Measurement of aspartic acid in oilseed rape leaves under herbicide stress using near infrared spectroscopy and chemometrics

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Abstract

Oilseed rape is used as both food and a renewable energy resource. Physiological parameters, such as the amino acid aspartic acid, can indicate the growth status of oilseed rape. Traditional detection methods are laborious, time consuming, costly, and not usable in the field. Here, we investigate near infrared spectroscopy (NIRS) as a fast and non-destructive detection method of aspartic acid in oilseed rape leaves under herbicide stress. Different spectral pre-processing methods were compared for optimal prediction performance. The variable selection methods were applied for relevant variable selection, including successive projections algorithm (SPA), Monte Carlo-uninformative variable elimination (MC-UVE) and random frog (RF). The selected effective wavelengths (EWs) were used as input by multiple linear regression (MLR), partial least squares (PLS) and least-square support vector machine (LS-SVM). The best predictive performance was achieved by SPA-LS-SVM (Raw) model using 22 EWs, and the prediction results were $R_p = 0.9962$ and RMSEP = 0.0339 for the prediction set. The result indicated that NIR combined with LS-SVM is a powerful new method to detect aspartic acid in oilseed rape leaves under herbicide stress.

Keywords: Agricultural techniques, Data mining, Mass spectroscopy applications, Agricultural engineering
1. Introduction

Nowadays, near infrared (NIR) spectroscopy combined with chemometrics is widely applied for the detection of plant growing information in precision agriculture (Yan et al., 2005). NIR is a fast and non-destructive method, which makes it a promising application in the in vivo detection and field dynamic monitoring. Along with the fast development of precision agriculture and wireless sensor networks for agriculture, developing a fast and dynamic detection method for plant growing information is a hotspot in the research field throughout the world. In the specific field of oilseed rape (*Brassica napus* L.), the growing information, especially under certain stress, is very important for a better understanding of the function mechanism and metabolic pathways (Zhou, 2001). NIR spectroscopy is quite a promising method for such a purpose. Some applications using NIR have been introduced into the oilseed rape study, such as the detection of chlorophyll of rape leaves (Fang et al., 2007; Wang et al., 2008), and the determination of acetolactate synthase (ALS) and protein content of oilseed rape leaves using visible/near infrared (400–2500 nm) spectra (Liu et al., 2008; Liu et al., 2009; Liu et al., 2011).

During the cultivation of oilseed rape, weed control is an important procedure for higher yield and better quality. Since the amount of labor for farming is showing a downward trend, more chemicals are applied to remove and control the weeds. Recently, a newly developed herbicide, named propyl 4-(2-(4,6-dimethoxypyrimidin-2-yloxy)benzylamino) benzoate (ZJ0273), has been applied to remove and control the weeds. ZJ0273 is an ALS (acetolactate synthase)-inhibiting herbicide, which is considered to be environmentally friendly (Tang et al., 2005; Chen et al., 2005). However, studies are necessary on the function mechanism and metabolic path of the herbicide on oilseed rape. Amino acids (like aspartic acid, valine and proline) are important parameters for the understanding of herbicide function mechanism and metabolic path during oilseed rape growth. Amino acid content in oilseed rape leaves could reflect the influence and effects of the herbicide.

Traditionally, amino acids are detected by high-performance liquid chromatography (HPLC) or automatic amino acid analyzer, which are laborious, time consuming, costly, infeasible methods for in-field monitoring. Hence, a fast and non-destructive amino acid detection method is quite necessary. NIR could be used as a fast and accurate method to determine the amino acid content. Therefore, NIR spectroscopy supplied an easy and convenient way to obtain the amino acid data which was quite useful to study the function mechanism and metabolic path of the herbicide on oilseed rape. However, to our knowledge, there have been no reports about the determination of aspartic acid in oilseed rape under the herbicide ZJ0273 stress using NIR spectroscopy.
The objectives of this study were to investigate the feasibility of using NIR for the amino acid detection, and compare the prediction performance of different spectral preprocessing methods, linear and nonlinear calibration methods using a wide wavelength region in the NIR with selection of effective wavelengths for the detection of aspartic acid in oilseed rape leaves under herbicide stress.

