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ROBUST SPECTRAL MODEL FOR LOW METAL CONCENTRATION MEASUREMENT IN AQUEOUS SOLUTION REVEALS THE IMPORTANCE OF WATER ABSORBANCE BANDS

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ABSTRACT

In this study, we focused on detection of metal ions at low concentration in aqueous solution by using NIRS. New "aquaphotomics" concept (Tsenkova, 2007) 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 NIRS. Although detectable, metals have no absorption in NIR region (Sakudo,et,al, 2007). However it 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 water matrix caused by metal can be detected by NIRS. In this study, we present NIR spectroscopy link to aquaphotomics as a tool to predict low concentration (0-10.mg L^{-1}) of Mg(II), Zn(II), Mn(II) and Cd(II).

Keywords : *NIR spectroscopy, spectral changes, absorbance*

1. INTRODUCTION

Near infrared spectroscopy has been extensively used to study water and water-solute interactions due to the low absorptivity of water in this region permitting higher pathlengths than other techniques. Bujis and Choppin (1963) studied the structure of water in the NIR between 1000 and 1300 nm and suggested three forms of water: water molecules with neither OH group bonded absorbing at 1160 nm, water with 1 O-H group H-bonded absorbing at 1200 nm, water with two O-Hs H-bonded absorbing at 1250 nm. They confirmed the cluster model proposed by Frank and Wen (1957) and adopted by Nemethy and Scheraga (1962).

The metal contamination of water poses hazardous risk to human and aquatic life. Therefore, detection of metal in water for scientific interest, is needed. The use of near infrared spectroscopy (NIRS) was explored to detection of metal ions in aqueous solution. Although there are no metal absorption in NIR region, but alteration of the vibrational mode of water matrix caused by metal can be detected by NIRS (Sakudo et.al, 2007).

The absorbance pattern produced by the absorbent at each water absorbance band is called the *water absorbance pattern* (WAP). *Water matrix Coordinates* (WAMACS) is introduced to capture and present the information about influence of different perturbation on the water absorbance in vis-NIR range for various samples. The aquaphotomics concept (Tsenkova, 1997) has become a powerful strategy to understand the spectral changed related to low concentration of solutes in aqueous solution.

The purpose of this study to determine low metal concentration using NIR spectroscopy and examine whether different metals displayed different effect on the vibration mode of water in the absence of organic matrices.

2. RESEARCH OBJECTIVES, BENEFITS AND LIMITATIONS

This study's objectives focus on exploring near-infrared spectroscopy (NIRS) as a tool to detect low concentrations of metal ions, such as Mg(II), Zn(II), Mn(II), and Cd(II), in aqueous solutions. The study aims to understand the structure of water and its interactions with solutes by using NIRS in the 1000–1300 nm range, following foundational work by Bujis and Choppin (1963) on water molecular forms based on OH bonding states. Additionally, the study applies the aquaphotomics concept to observe and interpret subtle spectral changes in water absorbance patterns (WAP) when metals are present. This allows researchers to assess how different metals impact the vibrational modes of water molecules, especially in the absence of other organic compounds. NIRS offers several benefits, including its non-destructive nature and ability to provide rapid results without complex sample preparation, making it highly suitable for water quality monitoring. Through aquaphotomics, the study can achieve enhanced sensitivity for detecting metal presence even at low concentrations by tracking water matrix coordinates (WAMACS) and examining changes in water's hydrogen bonding network. Furthermore, this research contributes valuable insights into water's molecular structure and the effects of solute presence on it, expanding the understanding of water-solute interactions. However, the study also encounters limitations, as metals do not directly absorb in the NIR region, making it necessary to rely on the secondary effects metals have on water's vibrational modes, which complicates data interpretation. Additionally, the presence of other solutes or contaminants may interfere with NIR spectral patterns, making it challenging to isolate metal-related changes. Finally, detecting low metal concentrations requires sophisticated modeling to accurately interpret spectral data, and this approach's success depends heavily on the models' sensitivity and specificity.

