Near infrared spectrometry of humic acid content in fertilizers at different levels of granularity

Xue Gong, Yuhuan Li¹, Yue Wang, Ruiyan Wang, Xiujie Yuan
Shandong Agricultural University.

¹ Email: yuhuan@sdau.edu.cn

Abstract. 【Objectives】 The adaptability of generally sampling tests and traditional method of chemometrics has trended to be more and more fragile in modern chemical enterprises which products chemical components required to be quickly measured with higher precision. Therefore it is a challenge to quickly and exactly calculate the humic acid contents in fertilizer industry while giving up traditional methodology. But it is possible currently that the combination of modern near-infrared spectroscopy and stoichiometry will become an effective means. 【Methods】 There were 74 samples randomly selected from humic acid raw materials, and strictly grading in four classes for each sample as 0.55mm, 0.25mm, 0.18mm, 0.15mm and exactly determining the humic acid content In light of the national criterion (GB/T11957-2001), and precisely surveying the near-infrared absorption spectra (NIRAS) data for 296 samples with the NicoletTMiNTM10 ft-ir spectrometer. So that the mathematical model was established using the 64 by Classical Least Square method (CLS), and the other 10 were verified. 【Results】 The result of the model verification shows that hyperspectral model has a good predictive effect on the fertilizer humic acid content. The model's coefficients of determination are all above 0.75. The relative errors are all below 0.35. The lowest RMSEP is 1.15. And the correlation coefficient can reach 0.812. 【Conclusions】 Finally the results show that the use of hyperspectral model can predict the humic acid content in humic acid fertilizers effectively. The powdery humic acid determination has overall good prediction effect based on CLS and NIRAS data, and the prediction precision is influenced by particle size; the finer grain diameter is, the higher the precision of the model. This study will provide the technical support for quick sampling of humic acid raw materials.

1. Introduction
Humic acid is a natural macromolecular substance which widely existing in soil organic matter, peat, lignite, weathered coal and marine sediments [1]. Promoting the growth of crops is one of the function of humid acid, but itself does not dissolve in water, can't be absorbed by crops directly. Therefore many kinds of humic acid fertilizers arise, like ammonium humate, potassium humate, humic acid compound fertilizer and so on [2]. The utilization rate of chemical fertilizers in China is far lower than that of developed countries [3]. Through researches, it has been found that humic acid fertilizers effectively promote the absorption of nitrogen, phosphorus, potassium and various trace elements in crops [4], and at the same time effectively promote the soil condition, the microbial activity and crop resistance, thereby decreasing the utilization of chemical fertilizers in crops. Previous studies were focused on optimizing the extraction process of humic acid. For example, D. Garcia [5] improved the raw materials required for the extraction of humic acid, and Jiang Chong-ju[6] improved the extraction conditions of humic acid. As for the improvement of humic acid fertilizers, like researches on
compound humic acid fertilizers by He Ping[7] and humic acid liquid foliar fertilizers by Zhou Chao[8].

With the development of the economy and the promotion of policies, at the same time, in order to improve the economic benefits of fertilizer production, the relevant government departments have carried out large-scale capital investment in soil testing and formula fertilization. However, under the influence of various factors, most of the funds are mainly used to update the soil and fertilizer testing equipment and improve the working environment of the soil testing department [9], and pay less attention to the innovation of soil fertilizer testing methods. However, the traditional separation and determination of humic acid in soils and fertilizers are time-consuming, labor-intensive and high cost, which is particularly unfavorable to the inspection of humic acid fertilizer products in the production line. Near-infrared hyperspectral analysis technology can be used for qualitative and quantitative analysis of the sample according to the spectral characteristics. The measurement process is simple and fast. In recent years, near-infrared hyperspectral analysis technology has been widely used in various directions, such as tracking organic carbon in rocks [10], qualitative analysis of rice seed mutants [11] and coffee beans [12], quantitative analysis of the pigment content in leaves [13] and extent of damage to blueberry [14], etc. However, near-infrared hyperspectral analysis techniques for the study of humic acid are mostly the determination of the humic acid evolution in the natural environment and content of humic acid, as well as the application of humic acid fertilizers. However, studies on fertilizer have not been contented testing for humic acid. The purpose of this paper is to establish a mathematical model of the chemically measured humic acid content and the near-infrared spectrum of the fertilizer measured by the instrument. Simultaneously, the effect of different particle sizes on the accuracy of the model is analyzed to provide the technical support for rapid determination of humic acid content in fertilizers and rapid fertilizer inspection.

