EPH - International Journal of Science And Engineering
ISSN (Online): 2454 2016
Volume 03 Issue 04 December 2017

DOI: https://doi.org/10.53555/eijse.v3i4.124

A STUDY CHARACTERISTICS AND DETECTION OF METALS ION IN AQUEOUS SOLUTION BY NEAR INFRARED SPECTRA AREA

Alfian Putra[1]*, Helmi[2], Syafruddin[3]
**[1, 2, 3] Chemical Engineering Department Polytechnic Lhokseumawe State*

****Corresponding Author:-***
Email: putraalf@yahoo.com

Abstract:-

This study was focused on detection of Magnesium (Mg,) Zinc (Zn), Cadmium (Cd) and Manganese (Mn) as minerals in aqueous solution using Near Infrared Spectroscopy (NIRS) and chemo metrics. 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 used in this research were contained metal diluted in aqueous solutions. Analyses were performed in the 680-1090 nm and 1110-1800 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 NIR System 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 Metals in aqueous solution with correlation coefficient ($R2_{pred.} > 0.7$). 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. 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.

Keywords: - *near infrared spectroscopy; magnesium (II), manganese (II), partial least square regression, regression vector*

INTRODUCTION

Pollution of ground water and soil with toxic heavy metals like mercury, cadmium, lead, zinc etc. pose a serious health risk. Because metals are non-degradable they tend to bioaccumulate as they move up the food chain. The main sources of soil and ground water pollution are improper waste dumping, agricultural chemicals, and industrial effluents (Chen *et al.,* 1998; Abollino et al., 2002). The toxicity of these heavy metals depends on their concentration and also on their speciation. There exists a need for rapid and wide scale monitoring of heavy metals in the environment. Simple, sensitive sensors that can measure multiple elements simultaneously would be of great significance for wide scale monitoring.

Heavy metals are particularly worrisome contaminants in foods and the environment. In general, they are not biodegradable and they have long biological half-lives. Heavy metals have potential for accumulation in humans from various plants and other natural sources, posing serious health hazards for conditions such as renal failure, symptoms of chronic toxicity, and liver damage. According to the World Health Organization (World Health Organization, 1995), lead, cadmium, chromium, and other heavy metals must be controlled in food sources in order to assure public safety.Lead and cadmium are among the most abundant heavy metals on earth, and are particularly toxic. Excessive concentrations of these metals in food is associated with the etiology of a number of diseases, especially with cardiovascular, renal, neurological, and bone diseases (Steenl and, *et al.,* 2000).

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

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 nondestructive 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) Near infrared (NIR) spectroscopy could be an alternative to monitoring of heavy metal presence in the water samples. 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. 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), aqueous solution (Berentsen, *et.al.,*1996), mineral in legume (Cozzolino and Moron, 2003), elemen in wine (Cozzolino, *et.al.,*2007). Near-infrared spectroscopy has been also used to predict metal in sample, nutrient metal content (Huang,*et.al.,*2008), Detection Zinc(II) (Asano*, et.al.,*2009), metal complex (Butler,*et.al.,*2007), total arsenic in prostrate amaranth (Font,*et.al.,*2003), heavy metal oxides glasses Garlamov,*et.al.,*1996) and metals in water (Sakudo *et.al.,*2006). The potential of NIR spectroscopy also was investigated for classification and character quantification of heavy metal in water.

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 behavior 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.

1. Material and Method

Sample Preparation, The metals were used in this study was obtained from standard solutions purchased from Wako (Tokyo). These metals are Cd (II), Zn (II), Mn (II) and Mg (II). Working stock solutions containing each metal at a concentration of 100 mg.L^{-1} were prepared by pure water. The concentration of each sample solution of Cd(II), Zn(II), Mn(II) and Mg(II) varied from 1 mg.L^{-1} to 10 mg.L^{-1} with 1 mg.L^{-1} step, these sample being prepared by direct dilution of the 100 mg.L^{-1}stock solution *NIR instrument:* The NIR spectra were recorded in the wavelength range 400-2500 nm at 2 nm intervals by spectroscopy (Nireco 6500). The spectral data were collected as the absorbance value [log (1/T)], where T= Transmittance. The cell was positioned in a cell holder in conjunction with a temperature bath to maintain temperature at 25^{0}C. Triplicate NIR spectra were taken from each sample.

Data Processing: Three consecutive spectra for each metal in three consecutive days were used in partial least squares (PLS) regression and soft independent modelling of class analogy (SIMCA) (Pirrouette 3.11, infometrix, Inc, Woodinville, WA, USA). Data for two days were used as data set and the rest of the data were used as prediction set. A matrix data set was constructed with rows representing metal samples and the columns corresponding to the absorbance in 400-2500 nm range. 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) (Bart *et.al*. 2006).