2. Materials and methods

2.1. Sample collection

Samples used in this experiment were oilseed rape (*Brassica napus*, cv. ZS758) planted in the farm of Zhejiang University, Hangzhou (30° 10′N, 120° 12′E). In order to make a full consideration of the effects of herbicide on oilseed rape leaf, three different concentrations (100, 200 and 500 mg/L) of herbicide ZJ2073 was foliar applied at the 5-leaf stage at the quantity of 500 L/ha. Simultaneously, oilseed rape leaves without herbicide treatment were kept as controls. Oilseed rape leaves were collected at three different times after herbicide treatment, and 80, 80 and 88 leaf samples were collected at each time. Some sample pre-treatment was performed before spectral collection. Firstly, the collected leaf samples were dried, milled and then sieved through 60-mesh. The whole oilseed rape leave sample was milled and sieved through 60-mesh and there was none left of the leaf sample. The oilseed rape leaf was milled in order to avoid the influence of different particle sizes. Besides, the oilseed rape leaf sieved through 60-mesh was also a necessary step in preparation stages to detect amino acid using the automatic analyzer. Secondly, each sample was separated into two categories. The first category was used for spectral scanning, and the second category was used for aspartic acid detection using traditional method by automatic amino acid analyzer. All samples were randomly divided into three sets, which were calibration set with 124 samples, validation set with 62 samples and prediction set with the remaining 62 samples. Each sample set included all herbicide concentration treatments (100, 200, 500 mg/L and the control group). The calibration and validation sets were only used for calibration stage. The validation set was used as the test set which played the same role of the samples of cross-validation method during calibration stage. The prediction set was applied for assessment and evaluation of the prediction performance of developed models.

2.2. Spectral acquisition

Spectral data of leaf samples within 1100–2500 nm were obtained by Foss NIR Systems 5000 spectrometer (Foss NIR Systems, Denmark). Before the spectral collection, the samples were taken out from the refrigerator until they were equalized to the room temperature at 20–23 °C. The room humidity was around...
50–60%. The diameter of the sample cell was 1 cm. The reflectance mode was used for spectral collection. The standard sample supplied by Foss Company was used to calibrate the Foss NIR Systems 5000 spectrometer. A total of 700 data points for each spectrum were collected within 1100–2500 nm with a 2 nm resolution. The reflectance spectra were collected for all leaf samples, and the spectral data were stored for later analyses.

2.3. Aspartic acid analysis

The reference method to measure aspartic acid was an automatic amino acid analyzer. The chemical pretreatment of oilseed rape leaf was based on the Lisiewska method (Lisiewska et al., 2008). The content of amino acids was determined using a HITACHI amino acid analyzer (Model: L-8900, Japan) under a normal analytical condition. Two aspartic acid values were obtained for each leaf sample, and the averaged value was used as the reference value for each leaf sample. The content of amino acids was expressed as mg/100 mg of dry matter (mg/100 mg DW).

2.4. Spectral pre-processing and effective wavelengths selection

Seven different spectral pre-processing methods were applied for better prediction performance in partial least squares (PLS) analysis models. These pre-processing methods included Savitzky-Golay smoothing (SG), standard normal variate (SNV), multiplicative scatter correction (MSC), first-derivative (1st-Der), second-derivative (2nd-Der) and de-trending. Spectral pre-processing was implemented by “The Unscrambler V 9.8” (CAMO AS, Oslo, Norway). Another pre-processing method, direct orthogonal signal correction (DOSC), was implemented by Matlab V7.0 (The Math Works, Natick, USA). These pre-processing methods were applied mainly to remove the spectral baseline shift, noise and light scatter influence (Chu et al., 2004; Westerhuis et al., 2001).