2. Materials and method

2.1. Data Sources

2.1.1. Determination of humic acid content. The object of this study was the humic acid fertilizer sample of Shandong Agricultural University Fertilizer Technology Co., Ltd. Seventy four samples of different products and different batches were randomly selected. Residues were used to determine the humic acid content in the fertilizer. Each sample was repeatedly measured 3 times, and the average value was taken as the humic acid content value of the sample.

2.1.2. Fertilizer Spectrometry. Fertilizer spectra were determined by NicoletTMiNTM10 FT-IR spectrometer of Thermo Fisher with a spectral range of 399-4000 cm⁻¹ (2.5–25 μm) and a resolution of 0.4 cm⁻¹. All the samples were passed through the sieves of 550μm, 250μm, 180μm, and 150μm to obtain four different particle size samples of 30-mesh, 60-mesh, 80-mesh, 100-mesh, respectively. Using the spectrometer measured a total of 296 samples for different particle sizes of different fertilizers. Before starting measurement, the instrument was warmed up for one hour. The near infrared spectral data of samples were directly collected without any treatment. Each measurement was scanned 16 times. Each sample was measured 3 times and the average value was taken as the spectral value of the sample.

2.2. Sample set division and data pretreatment

Four different kinds of granularity were modeled separately. In the 74 samples for each granularity, 64 were randomly selected as the calibration set, and the remaining 10 were used as validation set. Spectral pretreatment can reduce noise in the environment and eliminate spectral scattering and translation. Therefore, this study used TQ Analyst EZ Edition and SPSS software to perform multi-signal calibration [15] and first derivative [16] on spectral data.
2.3. Model establishment and testing
The mathematical model was established using the classical least square method (CLS) in the TQ analyst EZ Edition analysis software. The classical least squares method is to use m observations to obtain the most reliable value of n parameters and m observations under the principle of minimum sum of squared errors. The formula is as follows:

\[ y_i = b_0 + b_1x_{i1} + b_2x_{i2} + \cdots + b_mx_{im} + \epsilon_i (i = 1, 2, \cdots, n) \] (1)

Then use the determination coefficient (R²) to evaluate the fitting effect of the humic acid content and each characteristic spectral parameter. Use the root mean square error of prediction (RMSEP) and the relative error (RE) to evaluate the estimation accuracy and capability of the model. Use correlation coefficient to verify the correlation between the two variables. The above calculations are implemented by Excel and TQ Analyst EZ Edition analysis software.

3. Results and analysis

3.1. Characteristics of humic acid content in fertilizer
The humic acid content statistics in the fertilizer, Table 1 shows that fluctuation ranges of the calibration set and the verification set are 21.35-34.92 and 23.54-31.11, the average are 27.006 and 27.891, and the coefficient of variation are 9.65% and 9.38%. In short, the selected sample has a good representation.

| Statistical parameter | Sample number | Minimum (%) | Maximum (%) | Mean (%) | Standard deviation | Coefficient of variation |
|-----------------------|---------------|-------------|-------------|----------|--------------------|-------------------------|
| Calibration set       | 64            | 21.35       | 34.92       | 27.00    | 2.608              | 9.65                    |
| Testing set           | 10            | 23.54       | 31.11       | 27.89    | 2.618              | 9.38                    |

3.2. Establishment and evaluation of models under different levels of granularity
The pre-processed NIR spectra and humic acid content of each granularity humic acid fertilizer were modeled by the classical least squares method, 64 samples be randomly selected for the calibration set and then validated using the remaining 10 samples. According to the determination coefficient, relative error, root mean square error of prediction and correlation coefficient of the model, the optimal particle size level for humic acid content modelling prediction was selected. Table 2 shows that, in the different particle size humic acid prediction models, R² reach above 0.75, RE are between 0.1-0.35, RMSEP are all less than 3, and the correlation coefficient are between 0.1-0.85. Although the accuracy of modelling differs depending on the granularity, all four models have good predictive results.

