

Robust spectral model for low metal concentration measurement in aqueous solution reveals the importance of water absorbance bands

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Introduction

In this study, we focused on detection of metal ions at low concentration in aqueous solution by using near infrared (NIR) spectroscopy. The new “aquaphotomics” concept¹ has become a powerful strategy to understand the spectral changes related to small concentration of solutes in aqueous solution. To improve the model accuracy it is important to understand why it is possible to detect the object of interest using NIR spectroscopy. Although detectable, metals have no absorption in the NIR region.² However the detection of metals by NIR spectroscopy is perhaps due to their vibrational modes that are modulated by forming complexes with organic molecules containing C-H, N-H and O-H bonds. Therefore, alteration of the vibrational mode of the water matrix caused by metals can be detected by NIR spectroscopy. In this study, we present a NIR spectroscopy link to aquaphotomics as a tool to predict low concentrations (0–10 mg L⁻¹) of Mg(II), Zn(II), Mn(II) and Cd(II).

Materials and methods

All 0.1 M HNO₃ aqueous solutions that contained zinc (II) ions, manganese (II) ions, magnesium (II) ions and cadmium (II) ions, respectively, were purchased from Wako Pure Chemical Industries Japan (Tokyo). Test solutions containing metal ions were prepared by diluting the standard solutions with 0.1 M HNO₃. Working stock solutions containing each metal at a concentration of 10 mg L⁻¹ were prepared by direct dilution of the standard solution. A total of 99 transmittance spectra for each metal ion were scanned, using a NIRSystems Model 6500, in the range of 680–1090 nm, using 2 mm pathlength cuvette cell at 37° C in three consecutive days. Data for two days were used as a calibration set and the rest of the data were used as a prediction set. The calibration models were developed using partial least squares (PLS) regression method. Prior to

Table 1. Calibration and prediction statistics for four kinds of metal ions in 0.1M HNO₃ aqueous solution.

Metal Ion	Wavelength	Factor	Calibration		Validation		Prediction		RPD
	Range (nm)		R^2	SEC	R^2	SEV	R^2	SEP	
Cd (II)	680–1090	9	0.94	0.87	0.83	1.31	0.71	1.95	2.43
Mg (II)	680–1090	5	0.96	0.68	0.93	0.85	0.93	0.88	3.75
Mn (II)	680–1090	9	0.96	0.65	0.88	1.11	0.73	2.06	2.87
Zn (II)	680–1090	9	0.94	0.85	0.75	1.61	0.85	1.34	3.75

calibration, spectral data were mean centered and transformed using smoothing with 5–11 data-point windows. The optimum calibration models were determined by the lowest standard error of calibration (*SEC*) and standard error of prediction (*SEP*) and the highest R^2 (correlation coefficient). The ratio of *SEP* to standard deviation of reference values in the prediction set (*RPD*) was used to evaluate the accuracy of prediction.

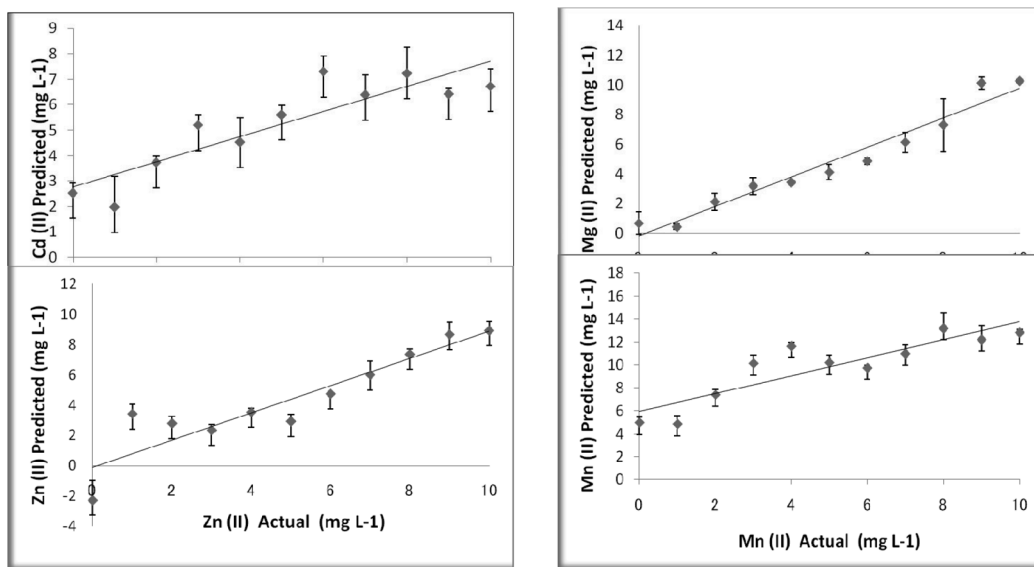


Figure 1. Calibration models for predicting the metal concentration using a leave-out step (3) validation procedure in the short infrared region, 680–1090 nm. Linear curves were obtained from each model respectively.

Results and discussion

The calibration and prediction statistics obtained in this study indicated the potential of NIR spectroscopy to predict metal ions in aqueous 0.1 M HNO₃ solution (Table 1).