3. RESEARCH METHODS

3.1 Materials

All 0.1 M HNO_3 aqueous solutions that contained Zinc (II) ion, Manganese (II) ion, Magnesium (II) ion and Cadmium (II), respectively, were purchased from Wako Pure Chemical Industries Japan (Tokyo). Test solutions containing metal ions were prepared by diluting the standard solution with 0.1 M HNO_3. 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 NIR Systems 6500 in the range of 680-1090 nm using 2 mm path length cuvette cell at 37^0C in three consecutive days. Data for two days were used as a data set and the rest of the data were used as a prediction set.

3.2 Methodology

The calibration models were developed using partial least squares (PLS) regression method. Prior to calibration, spectral data were mean centered and transformed using smooth with 5-11 data-points 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 standard error of Perforrnance to standard Deviation (RPD) was used to evaluate the accuracy of prediction.

4. RESULT AND DISCUSSION

The calibration and prediction statistics obtained in this study indicated the potential of NIRS to predict metal ions in aqueous 0.1 M HNO_3 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 correlation ($R^2_{pred.}$ > 0.7) (Conzolino, *et.al*, 2007). The RPD values were greater than 2 indicating that the models were appropriate for practical use.

Table 1. Calibration and prediction statistics for four kinds metal ions in 0.1M HNO_3 aqueous solution

Metal Ion	Wavelength Range (nm)	Factor	Calibration		Validation		Prediction		RPD
			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

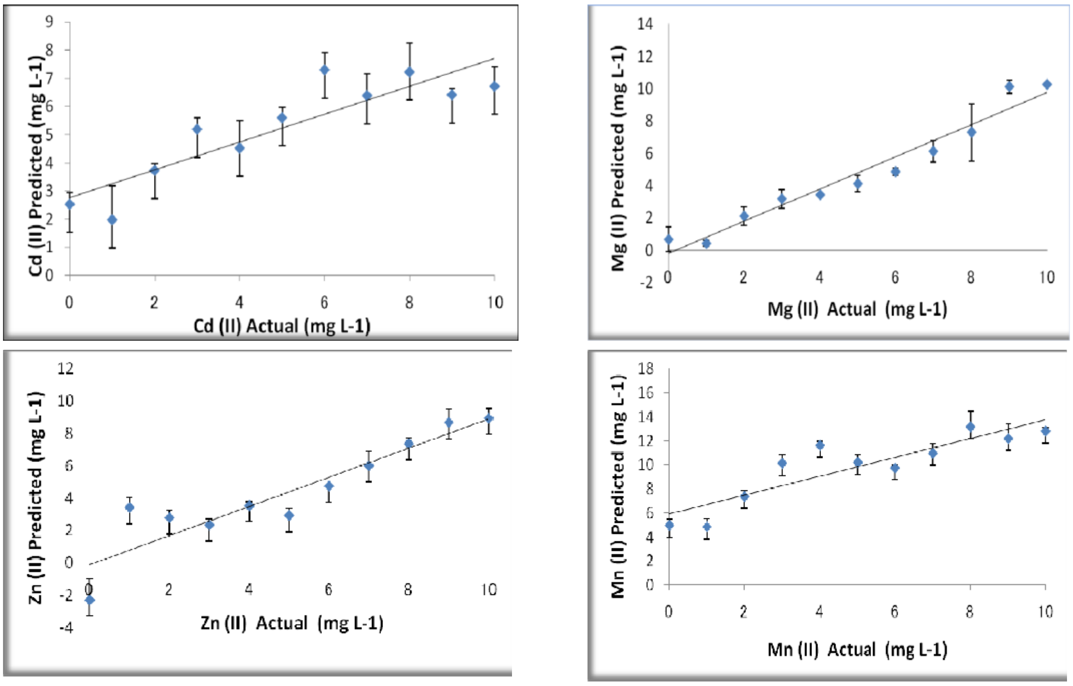

Figure 1. Calibration models for predicting the metal concentration using a leave-out step (3) validation procedure in the short infrared region, 680-1090 nm. Linear curves were obtained from the each model respectively.