Method analyses: All of metals divided 2 category, Cd (II) and Zn (II) representative from heavy metal, Mg (II) and Mn (II) representative from non-heavy metal. Based on Environmental Standard for drnking water suggest that Cd (II) < 0.005 mg.L^{-1}, Zn (II) < 5 mg.L^{-1}, Mg(II) < 8 mg.L^{-1} and Mn(II)<0.05 mg.L^{-1}. Thus In this study the concentration of each sample solution varied from 0 to 10 mg.L^{-1}with 1 mg.L^{-1}step. To clarify characteristic of metal, the experimental data suggested the use of Soft Independent Modelling Class Analogy (SIMCA) to qualitative information. To observation quantitative information partial least squares (PLS) regression model was used in this study.

2. Result and Discuss

Quantitative chemical analysis to detection metal in water the Partial-least square was constructed. Metal were used in this study are magnesium (Mg (II)), Manganese (Mn(II)), Cadmium (Cd(II)) and Zinc (Zn(II)). Data set is divided into model and test set according to the day to sample. The first and second day as calibration data set and rest as prediction data set, this aims to observe the consistency of spectra with the same conditions and equal treatment. In the calibration set there are 66 spectra (22 sample), and the test set (prediction set) 33 (11 sample) spectra for each metal. The complexity of the, PLS model was determined using validation (step 3). Prior to calibration, spectral data were mean centered and transformed using none and smooth with 5-25 data-point windows. To further focus the analysis, absorbance range is divided into two range 680-1090 nm and 1110-1800 nm. The optimal result for each model will be displayed on the following results.

Table 1. Statistic for the Partial Least-Squares Regression (PLS) Models metals in aqueous solution.

Metal Ion	Wavelength range (nm)	Factor	Calibration		Validation		Prediction		RPD
			R^2	SEC	R^2	SEV	R^2	SEP	
Mg(II)	680-1090	6	0.96	0.55	0.94	0.76	0.85	1.32	4.19
	1110-1800	7	0.94	0.85	0.86	1.18	0.76	1.76	2.71
Cd(II)	680-1090	11	0.98	0.41	0.86	1.22	0.94	0.77	2.61
	1110-1800	7	0.94	0.81	0.86	1.15	0.9	0.95	2.77
Mn(II)	680-1090	13	0.98	0.23	0.85	1.25	0.94	3.16	2.55
	1110-1800	11	0.98	0.38	0.92	0.88	0.9	6.84	3.62
Zn(II)	680-1090	10	0.96	0.56	0.9	0.94	0.71	2.2	3.54
	1110-1800	14	0.96	0.66	0.81	1.39	0.76	3.93	3.93

R^2: 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 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.(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).

Characteristic according to aqua gram

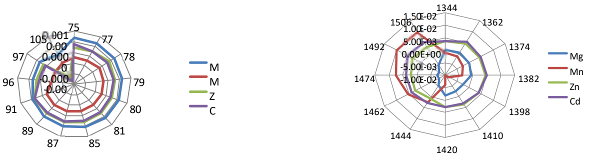


Figure 1: Differential average spectra for each metal and behavior for each metal in common wavelength.

The possible effects of water spectra change were explored by the searching 14 common wavelength at short range (680-1090 nm) and 13 common wavelength in the middle range (1110-1800 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 4.8 shows have character of metal at common wavelength, indicating that changes temperature affects all wavelengths with the different character. Cadmium and Zinc have similar character on any changes in temperature, whereas Mg and Mn show distinct characters.

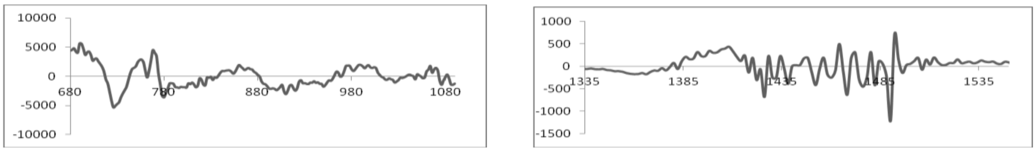
Regression Coefficient

Characteristic water absorbance pattern expressed by Water Matrix Coordinates (WAMACS) (Tsenkova, 2007), 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

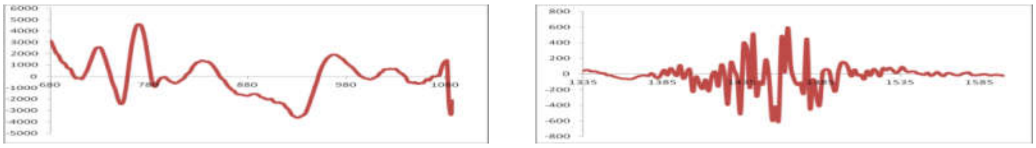
Figure.2.

