PAPER

Detection of K in soil using time-resolved laser-induced breakdown spectroscopy based on convolutional neural networks

View the article online for updates and enhancements.

Plasma Science and Technology

Detection of K in soil using time-resolved laser-induced breakdown spectroscopy based on convolutional neural networks

Chengxu LU (吕程序)[1], **Bo WANG (王博)**[1,2], **Xunpeng JIANG (姜训鹏)**[3], **Junning ZHANG (张俊宁)**[1], **Kang NIU (牛康)**[1] **and Yanwei YUAN (苑严伟)**[1]

[1] Chinese Academy of Agricultural Mechanization Sciences, Beijing 100083, People's Republic of China
[2] Jiangsu University, Zhenjiang 212013, People's Republic of China
[3] COFCO Feed Co. Ltd, Beijing 100029, People's Republic of China

E-mail: yyw215@163.com

Abstract

One of the technical bottlenecks of traditional laser-induced breakdown spectroscopy (LIBS) is the difficulty in quantitative detection caused by the matrix effect. To troubleshoot this problem, this paper investigated a combination of time-resolved LIBS and convolutional neural networks (CNNs) to improve K determination in soil. The time-resolved LIBS contained the information of both wavelength and time dimension. The spectra of wavelength dimension showed the characteristic emission lines of elements, and those of time dimension presented the plasma decay trend. The one-dimensional data of LIBS intensity from the emission line at 766.49 nm were extracted and correlated with the K concentration, showing a poor correlation of $R^2_c = 0.0967$, which is caused by the matrix effect of heterogeneous soil. For the wavelength dimension, the two-dimensional data of traditional integrated LIBS were extracted and analyzed by an artificial neural network (ANN), showing $R^2_v = 0.6318$ and the root mean square error of validation ($RMSEV$) = 0.6234. For the time dimension, the two-dimensional data of time-decay LIBS were extracted and analyzed by ANN, showing $R^2_v = 0.7366$ and $RMSEV = 0.7855$. These higher determination coefficients reveal that both the non-K emission lines of wavelength dimension and the spectral decay of time dimension could assist in quantitative detection of K. However, due to limited calibration samples, the two-dimensional models presented over-fitting. The three-dimensional data of time-resolved LIBS were analyzed by CNNs, which extracted and integrated the information of both the wavelength and time dimension, showing the $R^2_v = 0.9968$ and $RMSEV = 0.0785$. CNN analysis of time-resolved LIBS is capable of improving the determination of K in soil.

Keywords: quantitative detection, potassium (K), soil, time-resolved laser-induced breakdown spectroscopy (LIBS), convolutional neural networks (CNNs)

(Some figures may appear in colour only in the online journal)

1. Introduction

Soil is the basis for agricultural production and provides essential nutrients for crop growth. When a soil's nutrients cannot meet the crop's needs, they will be applied by fertilizer to increase the yield and enhance the quality of the crop. K is one of the macro-nutrient elements for plants; it contributes to the electrical neutralization of anionic charges, protein synthesis, control of membrane polarization and regulation of the osmotic potential [1]. Thus, the quantitative determination of K is of significant importance to estimate soil nutrient supplying capacity for crop production.

Traditionally, analytical techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [2], inductively coupled plasma mass spectrometry (ICP-MS) [3] and so on, have been used to determine the K concentration of

soil. However, these methods could not meet the precision farming needs of *in situ* and real-time detection. Laser-induced breakdown spectroscopy (LIBS) [4–9] with the advantages of real-time, non-contact, micro-destructive and multi-element, has been researched to determine K in soil.

