Evaluation of drainage by near infrared spectroscopy

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Introduction

Near infrared (NIR) absorption is derived from overtones and combinations of the fundamental vibrations of molecules found in the mid-IR region. Of major importance are the absorptions of the C–H, O–H and N–H groups. Therefore, the NIR technique is suitable for the determination of organic compounds. In addition, the determination in aqueous systems is possible since NIR absorption due to water is much lower than that in the mid-IR region. In our laboratory, spectral analysis for protein determination,[1–5] lipid oxidation[6] and moisture content[7] by NIR has been studied for years. However, only a few studies on the application of NIR techniques for environmental pollutions have been reported.[8–10]

Water pollutants in drainage mainly consist of organic compounds. Hence, total organic carbon (TOC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were generally used as the indices of pollution. However, these values are determined with a special analyser (TOC), titration method (COD) or microbe culture (BOD), which are time-consuming methods. Therefore, the development of simple and easy-to-use methods for the determination of water pollution is required. The authors reported the evaluation of water pollution by NIR spectroscopy in a model system with food components.[11] In this study, the relationship between NIR spectra and drainage was investigated in order to develop a method for the evaluation of drainage by NIR.

Materials and methods

Sample drainage and river water

Drainage, partially purified drainage, purified drainage and river water at various pollution levels were obtained at the Nara Purification Centre. Approximately 400 samples were used for calibration and 100 samples were used for prediction. The ranges of TOC, COD and BOD were 0–140, 0–100 and 0–220, respectively.

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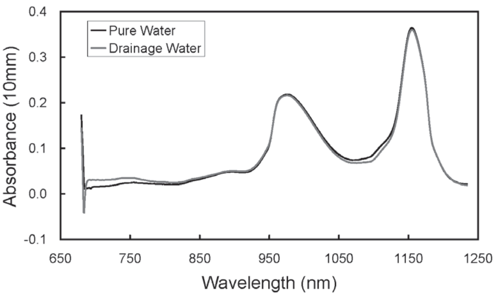
Determination of NIR spectra

NIR transmittance spectra (680–1235 and 1100–2500 nm) of the drainage were determined with an NIRSystems (Pacific Science) Model 6250 Research Composition Analyzer at 10–40°C. The 10 mm cuvette cell was used as a sample cell for 680–1235 nm and the 0.5 mm cuvette cell for 1100–2500 nm. Statistical analysis was performed using NSAS Ver. 3.27 (NIRSystems).



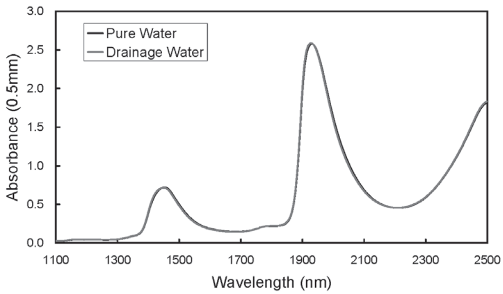


Figure 1. NIR raw spectra of water (TOC = 0) and drainage (TOC = 140) measured at 25°C in the region of (a) 680–1235 nm and (b)1100–2500 nm.

Table 1. Calibration using the short wavelength range of 680–1235 nm for determining TOC/COD/BOD.

Factor	TOC		COD		BOD	
	R	*SEC*	*R*	*SEC*	*R*	*SEC*
1	0.710	24.29	0.775	17.05	0.728	37.33
2	0.837	18.88	0.893	12.17	0.852	28.54
3	0.871	17.01	0.919	10.65	0.883	25.66
4	0.963	9.28	0.954	8.14	0.968	13.73
5	0.968	8.74	0.960	7.63	0.973	12.75
6	0.970	8.43	0.961	7.51	0.976	11.92
7	0.971	8.31	0.963	7.32	0.978	11.56
8	0.972	8.21	0.964	7.26	0.978	11.37
9	0.973	8.10	0.964	7.21	0.979	11.25
10	0.974	7.96	0.967	6.96	0.980	10.91
11	0.975	7.74	0.968	6.83	0.981	10.67
12	0.976	7.59	0.971	6.55	0.982	10.32
13	0.978	7.34	0.972	6.45	0.983	10.20
14	0.979	7.11	0.974	6.24	0.985	9.68
15	0.980	6.90	0.975	6.11	0.985	9.52

