Use of near-infrared spectroscopy for determining the characterization metal ion in aqueous solution

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Abstract. This study uses Aquaphotomics to measure Cadmium (Cd) and Magnesium (Mg) in aqueous solutions by analysing the changes in water spectra that occur due to water-metal interaction. Metals have no absorbance in the NIR spectral range, thus the methods developed so far have focused on detection of metal-organic complexes. Measurements were performed with Cd (II) and Mg(II) in 0.1 M HNO_3, in the 680-1090 nm (water second and third overtones) and 1110-1800 nm (water first overtone) spectral regions, and were subjected to partial least-square regression analysis. Metal ions were scanned by NIRSystem 6500 using cuvette cell with 2 mm path length, in three consecutive days. Data for two days were used as data set and the rest of the data were used as prediction set. 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 with correlation coefficient ($R^2_{pred.}$>0.7). The RPD (residual predictive deviation) or ratio of standard error of prediction to the standard deviation, values were greater than 2, indicating that the model is appropriate for practical use (Cozzolino,2007). By using water matrix coordinates (WAMACS) from regression coefficient, obtained a consistency specific wavelength for each metal.**.** These results showed that the PLS model were able to detect character metal ions in the NIR region of electromagnetic spectra with high accuracy even at very low concentrations (0-10 ppm).
Keywords: aquaphotomics, near infrared spectroscopy, cadmium (Cd), magnesium (Mg), partial least-square regression, regression coefficient, WAMACS

Introduction

Metals are non-degradable they tend to bio-accumulate as they move to up to the food chain and drink. The main sources of soil and ground water pollution are implore waste dumping, agriculture chemical and industrial effluents (Chen *et al.*, 1998). The toxicity of this metal depends on their concentration and also on their speciation. Cadmium and Zinc are heavy metal, and they are common in industrial pollutant and although some sources of pollution contaminate the environment exclusively with Cadmium, most cases of cadmium-polluted soils represent situations of multiple metal pollution. Both metals are harmful to plants at the relatively low concentration (Chakravarty *et al.*, 1992). The present investigation was undertaken to regenerate a *plant* tolerant of Cadmium and to ascertain the extent to which zinc can lower the toxicity of cadmium (Chakravarty *et al.*, 1997).

In general, the level of contamination by heavy metals is determined by instrumental analyses such as atomic absorption spectroscopy (AAS) (Apostoli *et al.*,200), inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Aleo *et al.*,2006) and inductively coupled plasma mass spectroscopy (ICP-MS) (Silanpaa and Oikari,1996). These methods can be used for the accurate estimation of amounts of individual heavy metals in a sample. However, evaluation of the heavy metal toxicity of a sample by the abovementioned methods is difficult because the toxicity depends on the total amount of the metals and other factors such as nature of the metal species, chemical content of the samples, and coexisting substances (Chen *et al.*, 2002). The presence of toxic substances other than heavy metals in the samples may also influence the obtained result. Hence,

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methods that are simpler and more sensitive are required to evaluate heavy metal toxicity in water (Asano *et al.*, 2009).

Traditional methods for trace metal ion detection include inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Campilo *et al.*, 1999), electrochemical method (Tsalev *et al.*, 1984), stripping potentiometry (Forrer *et al.*, 2005). Although these methods are excellent for Cd(II) detection, the instrumentation is expensive and not ideal for real time monitoring. Simple, sensitive sensors that are easy to work with would be of great significance for wide scale monitoring of metal presence. Near infrared spectroscopy (NIRS) could be an alternative for monitoring Cd and Mg presence. The most attractive features of NIRS analysis are its speed, minimal sample preparation and its being a non-destructive method, making it possible to conduct large numbers of analyses in a short time.

Near infra-red spectroscopy (NIRS) is a technique that uses the radiation absorbed by a set of samples in the region from 680 to 2500 nm (near infra-red region) to develop calibration curves which are related to sample properties. After calibration, the regression equation permits fast analysis of many other samples by prediction of data on the basis of the spectra. The most attractive features of analysis using NIRS are its speed, minimal sample preparation and its being a non-destructive method, making it possible to conduct large numbers of analyses in a short time. NIRS has been widely used for the last four decades as a fast and accurate method for qualitative and quantitative analysis of biological and non-biological materials in the agriculture, food, textile, petrochemical and pharmaceutical fields (Williams and Norris, 1987)

Unfortunately, NIR region are dominated by weak overtones and combination of vibration bands of atoms with strong molecular bonds containing nitrogen, oxygen and carbon attached to hydrogen and not found metal in this region. Although detectable, metals per se exhibit no absorption in the NIR region, since there vibrational modes are modulated by forming complexes with organic molecules containing C-H, N-H and O-H bonds (Malley *et al.*, 1997). A new concept "aquaphotomics"(Tsenkova, 2007) would became a powerful tool to understand the influence of water-metal ion interaction under various perturbations, and also to improve the model accuracy.