One-dimensional (1D) data of single characteristic emission lines have been used to determine K in soil. Hussain *et al* employed an emission line of 404.7 nm to analyze the soil collected from a greenhouse, showing a determination coefficient (R^2) of 0.9873 with a precision of around 2% [4]. Pareja *et al* prepared samples from three soils and one fertilizer, and built models with a 766.49 nm line of both LIBS and laser ablation-LIBS (LA-LIBS), presenting R^2 of 0.6656 and 0.8619, respectively. More soil samples of five types were collected and used to build an LA-LIBS model, showing $R^2 = 0.624$ [5]. It was demonstrated that different types of soils were effected by a complex matrix and presented a poor model precision. Meng *et al* mixed KNO_3 with one soil sample and used an emission line of 769.90 nm to quantify, showing a relative error of calibration under 5%. Another sample set with 12 different soil samples of certified reference material (CRM) was collected. A poor relationship between K concentration and spectral intensity was presented [6]. The LIBS model with a single variable is capable of determining K in soil of the simple type. However, for different types of soil with the complex matrix, it is difficult to build a precise model with only 1D emission line data.

More emission lines have been used to build quantitative models of K in the soil. Dong *et al* collected 60 agricultural soil samples and used the ratio of lines of Si at 476.85 nm and K at 766.49 nm to calibrate, showing a K predicted relative standard deviation of 9.26% [7]. Zhang *et al* prepared 13 simulated soil samples and selected a Li line of 812.66 nm as an internal standard. K lines of 766.49 nm and 769.90 nm were used to build the regression curve, showing an R^2 of 0.9337 [8]. Furthermore, two-dimensional (2D) data of traditional LIBS spectra in a region have been developed for a model. Yu *et al* collected five CRM soil samples to build a partial least squares (PLS) model with 338 spectral lines, presenting $R^2 = 0.9179$ and a root mean square error of validation ($RMSEV$) = 0.6134 [9]. Guezenoc *et al* collected 39 agricultural soils and built a PLS model with 97 spectral lines, presenting $R^2 = 0.84$ and $RMSEV = 1.49$ [10]. Models built with multi-variable 2D data of LIBS are capable of quantifying K in agricultural soil and different types of soil.

Compared to the model built with the 1D data of a single emission line, a model with 2D data of multi-variables introduces more information from multi-spectral lines. An abundance of spectral information could assist LIBS quantitative analysis and reduce the effect from the material matrix. Time-resolved spectroscopy is a method to further enrich LIBS information and to extend data dimension [11]. The formation and decay of plasma is a dynamic process, and the radiation intensity changes over time [12]. Time-resolved LIBS is a type of three-dimensional (3D) data, composed by spectra integrated at a set of time windows, and includes both wavelength and time dimension information. Several chemometrics methods, such as independent components

Table 1. CMR soil samples.

Sample No.	K concentration (%)	Soil type	Sample set
1	0.17	Latosols	Calibration
2	0.90	Red soil	
3	1.81	Fluvial sediments	
4	1.89	Loess	
5	2.01	Loess	
6	2.12	Sandy soil	
7	2.35	Fluvial sediments	
8	2.80	Aeolian soils	
9	0.54	Red soil	Validation
10	1.24	Yellow-red soil	
11	1.75	Saline-alkali soil	
12	2.19	Fluvial sediments	

analysis, multivariate curve resolution–alternating least squares etc [11, 13], have been used to mine time-resolved LIBS data. It is possible that further analysis of this 3D data has the potential to improve LIBS quantitative determination.

A convolutional neural network (CNN) is a type of machine learning method, which is inspired by the biological processes of the cat visual cortex. With the advantage of easy training and the capability to deal with both 2D and 3D data, it has been a powerful tool for image classification [14] and video action recognition [15]. Therefore, it was and further has been used to analyze spectroscopic data, such as Raman spectroscopy [16], near infrared spectroscopy [17], hyper spectroscopy [18] and so on. As CNNs present the state of the art for analysis of the transformed data in different orientations and scales, it was considered to adjust the LIBS spectral transformation caused by the matrix effect in this paper.

The aim of this paper is to troubleshoot the LIBS quantitative problem caused by the matrix effect using the method of combining time-resolved LIBS and CNNs. First, a typical 1D emission line was used to correlate with the K concentration to reveal the matrix effect of heterogeneous soil. Then, the 2D data of traditional LIBS and time-decay LIBS were analyzed by an artificial neural network (ANN) to discover the K concentration relationships with wavelength and time dimension spectral information, respectively. Finally, 3D time-resolved LIBS data were analyzed by CNNs to integrate both wavelength and time dimension information and would apply to the K determination of soil.

