

Frequency of use minute concentrations of cadmium in aqueous solution by near infrared spectroscopy and aquaphotomics

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Abstract. Cadmium (Cd) is a common industrial pollutant with long biological half-life, which makes it a cumulative toxicant. Near-infrared spectroscopy has been successfully used for quick and accurate assessment of Cd content in agricultural materials, but the development of a quick detection method for ground and drinking water samples is of equal importance for pollution monitoring. Metals have no absorbance in the NIR spectral range, thus the methods developed so far have focused on detection of metal-organic complexes. This study uses Aquaphotomics to measure Cd in aqueous solutions by analyzing the changes in water spectra that occur due to water-metal interaction. Measurements were performed with Cd (II) in 0.1 M HNO₃, 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. A concentration of Cd from 1 mg L⁻¹ to 10 mg L⁻¹ could be predicted by this model with average prediction correlation coefficient of 0.897. The model was tested by perturbations with temperature and other metal presence in the solution. The regression coefficient showed consistent peaks at 728, 752, 770, 780, 1362, 1430, 1444, 1472/1474 and 1484 nm under various perturbations, indicating that these water absorbance changes were due to Cd presence. The residual predictive deviation values (RPD) were greater than 2, indicating that the model is appropriate for practical use.

Keywords: near infrared spectroscopy, Cadmium, partial least-square regression, regression coefficient, WAP, WAMACS

Introduction

Cadmium (Cd) is a non-degradable heavy metal with long biological half-life (30 years) and to date there is no proven treatment for chronic cadmium intoxication (Malec et al., 2009). The main sources of pollution are improper waste dumping, agricultural chemicals and industrial effluents (Chen et al., 1998). After been released into the environment it ultimately gets transported into water and enters the food chain (Malec et al., 2009). Divalent Cd (II) ion is highly toxic when compared to its hexavalent counterparts. Cd readily dissolves in dilute nitric acid, HNO₃, making it a good solvent to study Cd in aqueous solution. Furthermore, 0.1 M HNO₃ protects the dissolved Cd from air oxidation (Mihit et al., 2010).

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 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.

Cadmium as such have no absorption in NIR range, but dissolved in organic matter, they actively form complexes with organic molecules. Alteration in the vibrational mode of organic complexes has been exploited for accurate detection of metals in agriculture materials and food, such as wines (Sauvage et al., 2002), legumes (Cozzolino and Moron, 2004), forage (Clark et al., 1989), grasses and hays (Saiga et al., 1989), heavy metal pollution (include Cd) (Pieponen, 1989), Cadmium and lead in the mussel *Mytilus galloprovincialis* (Font et al., 2006). NIRS has been also used to predict trace metal content in sediments or soils (Malley and Williams, 1997; Kemper and Sommer, 2002). Water

associates strongly with ions, organic monomers and polymers through hydrogen bonds. Therefore, the change in water absorption bands in the NIR region permits measurement of small quantities or of structural changes in other molecules in the system. This concept has been explored by Aquaphotomics, which has become a powerful strategy to understand water spectral changes related to small concentration of solutes (Tsenkova, 2007). Sakudo et al. reported successful detection of Cu(II), Mn(II), Zn(II) and Fe(III) in aqueous solution by NIRS (Sakudo et al., 2006). Despite using only direct NIR measurements of metal solutions, their findings are a good illustration of NIRS potential for metal detection without organic matrices.

The present study examines Cd(II) effect on the vibrational mode of water in the absence of organic solutes and apply Aquaphotomics concept as a tool to predict low metal concentration ($1-10 \text{ mgL}^{-1}$). For this purpose two particularly informative spectral regions have been selected, 680-1090 nm (water second and third overtones) and 1110-1800 nm (water first overtone). Further on, Cd detection under various perturbations has been performed, thus mimicking real life pollution monitoring conditions.

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) (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, 30 and 37°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 (Pirouette 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 centered 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)²⁷ and 1110-1800 nm (first water overtone)²⁷. 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.

Perturbations

Cd solutions were perturbed with temperature at 25, 30 and 37°C , and other metals (Mg (II), Mn (II) and Zn (II)). Metals were added as 5 mg L^{-1} concentration into increasing concentrations of Cd solutions ($0-10 \text{ mgL}^{-1}$ in 0.1 M HNO_3 with 1 mgL^{-1} step at 25°C). Respective spectral data of all perturbed solutions were taken.