Determination of TOC, COD and BOD

TOC was determined with a Shimadzu TOC-5000A TOC analyser. COD was determined by the potassium permanganate titration method. BOD was calculated from the difference in oxygen concentrations of water before and after a 5-day microbe incubation. Oxygen concentration was determined by oxygen electrode.

Regression analysis

A partial least squares (PLS) regression was used for calibration and prediction. All spectra measured at different temperatures were used for the calibration in order to obtain a robust calibration.

Results and Discussion

NIR spectra of water and drainage

Figure 1(a) and (b) show the NIR raw spectra of water (TOC = 0) and drainage (TOC = 140). In the region of 680–1235 nm [Figure 1(a)], the difference between water and drainage could be seen, while there was little difference in the region of 1100–2500 nm [Figure 1(b)].

Calibration for determining TOC/COD/BOD

Tables 1 and 2 show the correlation between the NIR raw spectra and TOC/COD/BOD in the wavelength range of 680–1235 and 1100–2500 nm, respectively. The samples of water and drainage were first determined by NIR spectrometer at 10–40°C and then TOC, COD and BOD were determined.

Table 2. Calibration using long wavelength range of 1100–2500 nm for determining TOC/COD/BOD.

Factor	TOC		COD		BOD	
	R	*SEC*	*R*	*SEC*	*R*	*SEC*
1	0.133	38.61	0.170	27.08	0.121	68.52
2	0.244	37.84	0.308	26.19	227	67.33
3	0.634	30.21	0.686	20.06	0.633	53.62
4	0.757	25.56	0.783	17.18	0.757	45.29
5	0.843	21.10	0.841	14.96	0.848	36.79
6	0.862	19.91	0.863	14.02	0.868	34.54
7	0.913	16.06	0.919	10.95	0.916	28.01
8	0.940	13.40	0.944	9.18	0.942	23.35
9	0.952	12.08	0.955	8.25	0.954	20.88
10	0.959	11.22	0.962	7.63	0.961	19.35
11	0.964	10.55	0.966	7.20	0.966	18.10
12	0.968	9.98	0.970	6.80	0.970	17.13
13	0.972	9.40	0.973	6.44	0.973	16.13
14	0.974	8.97	0.976	6.16	0.976	15.32
15	0.976	8.70	0.977	5.98	0.978	14.74

Table 3. Validation of the calibration equations developed.

Index	680–1235 nm				1100–2500 nm			
	Factor	*R*	*SEP*	Bias	Factor	*R*	*SEP*	Bias
TOC	6	0.960	4.99	3.46	11	0.187	70.0	–309
COD	6	0.892	5.55	8.60	10	0.211	58.8	–309
BOD	7	0.949	9.34	6.54	11	0.253	108.0	–559

Calibration was performed by PLS using 400 spectra measured at different temperatures to get a robust calibration against the change of temperature. As shown in Tables 1 and 2, good correlations between the NIR spectra and TOC/COD/BOD were obtained in both wavelength ranges, which suggests that the NIR raw spectra determined at different temperatures were highly correlated with TOC, COD and BOD.

Validation of the calibration equations developed

Table 3 shows the prediction statistics of NIR raw spectra for TOC, COD and BOD. Though good calibrations were obtained in both wavelength ranges, good predictions were obtained only in the range of 680–1235 nm. This result suggests that NIR spectroscopy can be used to evaluate the quality of drainage water by using the wavelength range of 680–1235 nm.

In this work, we examined the possibility of using NIR spectroscopy to evaluate drainage. NIR spectroscopy has a great advantage for this purpose, since it is simple and easy to use. Although some improvement is necessary for practical use, NIR evaluation of drainage may become useful in the future.

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