2. Experimental

2.1. Samples

As shown in table 1, 12 CRM soil samples (National Institute of Metrology, China) with a K concentration of 0.17%–2.80% were collected. To avoid splashing, each sample was placed

Figure 1. The LIBS instrument setup.

into an $\Phi\ 36 \times 5$ mm aluminum cap, and then the top of the cap was smoothed and pressed at 20 MPa for 1 min by a DY-30 tablet machine (Tianjin Keqi High & New technology corporation, China). Twelve samples were separated into two sets by the duplex method [19], resulting in eight samples for the calibration set and four samples for the validation set.

2.2. LIBS spectra collection

The LIBS instrument used in this work is shown in figure 1. A CFR200 Q-Switched Nd:YAG laser (Quantel laser, France) was employed as a light source to induce the plasma. The plasma was collected by an SR-OTP8024 fiber (Andor, UK), delivered to an SR500 Czerny-Turner spectrometer (Andor, UK), and sensed by an Istar intensified charge-coupled detector (Andor, UK). The spectral range was set to 723.62–808.24 nm, with a spectral resolution of 0.08 nm. The delay time between the laser pulse and the signal acquisition varied in the range of 0–98 μs with an interval of 1 μs, and the gate width was set to 1 μs. Each sample was scanned in triplicate.

2.3. Data analysis

All the calculations, analyses and graphics were performed in Matlab R2012b (The Mathworks Inc., USA).

2.3.1. 1D LIBS intensity. A wavelength of 766.64 nm was selected as the K characteristic emission line [5, 7]. The linear correlation was analyzed between the characteristic line intensity and K concentration.

2.3.2. 2D LIBS spectra. For the wavelength dimension, the fourth spectrum of each sample was extracted and analyzed by ANN. For the time dimension, the intensity decay curves were extracted at a wavelength of 766.64 nm and then analyzed by ANN.

2.3.3. 3D time-resolved LIBS. To compress the data and simplify the calculation, the raw time-resolved LIBS data were calculated with principal component analysis (PCA) using PLS Toolbox 6.7 (Eigenvector Research Inc., USA).

The size of the compressed matrix was set according to principal components (PCs) capturing 100.00% spectral variance of sample 1 [20]. The spectral matrix was optimized to 20×20; in other words, the spectral matrix was compressed to 20 spectral PCs and the first 20 delay time. The compressed data were pretreated by normalization to standardize the data, and then input to the CNNs.

The CNNs were programmed [21] as shown in figure 2. Convolutional kernels were optimized with 3×3, 5×5, 7×7, 9×9, 11×11 and 13×13, then set to 7×7 and initialized [22]. The rectified linear unit (ReLU) [23] was used as the activation function, and defined as:

$$f(x) = \begin{cases} x, & \text{if } x > 0 \\ ax, & \text{otherwise} \end{cases} \tag{1}$$

where x was the convoluted input data. A convolutional layer was expressed as:

$$y^j = f\left(\sum_i k^{ij} * x^j + b^j\right) \tag{2}$$

where x^j and y^j were the *i*th convoluted input and output data, k^{ij} and b^j were the convolutional kernel and bias parameter, respectively. In the convolution layer, 20 feature maps of 14×14 were obtained, and then processed by mean-pooling, which adopted the average value from each neuron cluster. The output of the pooling layer was rasterized and fully connected. The backpropagation was used to optimize k and b to minimize the error between the fully connected output layer and reference value. The CNNs were trained with an iteration of 3000 times.

The correlation coefficient (R), R^2 and root mean square error (RMSE) were used to evaluate the model performance.