Results and Discussion

Calibration model

The average correlation coefficient ($R^2_{pred.}$) is reported to be an indicator of a model successful practical usage when higher than 0.70.(Moron,*et.al.*,2003). The average $R^2_{pred.}$ of PLS model developed for Cd(II) in 0.1M NHO avg 0.945 (Table 1) and avg 0.88 for Cadmium and other metal as perturbations (Table 1). Chang et al.. define the residual predictive deviation (RPD) >2.0 as indicator of good prediction models²¹. 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.

Table 1. Calibration and prediction statistics for Partial Least-squares Regression (PLS) Model for Cadmium (II) in 0.1 M NHO₃ aqueous solution, indicating the coefficient of determination in Prediction (R^2_{Pred}) =Avg 0.945 and RPD (SD/SEV) >2 that the models are appropriate for practical use

Metal Ion	Wavelength Range	Factor	Calibration		Validation		Prediction		RPD
			R ²	SEC	R ²	SEC	R ²	SEC	
Cd(II)	680-1090	9	0.97	0.56	0.89	1.05	0.95	2.08	3.09
	1110-1800	16	0.98	0.48	0.82	1.38	0.94	4.29	2.36
Average			0.975	0.52	0.855	1.215	0.945	3.185	2.725

Metals as perturbations

Perturbation can be defined as evaluation of a physical system by applying small changes to selected parameters and re-estimating the resulting system (Tsenkova,2007).In the short NIR range (680-1090 nm), the regression coefficient for the different metal perturbations exhibit a consistent pattern of positive and negative peaks at 728,752,768,and 780 nm (Figure 1a), making this area most important for investigation of metal influence on water spectra. Similar characteristic absorbance bands were obtained by A.Sakudo et.al. in 710-750 nm short wavelength region (Sakudo et a. 2006). Important wavelengths in the middle NIR (1110-1800 nm) range were found at 1362,1404,1408,1434,1444,1472 and 1484 nm, a negative and positive peaks (Figure 1b). These results show the consistency with which Cd affects water spectra at certain wavelengths, so its presence has been predicted using these wavelengths as important variables in the regression vector for Cd.

Temperature as perturbations

The temperature change affects the vibration intensity of molecular bonds, therefore changes the spectrum. (Osborn,*et.al.*,1993). Temperature influences considerably spectral measurements. Baxter et al.. have reported that with increasing temperature the broad band, which can be seen as an overlay of many bands belonging to different cluster sizes of molecules formed by hydrogen bonding, is shifted towards lower energies as the degree of hydrogen bonding decreases (Baxter,*et.al.*,1996). These findings agree with our experimental data; NIR spectra of Cd (II) aqueous solution at different temperatures shifted towards lower absorbance as temperature increased (Figure 2).

In 680-1090 nm range, the spectral regression coefficients for different temperatures of Cd solution display consistent positive and negative peaks at 728,752, 770 and 778 nm (Fig. 3). Consistency is also visible in 1110 – 1800 nm range, with negative and positive peaks at 1362,1399,1408,1430,1444,1448,1462,1468,1472 and 1498 respectively (Figure 1). Figure 2 shows that, with a different temperature, in a particular wavelengths have consistency negative and positive peaks, which indicates the existence cadmium in the sample. It appears that Cd perturbrates water matrix in characteristic way at different temperatures. These results are consistent with the data on presence of other metals as perturbation in the regression coefficient (Figure 2). Therefore it can be speculated that the commonly observed peaks may be related to interaction between Cd(II) and water.