Characterization of heavy metal contamination in water is commonly based on to determination kind of metal. However, elements are present in various forms and these can strongly affect their behaviour in terms of biological availability, potential toxicity and mobility within the profile (Alloway, 1995). So the character of heavy metal to get initial information of heavy metal in unknown sample. The main purpose of this study is to examine whether NIR Spectroscopy could be to determine characteristic of heavy metals in aqueous solutions using partial least squares regression analysis.

Materials and Methods
Sample preparation
To minimize metal contamination of the sample, all glass or vessels to be used were immersed during one day in HNO_3 and then washed using deionized water from milliQ water purification system (Millipore, Molsheim, Germany). Standard solution of Cd(II) and Mg (II) (1000 mgL^{-1}) was purchased from Wako Pure Chemical Industries Japan (Tokyo, Japan). Working stock solutions of Cd(II) at 10 mgL^{-1} were prepared by direct dilution of the standard solution with 0.1 M HNO_3.

NIR spectra collection
The transmittance spectra were recorded by NIRSystem 6500 spectrophotometer (FossNIR-System, Laurel, USA) fitted with a quartz cuvette with 2 mm optical path length. The cuvette was positioned in a cell holder in conjunction with a temperature bath to maintain temperature at 25^{0}C. Three consecutive spectra for each metal concentration over the wavelength region of 400 - 2500 nm, in 2 nm steps, were registered. The spectral data were collected as absorbance value [log (1/T)], where T= transmittance.

Data processing
Three consecutive spectra for each solution were used to develop partial least squares (PLS) regression model (Pirrouette 3.11, Infometrix Inc., Woodinville, WA, USA). A

matrix data set was constructed with rows representing metal samples and the columns corresponding to the absorbance in 400-2500 nm range (data not shown). Prior to calibration, spectral data were mean centred and transformed using none and smooth transformation with 5-25 data-point windows. In the development of all calibration models twenty PLS factors were set up as maximum. The optimum number of PLS factors used in the models was determined by step-validation. To further focus the analysis, absorbance range was divided into two ranges: 680-1090 nm (second and third water overtone) and 1110-1800 nm (first water overtone) (Smith, 1991). The optimum calibration models were determined by the lowest standard error of calibration (SEC) and standard error of prediction (SEP) and the highest correlation coefficient (R^2). The ratio of standard error of Performance to Standard Deviation (RPD) was used to evaluate the accuracy of prediction.

Result and Discussion
Calibration model

The average correlation coefficient (R^2pred.) is reported to be an indicator of a model sucessful practical usage when higher than 0.70. (Moron *et al.*, 2003). Chang *et al.* define the residual predictive deviation (RPD)>2.0 as indicator of good prediction models (Chang, 2002). The average RPD value of the developed model is 2.725 (Table 1), thus the model presented can be considered as of acceptable accuracy for analytical purposes.

Tabel 1. Statistic for the Partial Least-Squares Regression (PLS) Models of Cd (II) and Mg(II) in 0.1 M HNO_3 solution.

Wavelength range (nm)	Metal	Factor	Calibration		Validation		Prediction		RPD
			R^2	SEC	R^2	SEV	R^2	SEP	
680-1090	Mg (II)	6	0.94	0.70	0.88	1.09	0.92	2.01	2.92
1110-1800		12	0.98	0.32	0.94	0.70	0.93	1.04	3.31
680-1090	Cd (II)	10	0.98	0.48	0.88	1.07	0.98	0.80	2.97
1110-1800		10	0.96	0.61	0.82	1.35	0.92	1.27	2.36

R²: Correlation Coefficient, SEC: Standard Error Calibration, SEV: Standard Error Validation, SEP: Standard Error Prediction, RPD: Standard Error of Performance to Standard Deviation

Calibration statistics included the standard error of calibration (SEC), the coefficient of determination in calibration (R^2CAL), the standard error of validation (SEV) and the coefficient of determination in validation (R^2VAL) (Shenk and Westerhaus, 1993). The satisfying the criteria for establishing the NIR model where R^2 >0.70 (Sauvage *et al.*, 2002). The prediction capacity of the models was assed using the ratio performance deviation (RPD) parameter or standard deviation reference of validation (Conzzolino and Moron, 2003). In that study, the RPD values obtained in accordance with the value in requiring, this show that the NIR equations obtained can be applied to unknown sample (Gonzales-Martin *et al.*, 2007).

The result obtained indicates that it is possible to determine metal these parameters using NIRS. It is also possible to measure the metals under difference perturbations affect. Near infrared region had considerable influence on the spectra due to the strong relationship between metal and water, mainly with O-H overtones (water) influenced by the presence of metal (Ko *et al.*, 2004).

