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Liquid Core Waveguide Spectrophotometry for the Sensitive Determination of Nitrite in River Water Samples

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A flow injection analysis system was built with a liquid core waveguide spectrophotometric detector using an 80 cm Teflon AF-1600 capillary tube (2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene). The system was applied to determine nitrite ion in river water samples. The lower limit of detection for nitrite was 2.1 nmol dm^{-3} (0.1 ng dm^{-3} as NO_2^-) and the relative standard deviation of measurements was typically 0.56% (n = 5) at 0.21 μmol dm^{-3}.

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Liquid core waveguides (LCWs) have been used to increase the length of the optical path, *i.e.*, the sensitivity of various spectroscopic measurements, such as spectrophotometry,[1–3] fluorometry[4] and Raman spectroscopy.[5] In particular, the use of Teflon AF (2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene), whose refractive indices (n_D = 1.29 (AF-2400) and n_D = 1.31 (AF-1600)) are lower than that of water (n_D = 1.33), has widened the applicability of the LCW technique to a great extent,[6–12] since the AF tubing can make it possible to form the LCW with water. Two types of LCWs using Teflon AF have been proposed. One is Teflon AF capillary tubing where a solvent-core and an AF-clad waveguide are formed (Type-1);[6–11] and the other is glass capillary tubing whose outer-surface is coated with Teflon AF (Type-2).[12] In the Type-2 LCW, whose principle was proposed by Tsunoda *et al.*,[13] total internal reflection occurs at the interface between the outer glass capillary surface and the Teflon AF coating. Recently, Zhang applied the Type-2 LCW to the spectrophotometric determination of nitrite with a FIA system, and achieved the detection limit of 2 nmol dm^{-3} nitrite with 4 m of the LCW.[14] Although the Type-2 LCW has various advantages, such as less adsorption of analytes to the cell surface, the Type-1 LCWs have so far mainly been used for analytical purposes because of their easier optical configuration. We also applied the Type-1 LCW (AF-2400) to the sensitive spectrophotometric determination of sulfur in steel samples.[15]

In this work, we built a flow-injection analysis (FIA) system with a Type-1 LCW spectrophotometric detector using AF-1600 tubing. Although the AF-2400 tubing has commonly been used for the LCW work because of its lower refractive index, we found it too fragile for routine use. Thus, we tried to use AF-1600 tubing, and found that it is more mechanically strong and flexible, and can still provide sufficiently high light transmittivity to form an LCW flow cell (80 cm). The LCW-FIA system was applied to the determination of nitrite in river water samples.

Experimental

Sulfanilamide, *N*-1-naphtylethylenediamine dihydrochloride and sodium nitrite were of analytical reagent-grade from Wako Pure Chemical Industries, Japan. Pure water used was prepared with a Milli-Q II system (Millipore, USA). A reagent solution containing 1% sulfanilamide and 0.1% *N*-1-naphtyl-ethylenediamine in 10% (v/v) HCl was prepared daily. Nitrite working-standard solutions were also prepared daily by diluting a 21 mmol dm^{-3} (1000 mg dm^{-3} as NO_2^-) stock nitrite standard solution. The stock solution was prepared by dissolving dried sodium nitrite in pure water.

Figure 1 shows a schematic diagram of the measurement system. Teflon AF-1600 tubing (n_D, 1.31; i.d., 0.45 mm; o.d., 0.60 mm; length, 80 cm; cell volume, 0.13 cm^3) was used as a liquid core waveguide (LCW) flow cell. It was coiled loosely to

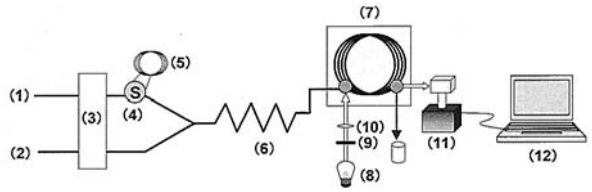

Fig. 1 Schematic diagram of the measurement system. (1) Carrier solution, pure water; (2) reagent solution, 1% sulfanilamide and 0.1% *N*-1-naphtylethylenediamine in 10% (v/v) HCl; (3) pump; (4) 6-way valve; (5) sample loop (0.50 cm^3); (6) reaction coil, PTFE tube (i.d., 0.50 mm; o.d., 1.0 mm; length, 5.0 m); (7) LCW, AF-1600 tubing (i.d., 0.45 mm; o.d., 0.60 mm, length, 80 cm; cell volume, 0.13 cm^3); (8) source light, Xe arc lamp; (9) IR cut filter; (10) convex lens; (11) multi-channel detector, USB2000; (12) PC.

