

Evaluation of water pollution by near infrared spectroscopy

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Introduction

Near infrared (NIR) absorptions are derived from overtones and combinations of the fundamental vibrations of molecules found in the mid-IR region. The absorptions by C–H, O–H and N–H groups are especially important. Therefore, the NIR technique is suitable for the determination of organic compounds. In addition, the determination in aqueous systems is possible since NIR absorption in water is much lower than that in the mid-IR region. The NIR technique has been widely used for food, agriculture, medicine, etc. In our laboratory, spectral analysis for protein determination,^{1–5} lipid oxidation⁶ and moisture content⁷ by NIR has been studied for many years. However, only a few studies on the application of NIR technique for environmental pollution have been reported.^{8–10}

The main source of water pollution is domestic drainage. Since the pollution by domestic drainage is mainly from organic compounds, the requirement is for the determination of organic compounds in drainage water. The indices of water pollution are biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). BOD and COD are the values of oxygen which are consumed to oxidise the organic compounds by microbes or chemically, respectively. These values are determined by microbe culture or titration method, which take a long time, require hazardous reagents (COD) and skill. TOC is usually determined by a TOC analyser, which determines carbon dioxide formed by the combustion of organic carbon. Therefore, the development of simple and easy methods for the determination of water pollution is required. In this work, we analysed the relationship between the water pollution indices (TOC and COD) and NIR spectra in a model system of domestic drainage by using several food components in order to develop a method for determination of the water pollution indices in domestic drainage by NIR spectroscopy.

Materials and methods

Materials

Ovalbumin, glycine and sucrose were purchased from Nacalai Tesque (Kyoto, Japan). Soluble starch was purchased from Merck (Germany).

Preparation of model drainage system

To prepare a model of a domestic drainage system, several kinds of food component were used. Each food component was dissolved in water to obtain 0–1% (every 0.2%) and 0–0.01% (every

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0.002%) solutions. Mixed solutions (0–1% and 0–0.01%) of all food components were also prepared. A 1% solution corresponds to approximately TOC = 5000 and COD = 8000.

Determination of NIR spectra

NIR transmittance spectra (680–1235 nm and 1100–2500 nm) of the model drainage solutions were determined in 1, 2, 4, 10, or 30 mm cuvette cells using an NIRSystems (Pacific Scientific) Model 6250 Research Composition Analyzer at 10, 20, 30 or 40°C. Statistical analysis was performed with NSAS v. 3.27 (NIRSystems).

Determination of TOC and COD

TOC was determined by Shimadzu TOC-5000A TOC Analyzer. COD was determined by potassium permanganate titration method.

Regression analysis

A partial least squares (PLS) regression analysis was used for calibration and prediction. All spectra of different food components, at different temperatures, were used for calibration in order to obtain a robust calibration.

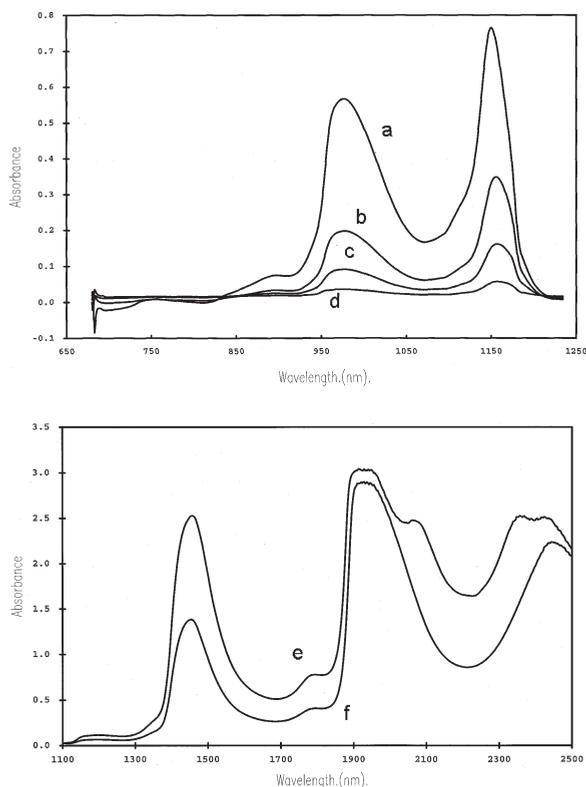


Figure 1. NIR raw spectra of water. The raw spectra of water was determined at 25°C in the region of (a) 680–1235 nm and (b) 1100–2500 nm. Light path: a, 30 mm; b, 10 mm; c, 4 mm; d, 1 mm; e, 2 mm; f, 1 mm

Table 1. Correlation between NIR Raw Spectra and TOC.

