr>
<td>6</td>
<td>ca. 100</td>
</tr>
<tr>
<td>8</td>
<td>ca. 100</td>
</tr>
</tbody>
</table>

### Table 2 pH and concentrations of TOC, IC, chloride, and nitrate in the river-water samples used for this study

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>TOC Concentration/mg L(^{-1})</th>
<th>IC Concentration/mg L(^{-1})</th>
<th>Cl(^-) Concentration/mg L(^{-1})</th>
<th>NO(_3) Concentration/mg L(^{-1})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiR1</td>
<td>0.502</td>
<td>2.99</td>
<td>3.80</td>
<td>0.809</td>
<td>6.0</td>
</tr>
<tr>
<td>HiR2</td>
<td>1.27</td>
<td>5.80</td>
<td>4.90</td>
<td>0.723</td>
<td>4.0</td>
</tr>
<tr>
<td>HiR3</td>
<td>1.54</td>
<td>9.36</td>
<td>10.7</td>
<td>2.08</td>
<td>4.5</td>
</tr>
<tr>
<td>HiR4</td>
<td>1.88</td>
<td>10.7</td>
<td>34.1</td>
<td>5.49</td>
<td>6.1</td>
</tr>
</tbody>
</table>

The proposed VUV LPT photoreactor was applied to actual river samples. The concentrations of TOC, IC, and the anions in the samples are presented in Table 2. When operated at 40 W with an irradiation time of 1 min, the DOM in the river water was decomposed almost completely. The values of the OC removal rates for HiR1, HiR2, HiR3, and HiR4 were 92, 98, 98, and 99%, respectively. It is noteworthy that rapid decomposition was achieved in the case of real river samples, but it required no additional chemicals or the facilities that are usually required for conventional VUV photoreactors.

Oxidizing reagent-free online TOC analyses of DOM in river water

The applicability of LPT photoreactors to online TOC analysis was examined without using decomposition reagents. A schematic diagram of the proposed analyzer is presented in Fig. 1(b). A comparison of the decomposition capability of LPT and HTCO reactors for online TOC analysis was performed. The performance of the proposed analyzer is summarized, respectively, in Table 3. A solution of phthalate was used as a test sample, because it is commonly used as a calibration solution for the determination of TOC in a sample solution by HTCO-type analyzers. Figure 4(a) presents a time-course of the NDIR signal intensity for 2 mg of C L\(^{-1}\). The intensity increased when the reactor lamp was turned on.
The conditions of instruments (except those of the decomposition reactors and pretreatment to remove IC from the sample solution) were kept identical between the two TOC analyzers. Values of the sensitivity and DLs were obtained using phthalate solutions of 390 μg C L\(^{-1}\). Values were determined by the TC-IC methods, described in the text. Values are standard deviations obtained from thrice-repeated analyses.

![NDIR signal profiles](image)

**Table 3** Analytical performance of the online TOC analyses using an LPT photoreactor and an HTCO reactor

<table>
<thead>
<tr>
<th></th>
<th>LPT reactor (this study)</th>
<th>HTCO reactor</th>
</tr>
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<tbody>
<tr>
<td>Sensitivity/ mV min per mg of C L(^{-1})</td>
<td>30.8 ± 0.4(^{c})</td>
<td>31.6 ± 1.4(^{c})</td>
</tr>
<tr>
<td>DLs of weight/μg of C</td>
<td>2.4</td>
<td>19</td>
</tr>
<tr>
<td>DLs of concentration/μg of C L(^{-1})</td>
<td>6.2</td>
<td>48</td>
</tr>
<tr>
<td>Analytical time per sample/min</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Determined TOC of river sample</td>
<td>1.85 ± 0.05(^{c})</td>
<td>1.88 ± 0.05(^{c})</td>
</tr>
<tr>
<td>HIr4/μg of C L(^{-1})</td>
<td></td>
<td></td>
</tr>
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</table>

The conditions of instruments (except those of the decomposition reactors and pretreatment to remove IC from the sample solution) were kept identical between the two TOC analyzers. Values of the sensitivity and DLs were obtained using phthalate solutions of 390 μL.

a. The analysis consisted of TC and IC measurements. Each measurement time was 5 min.

b. Values were determined by the TC-IC methods, described in the text.

c. Values are standard deviations obtained from thrice-repeated analyses.

although the intensity was maintained at the baseline level when the lamp was off. The absolute and concentration detection limit (DL) of the proposed analyzer was, respectively, 2.4 ng of carbon and 6.2 μg of carbon L\(^{-1}\). The two DLs were defined, respectively, as the weight and concentration of carbon that corresponded to the three-fold standard deviation of the values of the peak area for seven replicate analyses of a phthalate solution of 11 μg C L\(^{-1}\). The time-course of the NDIR intensity is shown in Fig. 4(b). Each DL was lower than that obtained using a HTCO-type analyzer (19 ng of carbon and 48 μg of carbon L\(^{-1}\), respectively). The calibration curve obtained using the proposed method was linear in the range of 6.2 μg to 10 mg of C L\(^{-1}\). The correlation coefficient between the detected peak area and the concentration of phthalate was 0.999. The sensitivity was almost equal to that obtained using the HTCO-type analyzer (Table 3). However, the linearity was not guaranteed at higher concentrations. The relative peak area observed at 20 mg of C L\(^{-1}\) was 76% of the area expected from the calibration curve. To extend the linear range, sample volume reduction or sample dilution is expected to be necessary. Those operations are frequently used in conventional TOC analyzers. We also analyzed an actual river sample (HiR4) containing the highest levels of coexisting substances among the river samples. As shown in Fig. 4(c), a peak corresponding to the concentration of the IC appeared under the lamp-off condition and a peak corresponding to the total concentration of dissolved carbon (TC), which consists of IC and TOC, appeared under the lamp-on condition. Therefore, the TOC concentration in the water was calculable based on the difference in the peak areas in the lamp-on and lamp-off conditions. The TOC determined using the developed system agreed well with that determined using a conventional HTCO analyzer (Table 3). In addition, the repeatability and analysis time were almost identical to those obtained using the conventional HTCO analyzer (Table 3). It is noteworthy that the LPT reactor achieved oxidizing reagent-free online TOC analyses of DOM in river water.

**Conclusions**

The proposed LPT photoreactor achieved a reagent-free and rapid decomposition of the DOM in river water. The online TOC analyzer equipped with an LPT reactor was also applicable to the rapid determination of TOC in real river samples without using any oxidizing reagents. The proposed method is not only simple, but it is easy to conduct. The excellent performance of this photoreactor is expected to contribute to the development of instruments for laboratory and on-site TOC analyses that require little maintenance, which reduce costs and chemicals, and which obviate facilities.

**Acknowledgements**

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**Supporting Information**

Additional information (Figs. S1 and S2) is available. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

**References**