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a diameter of approximately 13 cm and put in a laboratory-made plastic case. One end of the LCW was connected to both a light-source introduction and a sample-introduction device using a plastic T-joint (1/16 inch); the other end was connected to both photo-detection and sample-outlet devices. A Xe arc lamp (150 W) was used as the light source. The source light was passed through an IR cut filter, and then introduced into the LCW through a quartz glass rod (diameter, 1.5 mm; length, 20 mm). The IR cut filter was essential to prevent the formation of bubbles inside the LCW due to the local overheating of the LCW. The transmitted light was relayed to a multi-channel spectrometer (USB-2000, Ocean Optics Inc., USA) through another quartz rod. Its output was transferred to a personal computer for signal processing. A typical FIA system was used for sample introduction. A double plunger pump (DMX-2000, Sanuki Kogyo, Co., Japan) was used to send both the carrier solution and the reagent solution; one plunger sent the carrier solution and the other the reagent solution. The flow rate of each solution was typically 0.9 cm^3/min (the total flow rate, 1.8 cm^3/min). The sample solution (0.50 cm^3) was injected into the system through a six-way valve injector. Coiled PTFE tubing (i.d., 0.5 mm; o.d., 1.0 mm; length, 5 m; volume, 0.98 cm^3) was used as a mixing (reaction) coil of the carrier and reagent solutions. Nitrite ion was determined based on the typical spectrophotometric method, where nitrite was diazotized with sulfanilamide and coupled with *N*-1-naphtylethylenediamine to form a pink azo dye. The reagent conditions were basically the same as those in the literature.[16–18] For nitrite determination, the absorbance (A_{545}) of the azo dye at 545 nm and the absorbance (A_{670}) at 670 nm, where the azo dye does not absorb the light, were monitored at the same time to compensate for any change of the lamp power. The absorbance difference ($A_{545} - A_{670}$) was then used to quantify the nitrite in the samples. The baseline stability could be greatly improved by these two-wavelength measurements. Moreover, samples were injected at an interval of 2 min, *i.e.*, 30 injections per 1 h could be achieved. The system was periodically (once per *ca.* 50 injections) cleaned up by injecting a 0.01 mol dm^{-3} NaOH solution several times.

River water samples were collected from five sampling points of Kiryu-river from the upper course (#1) to the lower course (#5) near our laboratory. At sampling point #1, the river water is extremely clean, and is then gradually contaminated by human activities in Kiryu-city. The samples collected were immediately filtered with a 0.45 μm membrane filter, and then analyzed for nitrite within the same day of sampling.

Results and Discussion

In the wavelength range from 380 nm to 680 nm, a sufficient transmitted light intensity for the measurements was obtained with an 80 cm AF-1600 LCW capillary tube, when the carrier solution and the reagent solution were sent to the LCW. Although we did not try, the length of the LCW flow cell can be easily elongated to several meters. The lower and the upper limits of the wavelength range were mainly determined by the light transmittivity of the IR cut filter used; the range might be extended to the UV region, if the filter is not used. Moreover, the sensitivity enhancement factor of the LCW was examined with a dilute bromothymol blue (BTB) standard solution. An 80 cm long LCW detector was 88-times higher in the sensitivity than a conventional 1-cm cell spectrophotometer. The enhancement factor of 88 is almost the same as the cell length of the LCW. The typical baseline stability (3σ) was *ca.* 2×10^{-5} ΔAU (absorbance unit as a 1-cm cell). Waterbury *et al.*

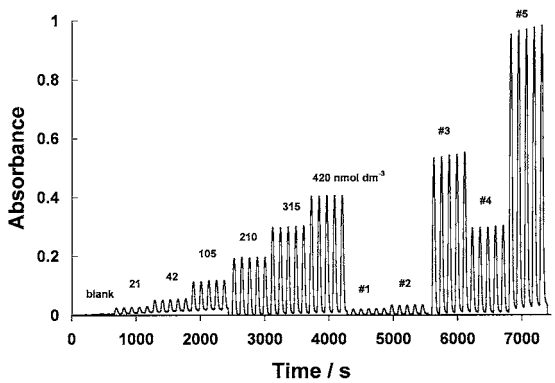

Fig. 2 Chart profile of nitrite determination in Kiryu-river samples. #1 to #5, sampling site number (see text in detail).

reported that the LCW was useful to enhance the sensitivity of an inexpensive field instrument using a detector of narrow dynamic range.[8,9] The dynamic range of the multi-channel detector used in this work also had a narrow dynamic range of 12 bits (4096 channels). The minimum detectable absorbance change could be calculated to *ca.* 10^{-4} ΔAU (= log (4000/3999)), when a 1-cm cell was used. Thus, we could extend the lower limit of the dynamic range of the system by at least one order of magnitude.