3. Results and discussion

3.1. LIBS spectra

The time-resolved LIBS spectra of soil sample 1 are described in figure 3. For the wavelength dimension, seven main peaks and several small peaks were found. Based on the NIST atomic spectra database, the main peaks originated from the atomic lines of 742.36 nm (N), 744.23 nm (N), 746.83 nm (N), 766.49 nm (K), 769.90 nm (K), 777.42 nm (O) and 795.54 nm (K). For the time dimension, the peak intensities decreased with time. The first spectrum (delay time of 0 μs) presented a high baseline from continuum emission. Self-reversal was found at the N line (746.86 nm) of the first spectrum (delay time of 0 μs) and O line (777.42 nm) of the first to third spectra (delay of 0, 1 and 2 μs).

3.2. Analysis of 1D LIBS intensity

As shown in figure 4, the 1D LIBS intensity at 766.49 nm regressed with the K concentration, resulting in $R^2_c = 0.0967$, *RMSEC* (root mean square error of calibration) $= 0.7447$, $R^2_v = 0.2700$ and *RMSEV* $= 0.6762$. This low R^2_c demonstrated that only the 1D LIBS peak intensity could not
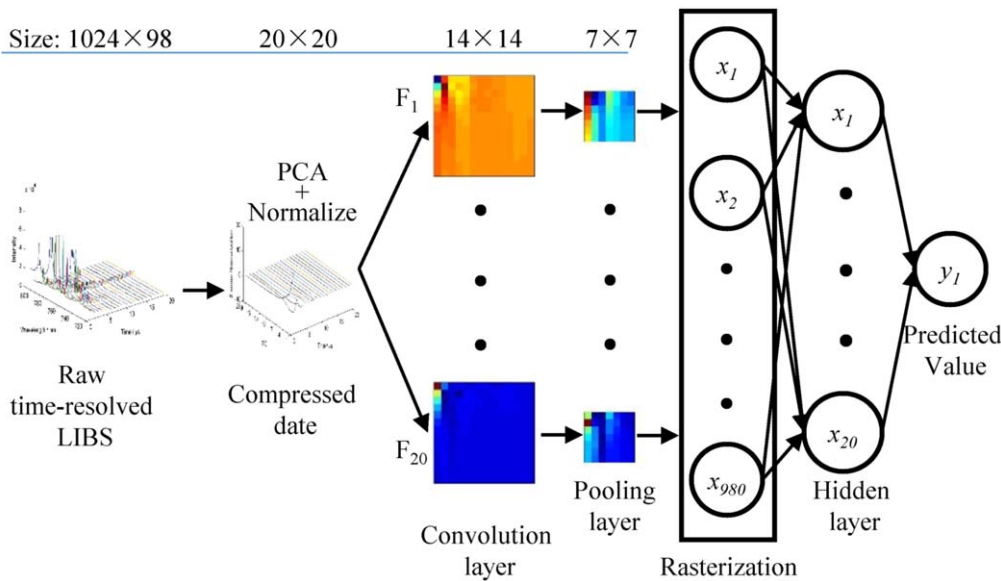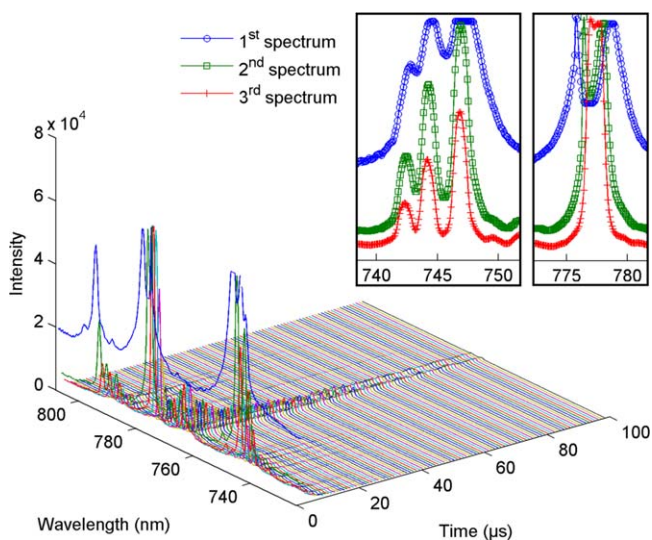
Figure 2. The structure of CNNs.

