

Frequency of use Minute concentrations of Cadmium and Magnesium in aqueous solution can be measured by Near Infrared Spectroscopy

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Abstract— *This study was focused on detection of Cadmium (Cd) and Manganese (Mg) in aqueous solution using Near Infrared Spectroscopy (NIRS). Although detectable, minerals have no absorption in NIR region, but alteration of the vibration mode of water matrix caused by minerals can be detected by NIRS. Artificial samples was used in this research were contained metal diluted in aqueous solutions. Analysis were performed in the 400-2500 nm region and were subjected to a partial least-square (PLS) regression analysis; validation was performed by mean center and transformed by smoothing. The metals were scanned by Fourier Transform Infrared Spectroscopy (FTIR), in three consecutive days. Data for two days were used as data set and the rest of the data were used as prediction set. These results showed that the PLS model were able to detect metal ions in the NIR region of electromagnetic spectra with high accuracy even at low concentrations (0 -10 ppm). PLS model provided a powerful tool for investigation of the vibration and interaction of a mineral with water.*

Keyword: *Near Infrared Spectroscopy, Magnesium(II), Cadmium(II), Partial Least Square Regression, Regresion Vector.*

I. INTRODUCTION

Traditional methods for trace metal ion detection include inductively coupled plasma atomic emission spectroscopy (ICP-AES) [1], electrochemical method, stripping potentiometry. 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.

Cadmium and magnesium as such have no absorbtion 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 [2], legumes [3], [4] grasses and hays [5], heavy metal pollution (include Cd) [6], Cadmium and lead in the mussel *Mytilus galloprovincialis* [7]. NIRS has been also used to predict trace metal content in sediments or soils [8].

To determine the unknown sample water bands involved in the models, water was analyzed under various perturbations and additional water bands were assigned based on loadings and regression vectors of the resulting data set. These observations were interpreted as an indication that water bands are widely-distributed in the NIR range. In this study to determine the potential of NIR spectroscopy with partial least square (PLS) to examine whether different metals Cd and mg displayed different characteristic on the vibration mode of water in the absence of organic matrices.

II. MATERIALS AND METHODS

A. Procedure

To minimize metal contamination of the sample, all glass or vessels to be used were immersed during one day in aqueous solution 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). Working stock solutions of Cd(II) and Mg (II) at 10 mgL⁻¹ were prepared by direct dilution of the standard solution with pure water.

B. NIR Spectra collection.

The transmittance spectra were recorded by FTIR. The cuvette was positioned in a cell holder in conjunction with a temperature bath to maintain temperature at 25⁰C. 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.

B. 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. 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.

III. RESULTS AND DISCUSSION

Calibration statistics included the standard error of calibration (SEC), the coefficient of determination in calibration (R²CAL), the standard error of validation (SEV) and the coefficient of determination in validation (R²VAL) [8]. The satisfying the criteria for establishing the NIR model where R² >0.70 [9]. The prediction capacity of the models was assed using the ratio performance deviation (RPD) parameter or standard deviation reference of validation [10] In those 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.[11]. 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[12]. The coefficient regression values and standard deviation of magnesium (Mg) and Cadmium (Cd) content in water sample calibration, validation and prediction set measured are presented by Table 1.

TABLE 1. STATISTIC FOR THE PARTIAL LEAST-SQUARES REGRESSION (PLS) MODELS OF MG(II) AND CD(II) IN AQUEOUS SOLUTIONS.

Metal	Factor	Calibration		Validation		Prediction		RPD
		R ²	SEC	R ²	SEV	R ²	SEP	
Mg	10	0,984	0,62	0,985	0,27	0,986	0,574	2,15
Cd	5	0,894	1,4	0,93	0,58	0,955	1,2	2,07

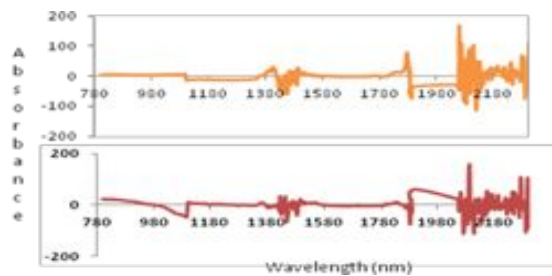


Fig.1. Regression coefficient for the Partial Least-squares (PLS) Base on NIR Spectra 780 -2280nm.

The regression coefficient shown that the existence of several consistencies in some absorbance bands, positive or negative peaks at around 1380-1580nm and 1780 -2200 nm Although the difference metals, 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. In these area the important wavelengths to predict metal present in the water.

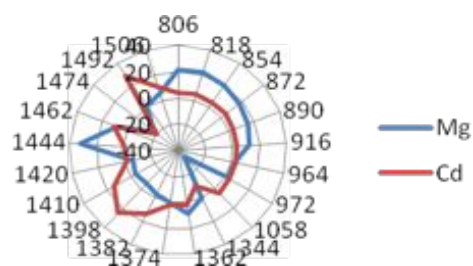


Fig.2. Differential average spectra for each metal and behavior for Mg and Cd in common wavelength

The possible effects of water spectra change were explored by the searching 21 common wavelength at short range (680-1800 nm). This spectra were done by subtracting spectra from average concentration 10 mg.L-1 and 0 mg.L-1 as subtracted spectra. Examination of the common wavelength for each metal is very interesting and informative. From the figure 2 shows the character of metal at common wavelength, Cd, very strong in 1398 (water) nm and 1493, and Mg strong in 1444, 806 and 1362 nm. These result indicated that the metals difference way to influence water spectra, and indicated the character of non-heavy metal and heavy metal in common bands.

IV. CONCLUSION

- 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.
- The potential of NIR spectroscopy was investigated for classification and character quantification of metal in aqueous solution. 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.

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