Development of the near infrared spectroscopy model for detecting herbicide concentrations contaminated in water

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Abstract. This research aims to develop the near infrared spectroscopy (NIR) models for detecting herbicide concentrations contaminated in water. Atrazine, the organochlorine herbicide, solution in the concentration range of 0-15 ppm were prepared in distilled water. Near infrared spectra were scanned by using Fourier transform spectrometer at wavenumbers of 12,500-4,000 cm⁻¹ (800-2,500 nm). Partial least square regression technique was used to establish the NIR models for detecting herbicide concentrations. The developed models showed high prediction potential of herbicide concentrations contaminated in water with the R² of 0.97, RMSEE of 0.899 ppm, bias of -0.0003 ppm and RPD of 5.43. This indicated that these models can apply to analyse contamination of atrazine in the natural water sources.

1. Introduction

Since Thailand is an agricultural country where exports various kinds of agricultural products, so there is the usage of the herbicides for controlling weed in plantation. The Office of Agricultural Economics of Thailand reports that the amount of the herbicide imported to Thailand gradually increases every year. The pesticides can mainly be categorized into 4 groups; organochlorine, organophosphate, carbamate and pytheroid. Among these, the organochlorines, i.e. DDT, dieldrin, aldrin, and atrazine are the most widely used [1]. Due to their long degradable period, they contaminate in environment especially in soil and water leading to the mutation of living organism, ecology and the quality of agricultural products which further affect the animal and human health [2-5].

There are several methods to detect these chemicals in water for example Gas Chromatography (GC) and High-Performance Liquid Chromatography (HPLC). However, such methods have many limitations i.e. (1) they are the stationary and complex equipment and (2) the specific analyzing column and method for detecting each chemical are required. Thus, it is not suitable for using in the farm or for detecting the pesticides contamination in the natural sources. The near infrared spectroscopy (NIR) is a less expensive equipment which can detect H-bond [6] which is 1 type of chemical bonding. The portable NIR is newly developed, so it is cheaper and less complicated to detect the chemical concentrations comparing to GC and HPLC. Brunet et al. [7] successfully determined organochlorine pesticide contaminated in soil by using NIR. However, the determination of organochlorine contaminated in water has still been not practical since NIR spectroscopy cannot
directly apply for quantitative analysis but the coupled mathematical model must always be established. Partial least square regression (PLS) is the most popular multivariate technique which has often been coupled with NIR spectroscopy for quantitative analysis.

Therefore, this work has studied the quantitative analysis of atrazine by using NIR and constructed the PLS models for predicting the atrazine contamination in water.

2. Methodology
2.1. Sample preparation
Atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4 diamine of 90% WG) was used in this work. The molecular structure of atrazine is shown in figure 1 [8]. Ten different concentrations of atrazine solution were prepared in the range of 0-15 ppm by dissolving the solid atrazine in distilled water. The prepared solution samples were kept in the amber glass bottles at the temperature of 25±2 ºC for analysis.

2.2 NIR spectra scanning
The solid atrazine was put into the quartz cup with the height of about 1 cm in order to attain the basis spectra of this solid sample. After that, the atrazine solution samples were analyzed by pouring them into the same cup and pushing them with ceramic probe during NIR spectra scanning. NIR spectra of the samples were recorded using the Fourier transform (FT)-NIR spectrometer (MPA, Bruker Ltd, Germany) with diffuse reflectance mode in the wavenumber range of 12,500-4,000 cm\(^{-1}\). Resolution of scanning was 8 cm\(^{-1}\). Each spectrum was acquired from averaging through 32 scans. Each concentration of atrazine solution was scanned 10 times. This experiment was done under room temperature of 25±2 ºC. The NIR absorbance values were displayed on log 1/R unit where R is reflectance of NIR radiation from the sample. Figure 2 shows NIR spectra obtained by scanning on sample.