Different spectral patterns for each metal shown in Figure 1 identified common water matrix coordinates (690-800 nm) (Tsenkona,2007). In this figure, regression coefficients at 752 nm were positive for Mg(II), Mn(II) and Zn(II), and negative for Cd(II). It could be explained with the fact that different metal perturbed the water matrix in a specific way, thus it was possible to observe difference 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 concentration range of 0-10.mg L^{-1} were successfully predicted by PLS models based on their respectively NIR spectra in the 680-1090 nm region and 2 mm path length.

The regression coefficients in these models registered positive and negartive peaks for Mg(II), Zn(II0 and Mn(II) at around 752-760 nm, while only one negative peak was observed for Cd(II) at the same absorbance band（Fig.2）.Those peaks were close to the water band (the third overtone of the O-H stretching mode of water that has been assigned to 760 nm), and the peaks at 752-760 nm may have been due to water absorbance (Sakudo,*et.al*, 2006). Although it is often difficult to assign wavelength to spesific metal absorpstion in the NIR region, the commonly observed peaks may be related to interaction between metals and water molecules (Fig.2).

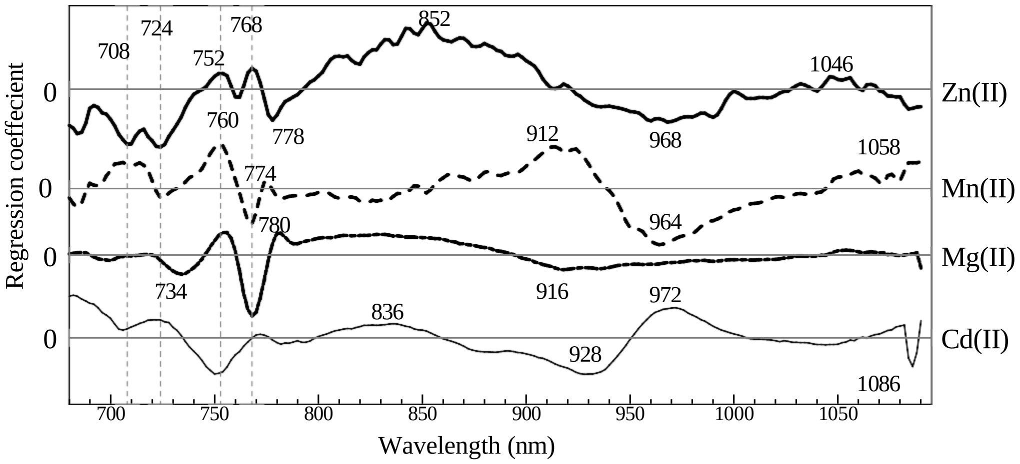

Figure 2. Regression coefficient the Partial Least Square (PLS) Models based on NIR spectra in the 680-1090 nm for metal in aqueous HNO_3.

In this study we show pure water spectra subtracted from the average spectra of Cd(II), Mg(II), Mn(II) and Zn(II) solution (Fig.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 regression vector and subtracted spectra and important absorbance bands were found in the region 720-778 nm. This shows that this region is the most important one to investigate the influence of metal to the water spectra.

The result showed that the concentration of metal ions from 0 to 10. mg L^{-1}could be predicted by PLSR model with reasonable correlation (R^2pred. > 0.7, SEP >2.0) (Table 1). The RPD values were greater than 2 indicating that the model is appropriate for practical use.

CONCLUSION

1. Calibration models for metals determination were successfully developed using 0.1 M HNO_3 aqueous solutions containing one kind of metal ion, Cd(II), Mg(II), Mn(II) and Zn(II), in the range of 0-10 mg L^{-1}.
2. PLS models provided a powerful tool for investigating the water-metal interaction.
3. It has been found that each metal in water solution has a different way to affect the spectra of water.

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