An efficient near infrared spectroscopy based on aquaphotomics technique for rapid determining the level of Cadmium in aqueous solution

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Abstract. Cadmium (Cd) is a common industrial pollutant with long biological half-life, which makes it as 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 equal important 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 (move to intro). This study focuses on the use of Aquaphotomics technique 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. It was found/determined that 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, 780, 1362, 1430,1444, 1472/1474 and 1484 nm under various perturbations, indicating that metal to influence the water spectra. The residual predictive deviation values (RPD) were greater than 2, indicating that the model is appropriate for practical use. The results suggested that this newly proposed approach is capable of detecting metal ion in a much simpler, rapid and reliable way.

1. Introduction

Cadmium (Cd) is a non-degradable heavy metal with long biological half-life (30 years) and until today 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 a 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 analysis in short time.

Cadmium as such have no absorbtsion 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 (Tsengkova,2007). Sakudo et al. recently 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 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). Furthermore, Cd detection under various perturbations has been performed, thus mimicking real life pollution monitoring conditions.

2. Procedure

2.1 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\(_3\).

2.2 NIR Spectra collection
The transmittance spectra were recorded by NIR System 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.

2.3 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 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 make the analysis more focus, absorbance range was divided into two ranges: 680-1090 nm (second and third water overtone) and 1110-1800 nm (first water overtone). 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 mgL$^{-1}$ in 0.1M NHO with 1 mgL$^{-1}$ step at 25°C). Respective spectral data of all perturbed solutions were taken.

3. Results

3.1 Calibration model
The average correlation coefficient ($R^2_{\text{pred.}}$) is reported to be an indicator of a model successful practical usage when it is higher than 0.70.(Moron, et.al., 2003). The average $R^2_{\text{pred.}}$ 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 2). Chang et al. define the residual predictive deviation (RPD) >2.0 as indicator of good prediction models. The average RPD value of the developed model is 2.725 (Table 1), thus the model presented can be considered as an 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 NHO$_3$ aqueous solution, indicating the coefficient of determination in Prediction ($R^2_{\text{pred}}$) =Avg 0.945 and RPD (SD/SEV) >2 that the models are appropriate for practical use.

| Metal Ion | Wavelength Range | Factor | Calibration R$^2$ | Validation R$^2$ | Prediction R$^2$ | RPD |
|-----------|------------------|--------|-------------------|------------------|------------------|-----|
| Cd(II)    | 680-1090         | 9      | 0.97              | 0.56             | 0.89             | 0.95 | 2.08 | 3.09 |
|           | 1110-1800        | 16     | 0.98              | 0.48             | 0.82             | 1.05 | 0.94 | 4.29 | 2.36 |
| Average   |                  |        | 0.975             | 0.52             | 0.855            | 1.215| 0.945| 3.185| 2.725 |
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 NHO₃ aqueous solution, these results indicate that the coefficient of determination in Prediction (R²_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 |
|-----------|------------------|--------|-------------|------------|------------|-----|
|           |                  |        | R²  | SEC | R²  | SEC | R² | SEC | R² | SEC | RPD |
| 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

R², correlation coefficient

SEC, standard error of calibration, RPD, standard error of performance to standard deviation

3.2 Metals as perturbations

Perturbation can be defined as evaluation of a physical system by applying small changes to selected parameters and re-estimating the resulted 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 become 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, negative and positive peaks (Figure 1b). These results showed the consistency which Cd affects water spectra at certain wavelengths, so its presence has been predicted by using these wavelengths as important variables in the regression vector for Cd.
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.

3.2 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 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 make the analysis more focus, absorbance range was divided into two ranges: 680-1090 nm (second and third water overtone) and 1110-1800 nm (first water overtone). 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 (R²). 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 mgL⁻¹ in 0.1M NHO with 1 mgL⁻¹ step at 25°C). Respective spectral data of all perturbed solutions were taken.

4. Discussion

4.1 Calibration model

The average correlation coefficient (R²pred.) is reported to be an indicator of a model successful practical usage when it is higher than 0.70.(Moron, et.al., 2003). The average R²pred. 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 2). Chang et al. define the residual predictive deviation (RPD) >2.0 as indicator of good prediction models. The average RPD value of the developed model is 2.725 (Table 1), thus the model presented can be considered as an acceptable accuracy for analytical purposes.
4.2 Temperature as perturbations

The temperature change affects the vibration intensity of molecular bonds, therefore it changes the spectrum. (Osborn, et al., 1993). Temperature influences considerably spectral measurements. Baxter et al. has reported that by increasing temperature the broad band, it can be seen as an overlay of many bands belonging to different cluster sizes of molecules formed by hydrogen bonding, it 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 3).

![Figure 2A](image1.png)

(a)

![Figure 2B](image2.png)

(b)

**Figure 2.** Spectral Cadmium in water: regression vector of the NIR Spectroscopy model for Cadmium in 0.1 M HNO₃ with temperatures as perturbations, the Water Matrix Coordinates (WAMACS) describes that consistency coordinates of Cadmium under various temperatures. (a) 680-1090 nm range, and (b) 1110-1800 nm range.

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 (Figure 2a). 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 2b). Figure 2 shows that, with a different temperature, in particular wavelengths its consistency have negative and positive peaks, which indicates the existence cadmium in the sample. It displays Cd perturbates 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 1). Therefore, it can be speculated that the commonly observed peaks may be related to the interaction between Cd (II) and water.
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.

### Table 3. Common wavelengths with WAMACS for Cd under various perturbations indicates the presence of cadmium with the occurrence of water spectra.

| Wavelength | WAMACS | CdMg | CdMn | CdZn | Cd 25°C | Cd 30°C | Cd 37°C |
|------------|--------|------|------|------|---------|---------|---------|
| 1110-1800 nm Range | | | | | | | |
| 1110-1800 nm Range | | | | | | | |

(+), Positive Peaks  
(-), Negative peaks C, Water matrix coordinate

Cd (II) affects the water spectra on a consistent basis (Table 3). 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 1 and 2) shows the influence of different perturbations on water absorbance. The presence of these perturbations also affects the spectra of water, however, some specific wavelengths showed consistency in the water matrix coordinates. These wavelengths showed high correlation value with Cd(II) (Figure 1 and 2), and in general they matched with 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 3). The finding of common absorbance bands with water in the regression vector for Cd (II) indicates that water-metal interaction plays very important role to understand metal presence in water. In this study, spectral analysis revealed the existence of specific WAPs for each perturbation at the same bands (WAMACS). Thus, using the consistency in the absorbance patterns, the presence of metal in the sample can be detected.

5. Conclusion

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 showed that NIRS could measure low concentrations of Cd by PLS model and using different perturbations that 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 aquaphotomic concept where Cd could be detected at particular wavelengths corresponding to the identified WAMACS. These results indicate that the interaction of NIR light and water is a useful tool for detecting metal in water and 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 such as 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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