a) 680-1090 nm *(b) 1110-1800 nm*

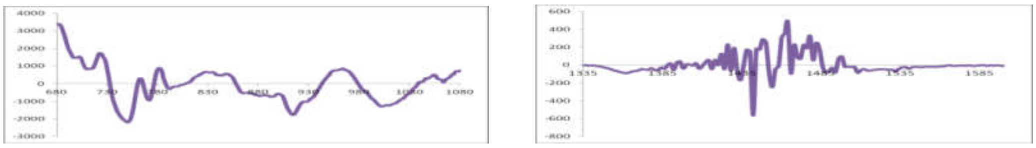
Cadmium



Zink



Manganese



Magnesium

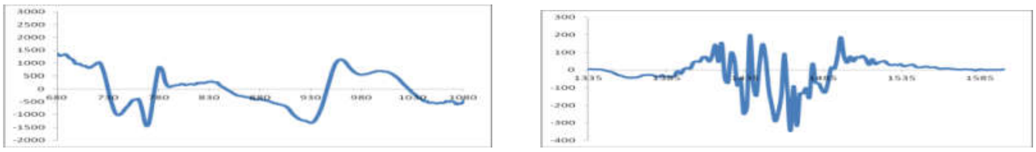


Figure 2: Regression coefficient for the Partial Least-squares (PLS) Model Based on NIR spectra in the (a) 680-1090 nm and (b) 1110-1800 nm region

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 metal, 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. With the consistency of particular wavelength its can detect of metal ion presence in a sample.

Conclusion

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.

References:

[1]. **Abe, H., Kusuma, T., Kawano, A, Iwamoto, M.,** (1995). In: Sprctrosc.Soc.Jpn **44,** 247; cited bu: Iwamoto, M., Kawano, S, Ozaki, J: An Overview of research and development of near infrared spectroscopy in Japan. Journal Near Infrared of Spectroscopy **3**, 179-189

[2]. **Berentsen S; Stolz T; Molt K** (1997). Analysis of aqueous solutions by near-infrared spectroscopy (NIRS) IV: One- and twocomponent systems of organic compounds in water, Journal of Molecular Structure, **410–411**, 581-585.

[3]. **Bart J C J** (2006), Plastic Additives: Advance Industrial Analysis, IOS Press, Amsterdam.

[4]. **Cozzolino D, Liu,L., Cynkai,W.U., Dambergs,R,G.,Janik,L.,Colby,C.B.,Gishen,M.,**(2007)Effectof temperature variation on the visible and near infrared spectra of wine and consequences on the partial least square calibrations developed to measure chemical composition, Analyta Chimica Acta, **588,** 224-230

[5]. **Cen H; He Y** (2007). Theory and application of near infrared reflectance spectroscopy in determination of food quality, Trends in Food Science and Technology, **18**, 72-83.

[6]. **Ozaki Y; McClure W F; Christy A A** (2007). Near-Infrared Spectroscopy in Food Science and Technology, Wiley-Intercience.

[7]. **Sakudo, A., Tsenkova,R., Tei,K., Onozuka,T., Yoshimura,E., Ikuta,K., Onodera,T,** (2006) Comparison of the vibration Mode of Metals in HNO_3 by Partial Least-Squares Regression Analysis of Near-InfraredSpectra,Bioschi.Biotechnol. Biochem, **70** (7), 1578-1583.

[8]. **Sakudo, A., Yoshimura,E., Tsenkova,R., Ikuta,K., Onodera,T.,** (2007), Native of metals in non-digested tissues by Partial Least Squares Regression analysis of visible and Near Infrared Spectra, The Journal of Toxicological Science **32** (2), 135-141

[9]. **Tsenkova, R,** (2000), Unpiblished data

[10]. **Tsenkova, R,** (2004), Method for Analysis with Visible and Near-infrared Spectroscopy, Patent Aplication No. 2004-065975, Japan

[11]. **Tsenkova, R** (2006). Aquaphotomics, NIR News, **17**, 11-12.

[12]. **Tsenkova,R** (2007). Aquaphotomics: Extended water mirror approach reveals peculiarities of prion protein alloforms, NIR News, **18**, 14-17.

[13]. **Williams, P.C.,** (1987). Variables affecting near-infrared reflectance spectroscopy analysis. In: Williams, P.C. and Norris, K., Editors, 1987. *Near-infrared technology in the agricultural and food industries*, American Association of Cereal Chemists Inc, St. Paul, MN, pp. 143–167.