Regression coefficient

To determine metal ion by NIR spectroscopy, with difference temperature showed completely by difference regression vectors, associated with changes in the water absorbance pattern caused by metal presence. Characteristic water absorbance pattern expressed by Water Matrix Coordinates (WAMACS) based on common water bands were found in regression vector. The spectra changes in the NIR spectra were consistent with compositional and structure change of absorbance pattern, this is shown in the Figure.1.
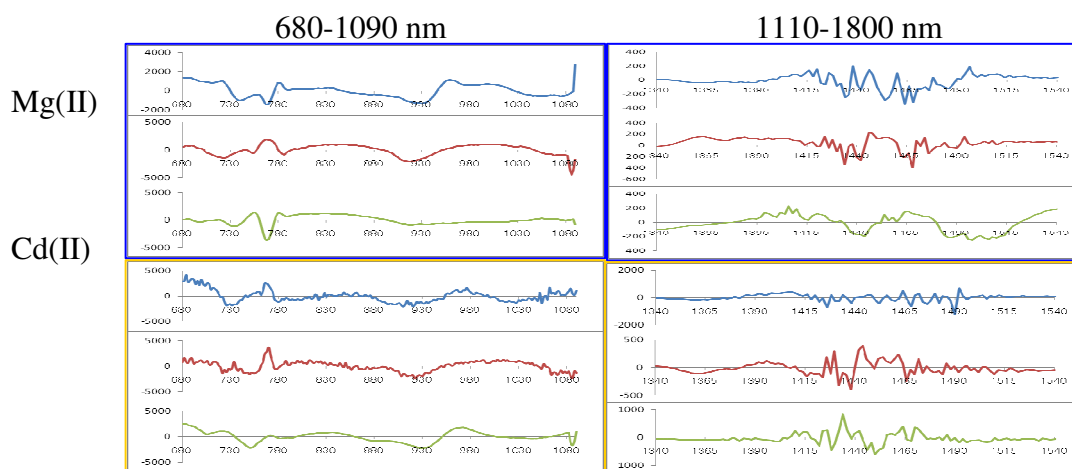
Figure 1. Regression coefficient for the Partial Least-squares (PLS) Model Based on NIR spectra in the (a) 680-1090 nm and (b) 1110-1800 nm region in 0.1 M HNO$_3$ solution.

The regression coefficient shown that the existence of several consistencies in some absorbance bands, positive or negative peaks at around 728-788 nm in 680-1090 nm range. In the 1110-1800 nm range shown that negative and positive peaks at 1362 nm and positive at 1408 nm. Although the difference metals and temperature were used as a perturbation, but there are several the same peaks for negative or positive. These result shown that the consistency of metal to affect the water spectra at a particular wavelength, so it can predict the possible presence metal at these wavelengths.

The results similar between the water band in regression vector and subtracted spectra at a short range, which the important wavelength is on 728-788 nm and the metal severely affected water spectra in the third overtone region. The presence of metal that affects the spectra of water. Therefore, the water spectra will be changes according to difference temperature and has the consistency at particular wavelength. With the consistency of particular wavelength its can detect of metal ion presence in a sample.

Consistency wavelength from a regression coefficient, PLS model its appeared differential spectra of water and metal. It is found in several important wavelengths in the form of coordinates these wavelengths were in good agreement with various well described vibration bands (symmetric stretching, v1; asymmetricstreching, v3 bending, v2). This band defined the WAMACS and allowed interpretation of the result with EWMA (extended water mirror approach). The consistency of these results allowed us to define the water absorbance patterns (WAPs). This spectral analysis proved that the existence of specific WAP for each metal at the same water bands (WAMACs).

However, from the results of the regression factor seen the difference in character between Mg (II) and Cd (II) at Figure 1. The Cd (II) is noisier than Mg (II) especially at wavelengths of 680-1090 nm. These results indicate that there is a difference characteristic of heavy metal and non-heavy metal.

Conclusions

The potential of NIR spectroscopy was investigated for classification and character quantification of metal. The results show that an NIR spectra analysis by our, PLS model provided a powerful tool for investigating the vibration and interaction of metal with water. PLS model provided a powerful tool for investigating the vibration and interaction of a metal with water, and shows the differences in the character of non-heavy metal and heavy metal in common bands. Water absorption bands in the NIR spectrum are influenced by metals for each metal has a different way to influenced of water spectra. The interaction of NIR light

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and water is the useful tool for detection of metal in water and for analysing water samples for cadmium and Magnesium contamination. The explanation is an excellent proves to the Aquaphotomics and this concept could be used for other purposes, too, like finding new water bands. However, further investigations are needed to determine the effect of metal valence, as interaction between cations and water may be influenced by valence.

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