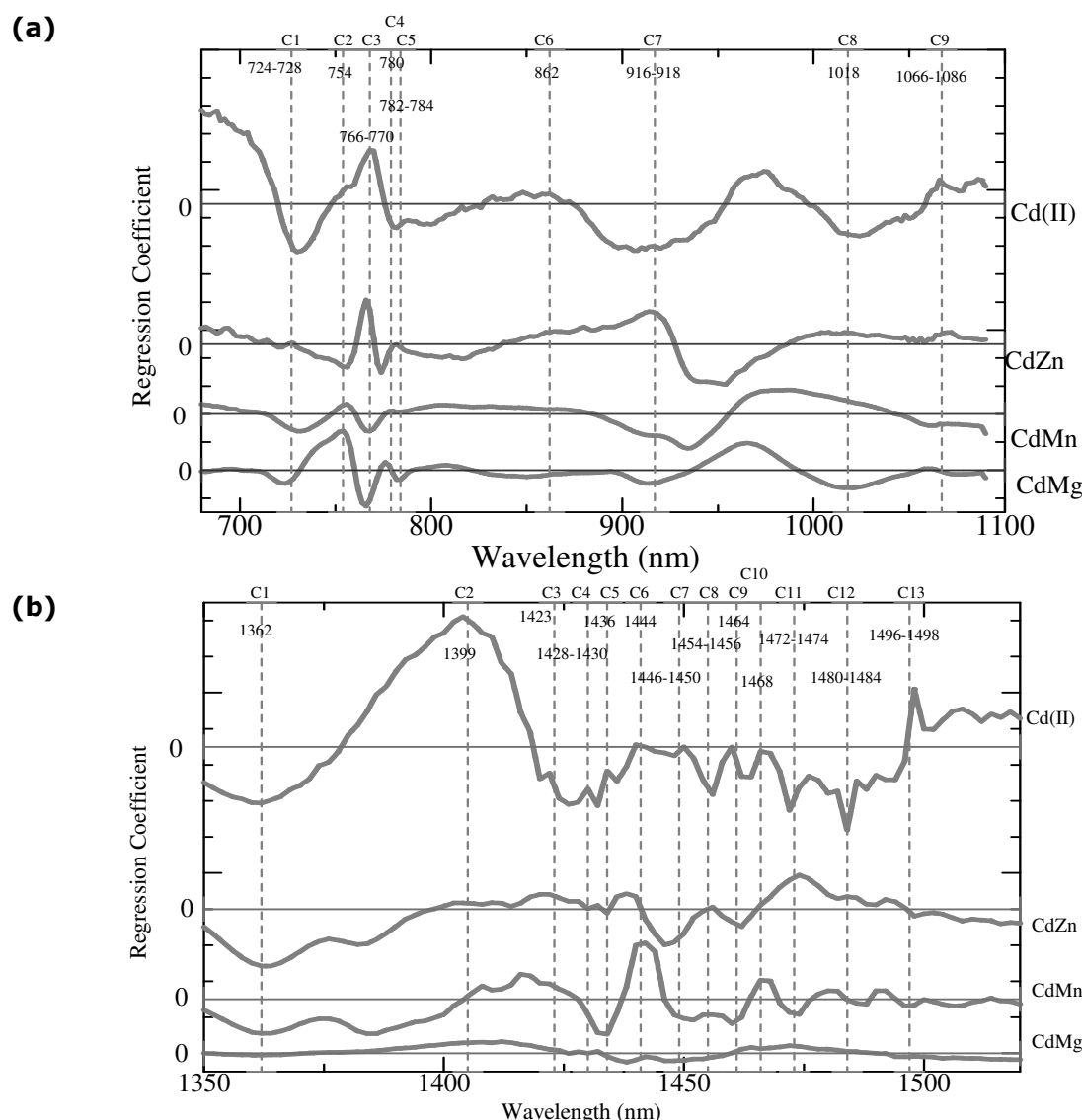


Figure 1. Spectral Cadmium in water : regression vector of the NIR Spectroscopy model for Cadmium in 0.1 M HNO₃ with other metals presence as perturbations, the Water Matrix Coordinates (WAMACS) describes that consistency coordinates of Cadmium under various perturbations. (a) 680-1090 nm range, and (b) 1110-1800 nm range.