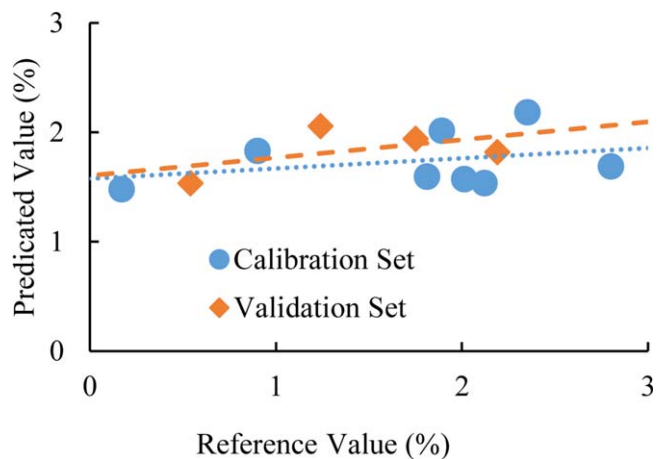**Figure 3.** The time-resolved LIBS of sample 1.

Figure 4. The regression result of the 1D data.

quantify the K in the soil. The samples used in this paper showed a high heterogeneity, which were collected from eight provinces of China and included eight different types. This led to a strong matrix effect [6] from both the chemical composition and physical properties [12] of the soil. It was difficult to build a K quantitative model using only LIBS peak intensity, especially for predicting different types of soil.

3.3. Analysis of 2D LIBS spectra

3.3.1. Spectra of the wavelength dimension. As the first three time-resolved spectra presented self-reversal at the emission lines of O and N, the fourth spectrum of time-resolved LIBS (figure 5(a)) was used as the integrated spectra. The fourth spectrum was collected with a time delay of 3 μs and a width of 1 μs; in other words, it was the integration of the time window of 3–4 μs. The ANN result of the fourth spectrum is presented in figure 5(b), showing $R^2_c = 1.0000$, $RMSEC = 0.0000$, $R^2_v = 0.6318$ and $RMSEV = 0.6234$. As only a limited eight samples were used to calibrate, the model performed over-fitting with significantly better results of calibration than that of independent validation. However, compared to the 1D LIBS intensity, the 2D data of the wavelength dimension performed better. In total, 1024 variables were employed in the model; the peaks of 766.49, 769.90 and 795.54 nm originated from K, and other variables originated from non-K. The non-K emission lines responded to the sample chemical component, assisted revision of the K peak transformation caused by the matrix effect, and still contributed to the K model.