Temperature	TOC					
	0–5000			0–50		
	Factor	<i>R</i>	<i>SEC</i>	Factor	<i>R</i>	<i>SEC</i>
All	15	0.961	377	13	0.906	5.67
10	14	0.985	272	12	0.982	2.87
20	13	0.987	254	14	0.960	4.69
30	6	0.917	557	10	0.958	4.17
40	12	0.972	363	9	0.934	5.12

NIR spectra were determined in the region of 680–235 nm by using 10-mm cuvette.

Table 2. Correlation between NIR Raw Spectra and COD.

Temperature	COD					
	0–8000			0–80		
	Factor	<i>R</i>	<i>SEC</i>	Factor	<i>R</i>	<i>SEC</i>
All	14	0.928	897	14	0.929	8.45
10	14	0.981	550	12	0.975	6.07
20	13	0.983	520	11	0.927	8.46
30	6	0.919	926	9	0.946	7.71
40	12	0.971	656	11	0.976	5.87

NIR spectra were determined in the region of 680–1235 nm by using 10 mm cuvette.

Results and discussion

NIR spectra of water

Figures 1(a,b) show the NIR raw spectra of water at different path lengths. In the region of 680–1235 nm [Figure 1(a)], 1 to 30 mm cuvettes can be used for determination, while the absorption of water is too high to use in the region of 1100–2500 nm [Figure 1(b)]. Therefore, the following analyses were carried out in the region of 680–1235 nm. In this region, the sensitivity was highest when using a 30 mm cuvette, but a 10 mm cuvette was used in the following analyses to save samples.

Correlation between NIR raw spectra and TOC/COD

Table 1 shows the correlation between the NIR raw spectra and TOC. The model samples of domestic drainage were first determined using an NIR spectrometer at 10–40°C and then determined by TOC analyser. Calibration was calculated by PLS using all individual and mixed samples. The spectra determined at different temperatures were used to obtain a robust calibration against the change of temperature. As shown in Table 1, a good correlation between the NIR spectra and TOC was obtained. The correlation coefficient (*R*) was 0.961 and 0.906 for the range of 0–5000 and 0–50, respectively, when the spectra determined at all temperatures were used.

Table 3. Calibration statistics of NIR raw, first derivative and second derivative spectra for TOC and COD.

Index	Raw			First Derivative			Second derivative		
	Factor	<i>R</i>	<i>SEC</i>	Factor	<i>R</i>	<i>SEC</i>	Factor	<i>R</i>	<i>SEC</i>
TOC (0–5000)	15	0.961	377	12	0.920	526	12	0.904	576
TOC (0–50)	13	0.906	5.67	12	0.916	5.39	12	0.817	7.71
COD (0–8000)	14	0.928	897	13	0.909	983	12	0.870	1162
COD (0–80)	14	0.929	8.45	11	0.886	10.42	11	0.841	12.18

NIR spectra were determined in the region of 680–1235 nm by using 10 mm cuvette.

Table 4. Calibration and Prediction Statistics of NIR Raw Spectra for TOC and COD.

Index	Factor	<i>R</i>	<i>SEC</i>	<i>SEP</i>	Bias
TOC (0–5000)	15	0.961	377	725	–247
COD (0–8000)	14	0.928	897	1340	286

Table 2 shows the correlation between the NIR raw spectra and COD. A good correlation between the NIR spectra and COD was also obtained. The correlation coefficient (*R*) was 0.928 and 0.929 for the range of 0–8000 and 0–80, respectively, when the spectra determined at all temperatures were used. These results demonstrate that the NIR raw spectra determined at different temperatures were highly correlated with TOC and COD, which means that a robust calibration against the change of temperature was obtained.

Effects of first and second derivatives

Table 3 shows the calibration statistics of the NIR raw, first derivative and second derivative spectra for TOC and COD. NIR spectra determined at all temperatures were used for calibration. As shown in Table 3, the correlation coefficient (*R*) and standard error of calibration (*SEC*) were somewhat worse when the first and second derivative spectra were used. Based on this result, the raw spectra were used for prediction.

Prediction of TOC and COD by NIR raw spectra

Table 4 shows the calibration and prediction statistics of NIR raw spectra for TOC (0–5000) and COD (0–8000). The calibration and prediction were carried out by using all individual and mixed samples determined at all temperatures. Though good calibrations were obtained for TOC and COD (*SEC*: 377 and 725, respectively), predictions were not so good [standard error of prediction (*SEP*): 725 and 1340, respectively]. In addition, the diluted samples could not be predicted (data not shown). These results may be due to the noise of the spectra or the error of determinations.

In this work, we demonstrated the possibility that the pollution of water derived from domestic drainage may be determined by NIR spectroscopy with a PLS calibration. Since NIR determination is simple, easy and speedy, this method has great advantages in the determination of water pollution.

However, much improvement is necessary for practical use. Further studies for improvement and application to other kinds of drainage are now in progress.

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