These results showed that the concentration of metal ions from 0 to 10 mg L⁻¹ could be predicted by PLSR model with reasonable correlations ($R^2_{\text{pred}} > 0.7$).³ The *RPD* values were greater than 2 indicating that the models were appropriate for practical use. Different spectral patterns for each metal shown in Figure 1 identified common water matrix coordinates (690–800 nm).¹

In this figure, regression coefficients at 752 nm were positive for Mg(II), Mn(II) and Zn(II), and negative for Cd(II). This could be explained by the fact that the different metals perturbed the water matrix in a specific way, which made it possible to observe differences in absorbance by changing metal concentration, even in the range from 0 to 10 mg L⁻¹. This new finding would further enrich the existing data base of water matrix coordinates called aquaphotome. The concentrations of Cd(II), Mg(II), Zn(II) and Mn(II) in the range of 0–10 mg L⁻¹ were successfully predicted by PLS models based on their NIR spectra in the 680–1090 nm region and 2 mm pathlength.

The regression coefficients in these models registered positive and negative peaks for Mg(II), Zn(II) and Mn(II) at around 752–760 nm, while only one negative peak was observed for Cd(II) at the same absorbance band (Figure 2).

Those peaks were close to the water band at 760 nm that has been assigned to the third overtone of the O-H stretching mode of water, and the peaks at 752–760 nm may have been due to water absorbance.⁴ Although it is often difficult to assign wavelengths to specific metal absorptions in the NIR region, the commonly observed peaks may be related to interaction between metals and water molecules.

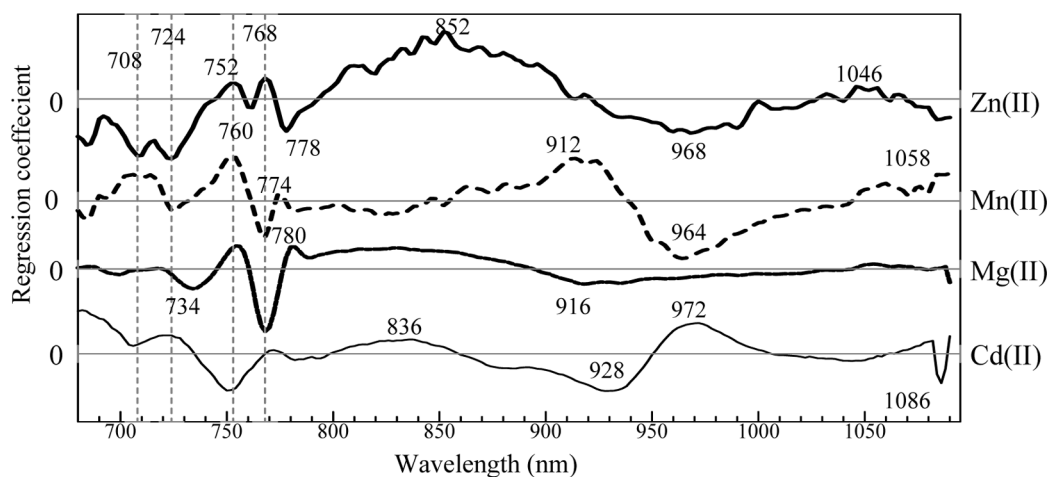


Figure 2. Regression coefficients for the partial least squares (PLS) Models based on NIR spectra in the 680–1090 nm for metal in aqueous HNO₃.

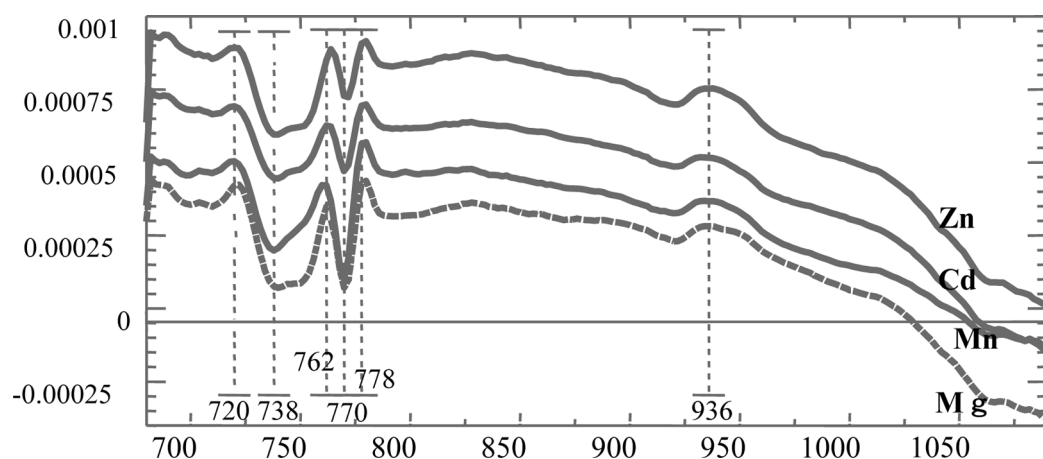


Figure 3. Difference spectra ΔA , short near infrared region, 680–1090 nm for metal in aqueous HNO_3 .

In this study we show pure water spectra subtracted from the the average spectra of Cd(II), Mg(II), Mn(II) and Zn(II) solution (Figure 3).

The potential of NIR spectroscopy was investigated for classification and quantification of metal in aqueous HNO_3 . The results showed consistency between the water absorbance band in the regression vector, and subtracted spectra and important absorbance bands were found in the region 720–778 nm. This shows that this region is a very important wavelength region to investigate the influence of metals on the water spectra.

Conclusion

Calibration models for metals determination were successfully developed using 0.1 M HNO_3 aqueous solutions containing different metal ions, Cd(II), Mg(II), Mn(II) and Zn(II), in the range of 0–10 mg L^{-1} .

1. PLS models provided a powerful tool for investigating the water-metal interaction.
2. It was found that each metal in water solution had a different way to affect the spectra of water.

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