3.3.2. Spectra of the time dimension. The plasma decay at the K emission line of 766.49 nm is shown in figure 6(a). During plasma decay, the intensity of K decreased at the beginning of ignition, and then turned to level off. The ANN result of the time-decay LIBS and K concentration is presented in figure 6(b), showing $R^2_c = 1.0000$,
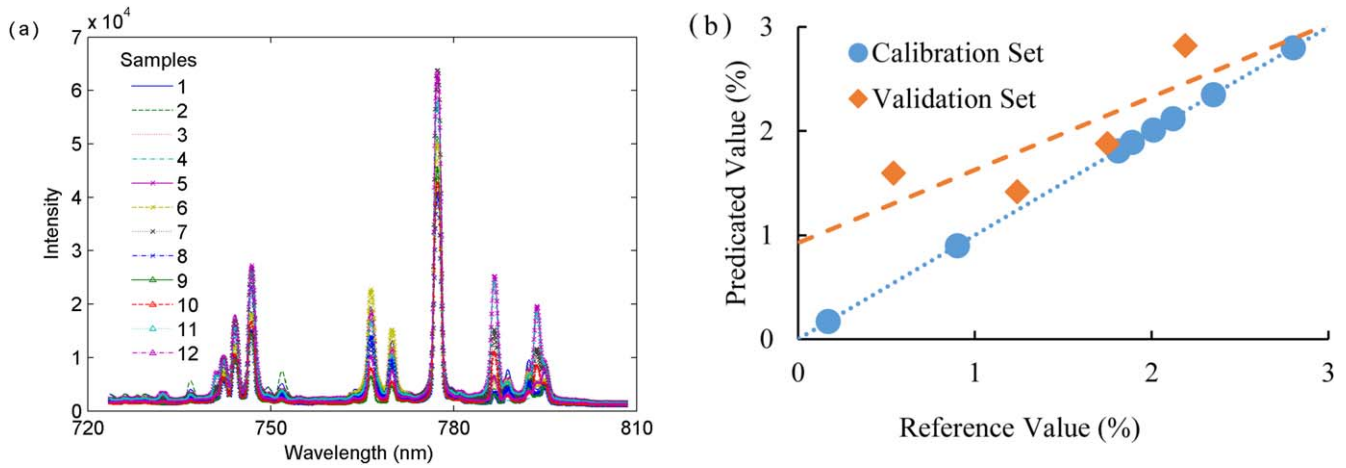
Figure 5. (a) The LIBS integrated at 3–4 μs, (b) The ANN result of integrated LIBS.
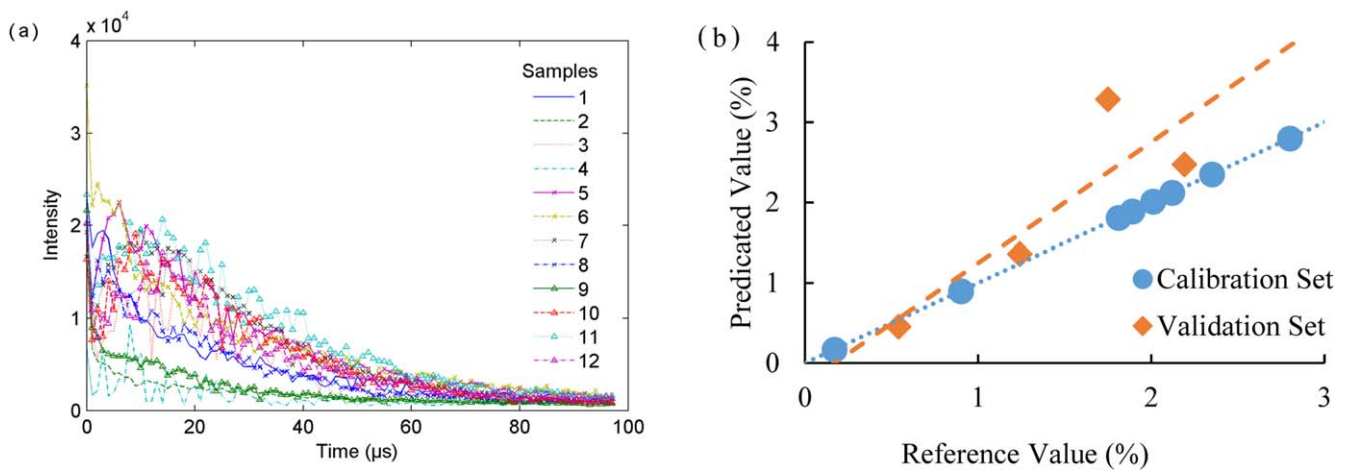

Figure 6. (a) The time-decay LIBS of 766.49 nm, (b) The ANN result of time-decay LIBS.
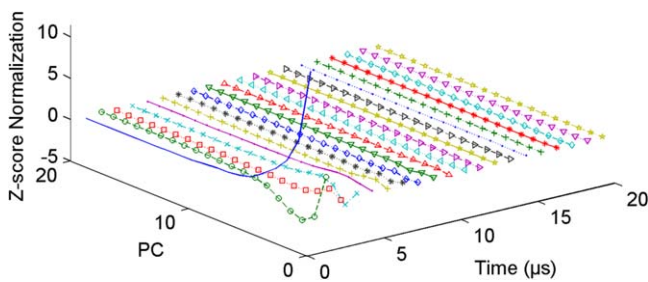

Figure 7. Normalized PCA scores of sample 1 time-resolved LIBS.