In the PLS models, the input data matrix was the full wavelength region including 700 variables (1100–2500 nm with 2 nm increment). The full wavelength region was a large data matrix, and thus the computation was complex with long computation time. In order to make a streamlined model, a relevant variable selection method was necessary before further comparison. Herein, a newly developed method called successive projections algorithm (SPA), was applied for comparison (Araújo et al., 2001; Galvão et al., 2008). SPA was able to choose the most informative wavelengths with least collinearity and redundancies though the projection procedure. SPA could make the relevant wavelengths in the sequential order of importance, which means that variables chosen earlier were more important. The selected relevant wavelengths were named as effective wavelengths (EWs).
Monte Carlo-uninformative variable elimination (MC-UVE) is a variable selection method combining Monte Carlo (MC) sampling and uninformative variable elimination (UVE). In MC-UVE, PLS models were built on the calibration set and the prediction set randomly divided by predefined times of MC sampling. The ratio of the mean and the standard deviation of the regression coefficients of each variable is used to evaluate the importance of the variables (Han et al., 2008).

Random frog (RF) is an efficient reversible jump Markov Chain Monte Carlo-like approach for variable selection. RF initializes a subset with a predefined number of variables ($V_0$) and a candidate subset with another number of variables ($V_*$). The initialized subset is updated by the candidate set with a certain probability at each iteration. The number of iterations should be predefined. After the finish of the iterations, the selection probability of each variable is calculated as the variable importance for variable selection (Li et al., 2012).

EWs were used as the input data matrix to develop calibration models using the following methods: multiple linear regression (MLR), partial least squares analysis (PLS) and least-squares support vector machine (LS-SVM).

### 2.5. MLR, PLS and LS-SVM methods

MLR and PLS analyses are widely utilized calibration methods for regression models in NIR technology. MLR applies input variables directly to develop a linear relationship between the spectral variables ($X$-variables) and aspartic acid ($Y$-variable) in oilseed rape leaves. During PLS, the latent variables (LVs) were first extracted from full wavelength region spectral variables and then used to develop a linear correlation between these LVs and chemical constituents (aspartic acid). The details of MLR and PLS can be found in the literature (Andrews, 1974; Geladi and Kowalski, 1986). MLR and PLS were implemented by “The Unscrambler V 9.8” (CAMO AS, Oslo, Norway).

LS-SVM is a newly developed statistical method, which is promising for handling both linear and nonlinear problems. The LS-SVM procedure reduces the computation time and requires a small sample database for a stable and robust model (Suykens and Vandewalle, 1999). Three steps are needed before performing LS-SVM. Firstly, the input data matrix should be selected. Herein, the selected EWs by SPA were applied as the input data matrix. Secondly, the kernel function should be suitable according to the input data and performing result. Herein, radial basis function (RBF) was recommended for kernel function for its ability of handling both linear and nonlinear relationships. Thirdly, the model parameters gamma ($\gamma$) and sig2 ($\sigma^2$) should be an optimal combination within a probable search region. Herein, the optimal combination of gamma ($\gamma$) and sig2 ($\sigma^2$) were settled by a two-step grid search technique. The details of
LS-SVM could be found in the literature (Suykens and Vandewalle, 1999; Liu et al., 2008). All calculations were performed using Matlab software V 7.0 (The Math Works, Natick, MA, USA). The free LS-SVM V 1.5 toolbox (Suykens, Leuven, Belgium) was applied with Matlab V7.0 to develop the LS-SVM models.

After the development of a calibration model, the prediction performance should be assessed, usually by the indices of correlation coefficient of prediction ($R_p$) and root mean square error of prediction (RMSEP). A good model should have a high $R_p$ (much closer to 1) and a low RMSEP (Liu et al., 2008).

3. Results and Discussion

3.1. Spectral features of oilseed rape leaves

The raw and preprocessed spectra of oilseed rape leaves under herbicide stress are shown in Figs. 1a–h. As shown in Fig. 1a, many peaks were observed within the region of 1100–2500 nm, which might be corresponding to chemical compositions with respect to the C–H, N–H or O–H bands (Workman Jr. and Weyer, 2007). The SG, SNV and MSC pre-processing (Figs. 1b–d) retained the main characteristic trends (peaks and valleys) in the spectral curves. There is not a lot of variation between samples and implications for the pre-processing methods of SG, SNV and MSC (Figs. 1b–d). The statistics of aspartic acid of leaf samples in calibration, validation and prediction sets are shown in Table 1. The calibration and validation sets included a large variation of aspartic acid, which was useful to build a stable and robust model.