Comparing the mathematical models under the four particle sizes, with the decrease of fertilizer particle size, the accuracy of modelling gradually becomes larger. For the 0.15mm humic acid fertilizer model, the determination coefficients of the calibration set and verification set are 0.979 and 0.895, which is the maximum value among the four models; the relative errors are 0.300 and 0.121, which is the smallest of the four models; the root mean square error of prediction is 1.15, which is the minimum value and the correlation coefficient is 0.812, which is the maximum value. As can be seen, the 0.15mm humic acid fertilizer samples have the highest modelling accuracy. Followed by the 0.18mm humic acid model, except for the relative error of the calibration set, its values were only inferior to 0.15mm humic acid fertilizer. For the 0.18mm humic acid fertilizer model, its other values are the third, except for the relative error of the calibration set and the determination coefficient of the verification set. As for the 0.6mm humic acid model, except for the validation set determination coefficient of 0.899, which higher than other granularity, the rest are the worst. It can be concluded
that the prediction accuracy of the model decreases with the increase of the fertilizer grain size and it is in the order 0.15mm > 0.18mm > 0.25mm > 0.6mm.

**Table 2.** Comparison of accuracy of verification and correction set models at different levels of granularity.

| Junior archivist (mm) | Calibration set | Testing set | Root mean square error of prediction (RMSEP) | Correlation coefficient |
|-----------------------|-----------------|-------------|---------------------------------------------|------------------------|
|                       | Determination coefficient (R²) | Relative error (RE) | Determination coefficient (R²) | Relative error (RE) |
| 0.60                  | 0.789           | 0.340       | 0.899                                      | 0.207                  | 2.69 | 0.151 |
| 0.25                  | 0.790           | 0.302       | 0.884                                      | 0.136                  | 1.35 | 0.533 |
| 0.18                  | 0.957           | 0.332       | 0.893                                      | 0.122                  | 1.28 | 0.755 |
| 0.15                  | 0.979           | 0.300       | 0.895                                      | 0.121                  | 1.15 | 0.812 |

Comparing the degree of fit of the humic acid content prediction model at the four particle sizes, figure 1 shows that the fitting degree of 0.15mm humic acid fertilizer model is the best, followed by 0.18mm. The 0.6mm humic acid prediction model has the most discrete data points of the calibration set and validation set, and it has the worst fitting degree.

**Figure 1.** The fitting degree of humic acid content obtained by the chemical and method under different granularity.
4. Conclusions
In this study 74 samples of humic acid fertilizers randomly selected as data sources, starting from the data of measured fertilizer spectrum and humic acid content, and then using the near-infrared absorption spectra of fertilizers at four different particle sizes after multiplicative signal correction and first-order derivative processing constructed four models of 0.6mm, 0.25mm, 0.18mm and 0.15mm by the classical least squares method to estimating the optimal fertilizer particle size for the model. The conclusions of the study are as follows:

(1) Near-infrared spectroscopy can be used to predict humic acid content in fertilizers. The determination coefficients of the models are all greater than 0.75, indicating that the accuracy of the model is high. The relative error of the models are less than 0.35, the RMSEP lower than 1.15, and the correlation coefficient be 0.815 at the maximum, indicating that the prediction result of the model is precise. This can change the method of sampling and chemical measurement humic acid fertilizers in factory production. The later method is not only inefficient, but also costly, and there is a phenomenon of missed detection. The use of near-infrared spectroscopy to test the humic acid content in fertilizer can effectively save manpower, material resources and time, and achieve the qualified inspection of fertilizer humic acid content on the production line.