$RMSEC = 0.0000$, $R^2_v = 0.7366$ and $RMSEV = 0.7855$. The model performed over-fitting also. Compared to the 1D data of the LIBS intensity integrated at one time window (figure 4), the time-decay LIBS model presented a significantly higher correlation with concentration. This demonstrated that LIBS information at the time dimension could assist quantitative detection of K in soil.

3.4. Analysis of 3D time-resolved LIBS

The normalized PCA scores of the time-resolved LIBS (figure 3) of sample 1 are shown in figure 7. A significant
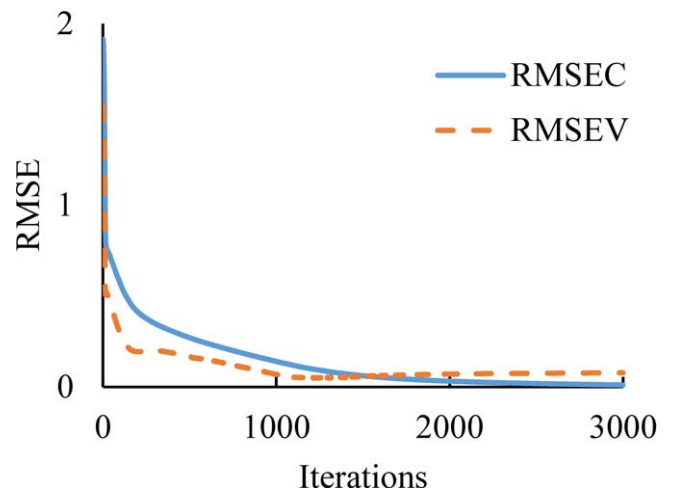

Figure 8. The CNNs iteration results.

score change was found at the PCs of 1–5 and the time delay of 0–3 μs. The matrix of 20 × 20 was used as the input layer of the CNNs, resulting in 99.6% data compression. As shown in figure 8, the CNNs iteration results of *RMSEC* and *RMSEV* plummeted at about the first 200 iterations, and then gradually
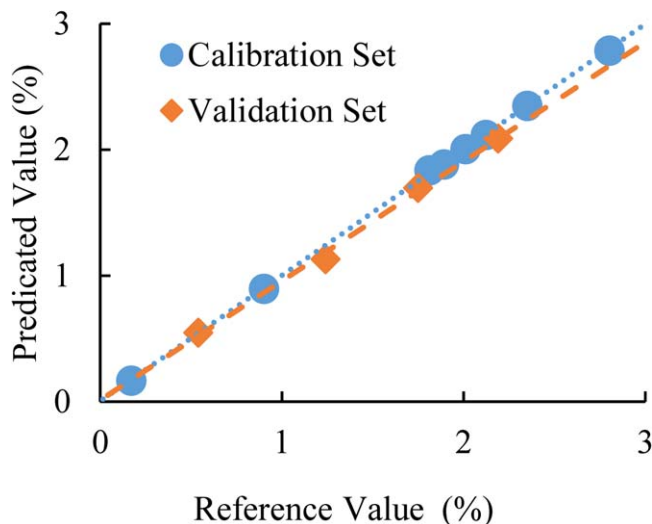
Figure 9. The CNNs model result.

decreased. The *RMSEC* consistently decreased to 3000 iterations, indicating the model optimization capability of backpropagation. While the *RMSEV* turned to level off after 1150 iterations, the iteration reached the optimized predictive result for independent external validation.

The CNNs model result is shown in figure 9, resulting in $R^2_c = 0.9998$, $RMSEC = 0.0114$, $R^2_v = 0.9968$ and $RMSEV = 0.0785$. The predicted result was much better than that of the 1D and 2D data. The time-resolved LIBS contained both wavelength and time dimension information, and this information was extracted and integrated by the CNNs. It is demonstrated that CNN analysis of time-resolved LIBS spectra is capable of improving the determination of the K concentration in soil.