3.2. The performance of PLS models

Different PLS models were developed using aforementioned pre-processed spectra. Different latent variables (LVs) were extracted and used during the PLS calibration. The prediction set was used to assess the prediction performance of developed models. The prediction results by PLS models are shown in Table 2. Optimal performance was achieved by 1st-Der spectra with $R_p = 0.9789$ and RMSEP = 0.0782. The scatter plots in the prediction set are shown in Fig. 2. A good prediction precision was achieved, but the number of input variables was 700. All 700 wavelengths were too many to be used directly for the development of portable instruments or sensors. Some type of effective wavelength selection procedure should be applied therefore to choose a small number of relevant variables from these 700 wavelengths. Herein, SPA, MC-UVE, RF were performed for such purpose.
Fig. 1. The raw and preprocessed spectra of oilseed rape leaves: (a) Raw; (b) SG; (c) SNV; (d) MSC; (e) 1st-Der; (f) 2nd-Der; (g) De-trending; (h) DOSC.
3.3. EWs selection

In the PLS models, the best spectral pre-processing method was 1st-Der. Hence, the 1st-Der spectra were applied for relevant variable selection. The Raw spectra were also used for relevant variable selection as a comparison. For SPA, the maximum number of selected variables was set to 30, and cross-validation was also applied in the selection process. For MC-UVE, the number of MC sampling was set as 10,000. For RF, the number iteration was set as 10,000. The selected EWs are shown in Table 3. From Table 3, it could be found that some wavelengths were selected similarly both by Raw and 1st-Der spectra. Some of the selected wavelengths were different by different selection methods due to the different selection principles and criterions. The wavelength around 1438 nm was thought to be caused by the first overtone of the N–H stretching vibration in protein (Workman Jr. and Weyer, 2007). The wavelengths of 2022, 2058 and

Table 1. Statistics of aspartic acid content of oilseed rape leaves.

| Set       | Number | Range (mg/100 g DW) | Mean (mg/100 g DW) | Standard deviation(mg/100 g DW) |
|-----------|--------|---------------------|--------------------|---------------------------------|
| Calibration | 124    | 0.926-2.746         | 1.773              | 0.3810                          |
| Validation | 62     | 0.937-2.579         | 1.775              | 0.3803                          |
| Prediction | 62     | 0.932-2.662         | 1.773              | 0.3849                          |

DW: dry matter.

Table 2. Prediction results of aspartic acid by the PLS model with different pre-processing methods.

| Model | Treatment | LV/EW/(γ, σ²) | Calibration | Prediction |
|-------|-----------|----------------|-------------|------------|
|       |           |                | Rc | RMSEC | Rp | RMSEP |
| PLS   | Raw       | 8/700/-        | 0.9715 | 0.0899 | 0.9766 | 0.0824 |
|       | SG        | 7/700/-        | 0.9675 | 0.0956 | 0.9681 | 0.0958 |
|       | SNV       | 5/700/-        | 0.9619 | 0.1037 | 0.9631 | 0.1029 |
|       | MSC       | 5/700/-        | 0.9625 | 0.1030 | 0.9637 | 0.1021 |
|       | 1st-Der   | 6/700/-        | 0.9768 | 0.0813 | 0.9789 | 0.0782 |
|       | 2nd-Der   | 4/700/-        | 0.9882 | 0.0582 | 0.9599 | 0.1111 |
|       | De-trending | 6/700/-      | 0.9687 | 0.0941 | 0.9731 | 0.0881 |
|       | DOSC      | 6/700/-        | 0.9669 | 0.0968 | 0.9680 | 0.0958 |

LV: latent variable in PLS model; EW: effective wavelengths used in the models; (γ, σ²): parameters of LS-SVM.