(2) The smaller the particle size of the humic acid fertilizer is, the higher the accuracy of its modeling prediction. The fertilizer samples in this study were ground into 4 different particle sizes by different sieves, and making the modeling predictions separately. The results showed that the smaller the particle size of fertilizer samples, the higher the precision of modeling (0.15mm > 0.18mm > 0.25mm > 0.6mm). This conclusion can be applied not only to fertilizers but also all the solid samples. Thus in the future research, solid samples can be ground more precisely to improve the accuracy of the spectral inversion model.

(3) In the increasingly fierce economic competition, the quality of fertilizers, especially the quality of new humic acid fertilizers, has a significant impact on trade volume and market sales. Inefficient quality inspections affect production efficiency and increase costs. Using the near-infrared spectroscopy predictive model to assess the humic acid content in the fertilizer, which can achieve real-time quality inspection and greatly improve the efficiency as well as increase revenue while ensuring product quality.

Acknowledgement
Shandong Province Major Science and Technology Innovation Project(2017GXGC0306);
Funds of Shandong “Double Tops” Program(SYL2017XTTD02);
Shandong Key Research and Development Project(2015GNC110010)

References
[1] Romero E, Plaza C, Senesi N, et al. 2007 Humic acid-like fractions in raw and vermicomposted winery and distillery wastes [J] Geoderma 139(3-4) 397-406
[2] Chen XJ 2017 Advances in production and application of humic acid [J] Modern Salt and Chemical Industry 44(05) 1-3+10
[3] Shi B,Zhang WX 2015 Role of Humic Acid in Agricultural Production and Soil Remediation Field and Proposal [J] Chemical Fertilizer Industry 42(03) 86-89
[4] LIU XM , ZHANG FD, et al. 2005 N , P and K adsorption and desorption characteristics of humic acids made from the airslake-coal [J] Journal of Plant Nutrition and Fertilizers 05 641-646
[5] Garcia JC D,Abad M 1996 A comparison between alkaline and decomplexing reagents to extract humic acid from low rank coals [J] Fuel Processing Technology 48 51-60
[6] Jiang CJ, Liu DQ et al. 1997 Studies on degradation of peat under pressure [J] Journal of Natural Science of Heilongjiang University 02 109-112
[7] He P, Yang J, et al. 1997 Effects of humic acid compound fertilizer on tomato yield, quality and physical activity [J] Chinese Journal of Soil Science 06 38-40
[8] Zhou C, Zhou CY, et al. 2013 Effects of humic acid liquid foliar fertilizer on yield and quality of greenhouse watermelon [J] Heilongjiang Agricultural Sciences 09 36-38

[9] Gong Ning, Deng Fan, Li Guoliang, et al. 2012 Analysis of Soil Fertilizer Detection Technology[J] Beijing Agriculture 33

[10] Pisapia C, Jamme F, Duponchel L, et al. 2018 Tracking hidden organic carbon in rocks using chemometrics and hyperspectral imaging [J] Scientific Reports 8(2393)

[11] Feng X, Peng C, Chen Y, et al. 2017 Discrimination of CRISPR/Cas9-induced mutants of rice seeds using near-infrared hyperspectral imaging [J] Sci Rep 7(1)

[12] Zhang C, Liu F, He Y 2018 Identification of coffee bean varieties using hyperspectral imaging: influence of preprocessing methods and pixel-wise spectra analysis [J] Scientific Reports 8(1)

[13] Jiang Y, Li C Y, Fumiomi Takeda. Nondestructive Detection and Quantification of Blueberry Bruising using Near-infrared (NIR) Hyperspectral Reflectance Imaging:[J]. Scientific Reports, 2016, 6:35679.

[14] Yu J, Li C, Fumiomi T 2016 Nondestructive Detection and Quantification of Blueberry Bruising using Near-infrared (NIR) Hyperspectral Reflectance Imaging [J] Scientific Reports 6 35679

[15] Afseth N K, Kohler A 2012 Extended multiplicative signal correction in vibrational spectroscopy, a tutorial [J] Chemometrics & Intelligent Laboratory Systems 117(6) 92-99

[16] Luo JW, Ying K, Bai J 2005 Savitzky-Golay smoothing and differentiation filter for even number data Signal Processing 85 1429–1434