2.3 Repeatability and reproducibility
Repeatability and reproducibility are the indicators used for reporting the overall precision that was evaluated in this research. Repeatability was calculated to explain the variation of NIR spectrometer which was tested by measurement of NIR spectra of distilled water with 10 duplicates under the same conditions. Mean and standard deviation (SD) of absorbance values at 5155 cm\(^{-1}\) (absorbance peaks of water [9]) were calculated for reporting repeatability. Reproducibility is defined as the ability that the experiment can completely be reproduced implying the precision of analytical method in different conditions. In this work, the reproducibility was tested for investigating precision of NIR by scanning on the samples at different concentrations. The absorbance of water at 5155 cm\(^{-1}\) was mainly focused by scanning 10 times of each sample concentration. After that, mean and SD were calculated from these 10 absorbance values for reporting reproducibility.
2.4 NIR model development

One hundred spectra of atrazine contaminated in water at 10 different concentrations were used to develop NIR models. Multivariate technique of partial least square regression (PLS) was applied to create models with full cross validation. Near infrared spectra either non-treatment or treatment were used to create the NIR spectroscopy models with the OPUS software V. 7.0.129 (Bruker Optik GmbH, German). The following pre-treatment techniques were applied i.e., constant offset elimination, straight line subtraction, vector normalisation (SNV), min-max normalization, multiplicative scatter correction (MSC), first derivatives, second derivatives, first derivatives + straight line subtraction, first derivatives + SNV and first derivatives + MSC. The OPUS software was used for selecting the optimum model with the default optimisation command which was based on combination of the number of PLS factors, the wavenumber ranges and the pre-treatment methods. The model provided from the minimum RMSECV (root mean square error of cross validation) was selected to be the optimum model. The potential of NIR spectroscopy model was then evaluated by statistical terms of coefficient of determination ($R^2$) root mean square error of estimation (RMSEE), ratio of prediction to deviation (RPD) and bias.

3. Results and discussion

Figure 3 shows raw and second derivative spectra of solid atrazine. The prominent peaks at 11110, 8370, 7170, 6170, 5900, 5155, 4810, 4385 and 4065 cm$^{-1}$ (900, 1195, 1395, 1620, 1695, 1940, 2080, 2280 and 2460 nm) was obtained in raw spectra. Three peaks at 11110, 8370, 5900 and 4385 cm$^{-1}$ are the overtone and combination of CH$_3$ stretching [9] while CH$_3$ is an important component of atrazine. Two absorbance peaks of CH$_2$ were observed at 7170 and 6170 cm$^{-1}$ which are the vibration bands of C-H combination and overtone starchying [9]. The vibration band of CH$_2$ detected in the atrazine spectra might be the chemical compound of starchy. The occurrence of combination of starchy around 4810 and 4065 cm$^{-1}$ [9] confirmed that atrazine sample is mixed with starch. Absorbance peak of water was detected at 5155 cm$^{-1}$ which is the vibration band of O-H combination.

Figure 4 shows raw and second derivative spectra of the atrazine solution. The raw spectrum shows evident absorbance peaks around 6870 and 5155 cm$^{-1}$. Both prominent peaks are the overtone and combination bands of water [9]. By the second derivation, NIR spectra was solved about scattering and solving bleary peak in NIR raw spectrum. Some interested peaks were observed at 7170, 4385 and 4065 cm$^{-1}$ after treating spectra with second derivative technique which are the vibration bands of the combinations of CH$_2$, CH$_3$ and starch, respectively [9].

Figure 3. Raw (a) and second derivative (b) spectra of solid atrazine.
Figure 4. Raw (a) and second derivative (b) spectra of atrazine solution.