Rc: correlation coefficient of calibration; Rp: correlation coefficient of prediction; RMSEC: root mean square error of calibration; RMSEP: root mean square error of prediction.
2098 nm might be due to the combinations or combination transitions of N–H stretch, N–H in plane bend, C=O stretch and C–N stretch (Daszykowski et al., 2008). The wavelengths of 2178, 2180, 2232 and 2272 nm might be due to the N–H stretch and N–H in plane bending motion (Cowe et al., 1988). The wavelength of 2308 nm could be related to the stretch and deformation vibrations of the methylene group (Daszykowski et al., 2008). All selected EWs in Raw or 1st-Der spectra were applied as inputs of the MLR, PLS and LS-SVM models. This calibration method was a newly proposed combination calibration method in a previous study (Liu et al., 2008a). The developed calibration models using EWs were utilized for the fast determination of aspartic acid in oilseed rape leaves under herbicide stress.

Table 3. Selected EWs by SPA, MC-UVE and RF.

| Treatment | No. | Selected EWs (nm) |
|-----------|-----|-------------------|
| SPA Raw   | 22  | 2304, 2272, 1410, 2372, 1190, 1730, 2098, 1528, 1438, 2058, 1692, 1104, 1878, 2022, 2234, 2178, 2290, 1344, 2352, 1818, 1994, 1942 |
| 1st-Der   | 17  | 1684, 1950, 2180, 2232, 1298, 1720, 2308, 1534, 1528, 2326, 2096, 2492, 1110, 2442, 1310, 2336, 2276 |
| MC-UVE Raw | 22  | 1444, 1446, 2038, 1442, 2036, 2108, 1448, 2032, 1512, 2110, 1760, 1828, 1440, 2106, 1510, 1504, 1506, 2298, 2034, 1932, 1830, 1436 |
| 1st-Der   | 22  | 1248, 1146, 1430, 1330, 1144, 1328, 1246, 1428, 1660, 1148, 1250, 1714, 1658, 1712, 2284, 1432, 2384, 2382, 1662, 1224, 1716, 2286 |
| RF Raw    | 22  | 1334, 1340, 1828, 1252, 1328, 1140, 1244, 1254, 1326, 1816, 1336, 1804, 1142, 1246, 1830, 2198, 1342, 2200, 1332, 2362, 2202, 2082 |
| 1st-Der   | 26  | 1146, 1714, 1834, 1836, 1256, 1300, 2342, 1154, 1328, 1166, 1330, 1658, 2384, 1470, 1390, 1468, 1660, 2284, 1338, 1824, 1144, 1236, 1388, 1686, 1744, 2344 |

No.: number of selected effective wavelengths.
3.4. Calibration models using EWs

The MLR, PLS and LS-SVM models using EWs selected by SPA, MC-UVE and RF were developed for aspartic acid detection (Liu et al., 2008). The results of MLR, PLS and LS-SVM models using EWs selected by SPA, MC-UVE and RF shown in Table 4 are all satisfactory with $R_c$ and $R_p$ over 0.95. For EWs selected by SPA and MC-UVE, the calibration models using EWs selected from the Raw spectra performed slightly better. The LS-SVM models performed better than the corresponding MLR and PLS models. For EWs selected by RF, the RF-MLR (1st-Der) and RF-PLS (1st-Der) models performed slightly better than the RF-MLR (Raw) and RF-PLS (Raw) models. The RF-LS-SVM (1st-Der) performed slightly better than RF-LS-SVM (Raw). It could be observed from Table 4 that LS-SVM models performed best among all models, and models using EWs selected by SPA performed best among all variable selection methods. SPA-LS-SVM (Raw) obtained the best results with $R_p = 0.9962$ and RMSEP = 0.0339. The scatter plots of the prediction set by SPA-LS-SVM (Raw) are shown in Fig. 3. Comparing Fig. 3 with Fig. 2, the distribution of the