4. Conclusions

The 1D data were extracted from the LIBS intensity at an emission line of 766.49 nm, and then correlated with the K concentration. A poor correlation of $R^2_c = 0.0967$ was found, revealing the matrix effect of heterogeneous soil. This demonstrated that it was difficult to build a K quantitative model using only LIBS peak intensity. The 2D wavelength and time dimension data were extracted and analyzed by ANN, resulting in $R^2_v = 0.6318$, $RMSEV = 0.6234$ and $R^2_v = 0.7366$, $RMSEV = 0.7855$, respectively. Due to limited calibration sample numbers, the models performed overfitting. However, the model of wavelength dimension indicated that non-K emission lines could assist in the revision of the K emission line transformation caused by the matrix effect, and the model of time dimension demonstrated that time-resolved LIBS information could assist in the quantitative detection of K in the soil. The 3D data of time-resolved

LIBS were analyzed by CNNs, showing $R^2_v = 0.9968$ and $RMSEV = 0.0785$. The CNNs extracted and integrated the information of both the wavelength and time dimension, which was more helpful in improving the model performance than that of traditional 2D LIBS. CNNs analysis of time-resolved LIBS spectra is capable of improving the determination of K in soil.

References

[1] Chérel I *et al* 2014 *J. Exp. Bot.* **65** 833
[2] ISO 2009 Soil quality—Determination of trace elements in extracts of soil by ICP –AES: ISO 22036 2008 https://iso.org/standard/40653.html
[3] ISO 2013 Soil quality—Determination of trace elements using ICP-MS: ISO/TS 16965 2013 https://iso.org/standard/58056.html
[4] Hussain T *et al* 2007 *Environ. Monit. Assess.* **124** 131
[5] Pareja J *et al* 2013 *Appl. Opt.* **52** 2470
[6] Meng D S *et al* 2014 *Chin. J. Lasers* **41** 0515003 (in Chinese)
[7] Dong D M *et al* 2013 *Spectrosc. Spectr. Anal.* **33** 785 (in Chinese)
[8] Zhang J N *et al* 2014 *Trans. Chin. Soc. Agric. Mach.* **45** 294 (in Chinese)
[9] Yu K *et al* 2017 *Spectrosc. Spectr. Anal.* **37** 2879 (in Chinese)
[10] Guezenoc J *et al* 2017 *Spectrochim. Acta Part* B **134** 6
[11] El Rakwe M *et al* 2017 *J. Chemom.* **31** e2869
[12] Noll R 2012 *Laser-Induced Breakdown Spectroscopy* (Berlin, Heidelberg: Springer)
[13] Bredice F *et al* 2017 *Spectrochim. Acta Part* B **135** 48
[14] Rawat W and Wang Z H 2017 *Neur. Comput.* **29** 2352
[15] Yao G L, Lei T and Zhong J D 2018 *Patt. Recognit. Lett.* (https://doi.org/10.1016/j.patrec.2018.05.018)
[16] Liu J C *et al* 2017 *Analyst* **142** 4067
[17] Hiwa S *et al* 2016 *Comput. Intell. Neurosci.* **2016** 1841945
[18] Windrim L *et al* 2017 *IEEE Trans. Geosci. Remote Sens.* **56** 2798
[19] Snee R D 1977 *Technometrics* **19** 415
[20] Wang C *et al* 2018 *Spectrosc. Spectr. Anal.* **38** 36 (in Chinese)
[21] Kim P 2017 *MATLAB Deep Learning: with Machine Learning, Neural Networks and Artificial Intelligence* (Berkeley, CA: Springer)
[22] Glotot X and Bengio Y 2010 Understanding the difficulty of training deep feedforward neural networks *Proc. of the 13th Int. Conf. on Artificial Intelligence and Statistics* (Chia Laguna Resort, Sardinia, Italy: AISTATS)
[23] Maas A L, Hannun A Y and Ng A Y 2013 Rectifier nonlinearities improve neural network acoustic models *Proc. of the 30th Int. Conf. on Machine Learning Workshop on Deep Learning* (Atlanta, GA, USA: ICML)