Table 1 shows the repeatability and reproducibility. The mean and SD of repeatability of FT-NIR spectrometer were 1.430 and 0.002 respectively. These results indicated high precision of FT-NIR spectrometer. Reproducibility of samples of atrazine solution at different concentrations showed SD value varying between 0.039 and 0.105. SD/mean reveals the variance of the experiments. It can be seen also from table 1 that SD/mean values of each concentration were less than 8%. This implies that the experiments had low variance, so the NIR model obtained from this experiment could be predicable.

The NIR results of atrazine concentration detection are shown in table 2. The optimum model was developed with NIR spectra in the range of 9304 to 4243 cm⁻¹ which was preprocessed with multiplicative scatter correction (MSC) technique. The optimum model showed high potential with $R^2$ of 0.97; RMSEE of 0.899 ppm; bias of -0.0003 ppm and RPD of 5.43. Williams [10] recommended that NIR spectroscopy models with $R^2 > 0.960$ and RPD > 5.0 are usable in most application and can be used in quality control [11]. Therefore, this point specified that the developed model in this work can apply to detect atrazine concentrations contaminated in water. Scatter plot of prediction and reference from NIR spectroscopy model is shown in figure 5.

Table 1. Repeatability and reproducibility obtained by scanning 10 times of each sample concentration.

| Overall precision test | Absorbance value at 5155 cm⁻¹ | (SD/Mean)=100% |
|------------------------|-------------------------------|-----------------|
|                        | Mean  | SD   |                    |                 |
| Repeatability Distilled water | 1.430 | 0.002 | 0.140             |
| Reproducibility 0       | 1.430 | 0.039 | 2.727             |
| (Concentration of atrazine in the solution, ppm) 1.5 | 1.424 | 0.049 | 3.441             |
|                        | 3     | 1.415 | 0.080 | 5.654             |
|                        | 4.5   | 1.439 | 0.063 | 4.378             |
|                        | 6     | 1.456 | 0.105 | 7.212             |
|                        | 7.5   | 1.480 | 0.073 | 4.932             |
|                        | 9     | 1.454 | 0.089 | 6.121             |
|                        | 10.5  | 1.471 | 0.079 | 5.370             |
|                        | 12    | 1.441 | 0.075 | 5.205             |
|                        | 13.5  | 1.427 | 0.072 | 5.046             |
|                        | 15    | 1.459 | 0.079 | 5.415             |
Regression coefficient of PLS model for detecting atrazine concentrations is shown in figure 6. Ten dominant regression coefficient values were attained at the wavenumbers of 8750, 8680, 7350, 7170, 5900, 5495, 5265, 5155, 4565 and 4240 cm\(^{-1}\), (1143, 1152, 1360, 1695, 1820, 1900, 1940, 2190 and 2358 nm). Among these, 3 peaks at 7170 cm\(^{-1}\), 5900 cm\(^{-1}\) and 5155 cm\(^{-1}\) were also observed in spectra plots of solid atrazine as shown in figure 3. Vibration bonds of these peaks were explained in the section of Results and discussion. This confirmed that NIR vibration bands of CH\(_3\), CH\(_2\) and H\(_2\)O affected the PLS model for detecting atrazine concentrations. In addition, C-H combination and overtone stretching of CH\(_3\) and CH\(_2\) were obtained around 8680 cm\(^{-1}\), 7350 cm\(^{-1}\) and 4565 cm\(^{-1}\) [10]. The regression coefficient peak at 8750 cm\(^{-1}\) was C-H stretching second overtone of aromatic [10]. The evident peaks around 5265 cm\(^{-1}\) and 4240 cm\(^{-1}\) were vibration bonds of starch and cellulose respectively.

Figure 5. The scatter plot of prediction and reference from NIR spectroscopy model.

Figure 6. Regression coefficient of PLS model for detecting atrazine concentrations contaminated in water.
4. Conclusion
The near infrared spectroscopy model developed with partial least square regression (PLS) technique showed high potential for detecting atrazine concentrations contaminated in water with $R^2$ of 0.97. This indicated that this model may be applied to analyse contamination of atrazine in the natural water sources.

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