| Model           | Treatment | LV/EW/($\gamma$, $\sigma^2$) | Calibration | Prediction |
|-----------------|-----------|--------------------------------|-------------|------------|
|                 |           |                                | $R_c$ | RMSEC | $R_p$ | RMSEP |
| SPA-MLR         | Raw       | -/22/-                         | 0.9811 | 0.0734 | 0.9833 | 0.0709 |
|                 | 1st-Der   | -/17/-                         | 0.9692 | 0.0934 | 0.9720 | 0.0898 |
| SPA-PLS         | Raw       | 7/22/-                         | 0.9754 | 0.0837 | 0.9747 | 0.0854 |
|                 | 1st-Der   | 5/17/-                         | 0.9703 | 0.0918 | 0.9749 | 0.0860 |
| SPA-LS-SVM      | Raw       | -22/(7.1×10$^4$, 171.6)       | 0.9936 | 0.0428 | 0.9962 | 0.0339 |
|                 | 1st-Der   | -17/(749.0, 427.7)             | 0.9907 | 0.0516 | 0.9871 | 0.0613 |
| MC-UVE-MLR      | Raw       | -/22/-                         | 0.9706 | 0.0914 | 0.9647 | 0.1009 |
|                 | 1st-Der   | -/22/-                         | 0.9682 | 0.0949 | 0.9551 | 0.1145 |
| MC-UVE-PLS      | Raw       | 5/22/-                         | 0.9509 | 0.1174 | 0.9554 | 0.1130 |
|                 | 1st-Der   | 5/22/-                         | 0.9545 | 0.1131 | 0.9516 | 0.1175 |
| MC-UVE-LS-SVM   | Raw       | -22/(143.8, 4.2)               | 0.9968 | 0.0306 | 0.9840 | 0.0715 |
|                 | 1st-Der   | -22/(56.8, 19.0)               | 0.9962 | 0.0336 | 0.9832 | 0.0736 |
| RF-MLR          | Raw       | -/22/-                         | 0.9771 | 0.0807 | 0.9632 | 0.1046 |
|                 | 1st-Der   | -/26/-                         | 0.9872 | 0.0604 | 0.9634 | 0.1038 |
| RF-PLS          | Raw       | 5/22/-                         | 0.9582 | 0.1085 | 0.9569 | 0.1109 |
|                 | 1st-Der   | 6/26-                          | 0.9759 | 0.0828 | 0.9679 | 0.0960 |
| RF-LS-SVM       | Raw       | -26/(9.9×10$^4$, 110.3)       | 0.9903 | 0.0528 | 0.9889 | 0.0569 |
|                 | 1st-Der   | -26/(4.9×10$^4$, 7.5×103)     | 0.9895 | 0.0549 | 0.9730 | 0.0891 |
prediction plots was closer to the regression line in Fig. 3, which also indicated a better prediction performance in Fig. 3.

The models based on EWs selected by SPA, MC-UVE and RF obtained acceptable prediction results as compared with full spectra models. The number of wavelengths reduced at least 96.29% by wavelength selection. The prediction results of calibration model using EWs were similar or better than the full spectra calibration models. This indicated that SPA, MC-UVE and RF were effective method for wavelength selection. These selected EWs would also be important and helpful for the development of a portable instrument, which is essential to achieve field monitoring of oilseed rape growth status and the study of herbicide function mechanism and metabolic pathway in oilseed rape under herbicide stress.

4. Conclusion

After comparing different spectral pre-processing methods (Raw, SG, SNV, MSC, 1st-Der, 2nd-Der, de-trending and DOSC), an optimal PLS (1st-Der) model was obtained for the determination of aspartic acid in oilseed rape leaves under herbicide stress, and the prediction results were $R_p = 0.9789$ and RMSEP = 0.0782. Comparing all linear and nonlinear models (MLR, PLS and LS-SVM) using effective wavelengths extracted by SPA, MC-UVE and RF, the best model was SPA-LS-SVM (Raw) with $R_p = 0.9962$ and RMSEP = 0.0339, which was also the best one in all developed models. The overall results indicated that near infrared spectroscopy integrated with SPA-LS-SVM could be successfully applied for the detection of aspartic acid. The obtained calibration model was helpful for the fast detection of aspartic acid, which provides a short cut to obtain the basic physiological data for the herbicide effects, function mechanism and metabolic pathways in oilseed rape leaves. The selected effective wavelengths would be useful for portable instrument development and the field monitoring of oilseed rape growing status.
Declarations

Author contribution statement

Chu Zhang, Wenwen Kong, Fei Liu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Yong He: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Competing interest statement

The authors declare no conflict of interest.

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Additional information

No additional information is available for this paper.

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