The flow rate was optimized in line with the LCW flow cell. In the range of the total flow rate from 1.0 to 8.0 cm^3/min examined, almost no change in the peak absorbance of the dye was observed; thus, the total flow rate was set at 1.8 cm^3/min throughout the experiments, considering the trade-off of the reagent consumption and the sample throughput. The lower limit of detection for the nitrite (= 3σ of baseline fluctuation) was 2.1 nmol dm^{-3}, and the calibration curve was linear up to 0.63 μmol dm^{-3}. This value of the lower limit of detection was as low as that obtained by Zhang using a 4 m of LCW.[14] That is, our system (LLW, 80 cm) showed *ca.* 5-times better performance than Zhang's system (LLW, 4 m). This may partly be because his LLW is classified as Type-2, as mentioned above, and the effective cell-length (the sensitivity) of the Type-2 LLW is known to usually be as short as half the physical cell-length,[13] although we cannot at present fully explain the reason for the difference in the performance. The relative standard deviation of the measurements was typically 0.56% (n = 5) at 0.21 μmol dm^{-3}. Figure 2 shows the typical chart profile of the nitrite determination in river water by the present system. Even in the cleanest river water sample (#1), the nitrite concentration could be determined. (Although the signals of the samples #3 and #5 were over the range of the calibration graph, the actual quantification was performed with the diluted samples.) The recovery using the method for the river water samples was typically 104.3% (σ = 4.9%). Figure 3 shows the seasonal change (the autumn of 2003 to the winter of 2004) of the nitrite concentration in Kiryu-river obtained by the present method. This figure may show the applicability of this system to the routine analysis of river water samples for nitrite. Although the main subject of this paper is LCW spectrophotometry, we would like to add brief comments on the nitrite level in Kiryu-river shown in Fig. 3. Firstly, there is a large difference in the nitrite level between sampling points #1 and #2, and #3 to #5. This is due to the existence of a water reservoir with Umeda-dam between them. Secondly, the nitrite level of #3 is higher than that of #4. This may be due to that a cleaner branch

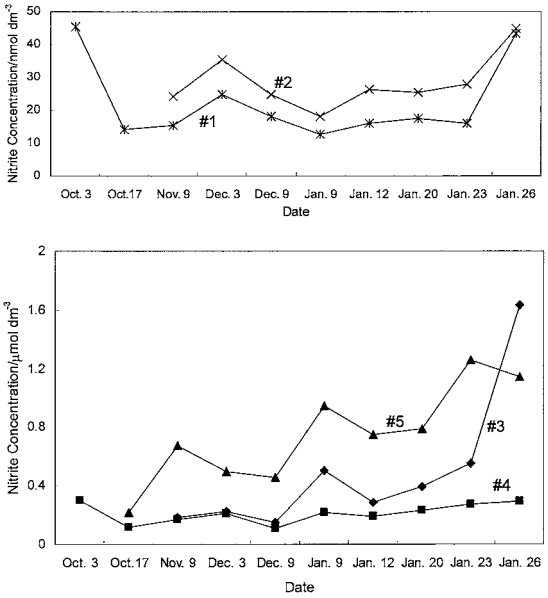

Fig. 3 Seasonal change of the nitrite concentration in Kiryu-river. #1 to #5, sampling site number (see text in detail). Water samples were collected from the autumn of 2003 to the winter of 2004.

merges into Kiryu-river just at the upper point of #4. Thirdly, the nitrite level in winter is generally higher than that in autumn. This may be due to less rainfall in winter, resulting in the concentration of chemicals in river water.

Conclusively, the AF-1600 LCW flow cell is useful for signal enhancement in spectrophotometry. In particular, the combination of the LCW and the inexpensive multi-channel detector of narrow dynamic range can provide highly sensitive and convenient routine analytical systems.

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