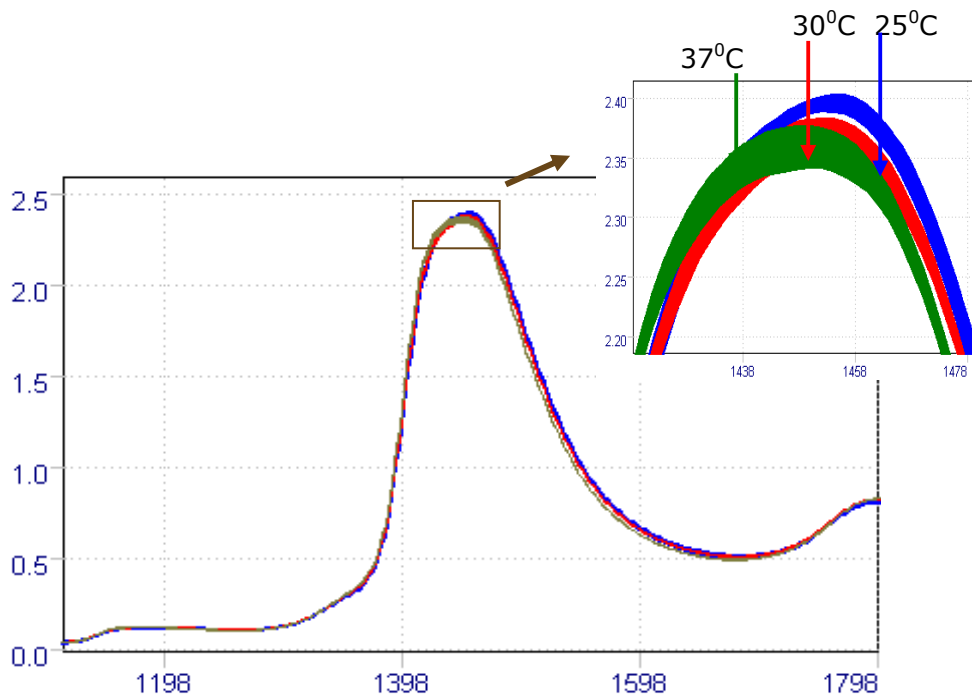


Figure 2. NIR Spectra of Cd (II) at 25°C (blue), 30°C (red) and 37°C (blue), The increase of temperature makes the spectra shift to the short wavelength direction, indicated that the change of water structural patterns.

Water matrix absorbance coordinates, WAMACS

The term Water Matrix Coordinates (WAMACS) represents the influence of different perturbations on the water absorbance in NIR range.⁴ Finding common absorbance bands with WAMACS in the regression vector for Cd(II) is important for understanding water-metal interaction.

Cd(II) affects the water spectra on a consistent basis (Fig. 3 and 5). Regression coefficients reveal several consistent wavelengths activated under perturbations with temperature and other metals (728, 752/754, 780, 1362, 1407/1408, 1432, 1452/1455, 1472/1474 and 1486/1488 nm). The regression vector (Figure 3 and 5) shows the influence of different perturbations on water absorbance. The presence of these perturbations also affects the spectra of water, however, some specific wavelengths show consistency in the water matrix coordinates. These wavelengths showed high correlation value with Cd(II) (Fig. 3 and 5), and in general they matched positive and negative peaks in the correlation plots corresponding to coordinates $C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9$ and C_{10} in Water matrix coordinates (WAMACS) (Table 2). The finding of common absorbance bands with water in the regression vector for Cd (II) indicates that water-metal interaction play very important role to understanding metal presence in a water. In this study, spectral analysis revealed the existence of specific WAPs for each perurbations at the same bands (WAMACs). Thus, using the consistency in the absorbance patterns, the presence of metal in the sample can be detected.

Table 2. Calibration and prediction statistics for Partial Least-squares Regression (PLS) Model for Cadmium (II) and (Mg,Zn and Mn) perturbation in 0.1 M HNO_3 aqueous solution, these results indicate that the coefficient of determination in Prediction (R^2_{Pred}) = Avg 0.88 and RPD (SD/SEV) >2 that the models are appropriate for practical use.

Metal Ion	Wavelength Range	Factor	Calibration		Validation		Prediction		RPD
			R^2	SEC	R^2	SEC	R^2	SEC	
CdMg	680-1090	9	0.93	0.91	0.83	1.31	0.9	4.3	2.44
	1110-1800	8	0.92	0.93	0.71	1.52	0.84	1.73	2.1
CdZn	680-1090	15	0.99	0.18	0.95	0.71	0.81	2.71	4.5
	1110-1800	11	0.97	0.61	0.84	1.30	0.82	3.33	2.46
CdMn	680-1090	13	0.93	0.94	0.73	1.58	0.97	1.47	2.02
	1110-1800	15	0.98	0.41	0.76	1.57	0.96	1.41	2.03
Average			0.95	0.66	0.80	1.33	0.88	2.49	2.59

Concentration of Cadmium: 0 - 10 mg.L^{-1} (1 mg.L^{-1} ,step), CdNx, Cd(II) + 5 mg/L concentration of metal Nx, Factor, Maximum factor used, R^2 , correlation coefficient SEC, standard error of calibration, RPD, standard error of performance to standard deviation

Conclusions

Considering Cd toxicity, quick and reliable environmental monitoring is primordial. The potential of NIR spectroscopy was investigated for identification and quantification of Cd(II) in aqueous HNO_3 . The results show that NIRS could measure low concentrations of Cd by PLS model and using different perturbations provided a useful tool for investigating the interaction of metal with water and its quantitative detection, with average coefficient of prediction (R^2_{Pred}) = 0.945. This can be explained with the concept of aquaphotomics, where Cd could be detected at particular wavelengths corresponding to already identified WAMACS. These results indicate that the interaction of NIR light and water is the a useful tool for detection of metal in water and for analyzing water samples for cadmium contamination. The explanation is an excellent prove 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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