STUDY ON DETECTION TECHNOLOGY OF PESTICIDE RESIDUES IN VEGETABLES BASED ON NIR

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Abstract: A quantitative technology based on near infrared spectroscopy (NIR) is proposed to detect pesticide (chlorpyrifos) residues in vegetables in the paper. There are three groups of samples (totally 100 unit, concentration from 0.1mg/kg to 4mg/kg) used in the experiment. The first group sample is confected to simulate vegetable juice to validate feasibility of the NIR quantitative method. As shown in this work, the first NIR model has good indexes (R2 is 0.9807, RMSEP is 0.149). Next the second group sample is confected by adding material standards of 1 mg/ml of chlorpyrifos to spinage juice. The second NIR model also has good performance (R2 is 0.9858, RMSEP is 0.207). The third group sample is confected as the second group to validate repeatability of the detection method based on NIR. The third model is also excellent (R2 is 0.9986, RMSEP is 0.0485). The exploratory experiment results indicate the detection technology of pesticide residue in vegetables based on NIR is feasible in the given conditions. But supposed to the natural vegetable samples that include pesticide residue, the method should to be validated more.

Keywords: NIR, Pesticide Residue, Detection, Spinage

1. INTRODUCTION

The invention and use of pesticides has greatly enhanced the crop yield. However, with the widely and unreasonable use of pesticide the negative impact is increasingly exposed, especially poisoning incidents occur from time to time caused by pesticide residues in vegetables. The detection technology of pesticide residues gets great attention. At present there are some traditional chemical method to detect pesticide residues, such as GC，PLC and CG-MS (Wang, et al, 2006). But these methods are time-consuming and complex. Otherwise chemical methods need consume chemical and destroy the estimate sample. So it's unfit for the national supervise department to execute the inspect task locally.

Near infrared spectrometry is fast developed after ninety in twentieth century in China. The NIR-based (Near Infrared Spectroscopy analysis) technology is recommended for agricultural products detection because it is a fast, lossless and sustainable technology. At present, Pierre Billeen had been using near-infrared detection of pesticides used in seed dressing, and achieved good results (Pierre, et al, 2000). Wen-Xiu Li, such as the use of high pesticide residues in vegetables dichlorvos trichlorfon and the infrared absorption of solvent juice, vegetables directly on the pesticide residue was detected (LI, et al, 2004). Xiang-Yang Zhou, analyzed a variety of vegetable samples near-infrared spectra of the differences in the use of phosphorus-containing group characteristic absorption frequency of the area to identify, and GC-MS method than the right, made with the differential effects (ZHOU ,et al, 2004).

Pesticide residues detection belongs to trace detection. This paper does exploratory studies about quantitative detection technology of pesticide (chlorpyrifos) residues in vegetables based on near infrared Spectroscopy.

2. THEROY

Near-infrared is the electromagnetic wave between the middle-infrared and visible. Its wavelength range is between 800nm to 2500nm.

Near infrared spectroscopy is the absorption spectrum which is mainly obtained by organic molecules hydrogen group (C-H, N-H, O-H, etc.) stretching at all levels and frequency of these groups of stretching and bending of the frequency of vibration. The spectrum of areas include almost all of the hydrogen-containing organic compounds in the group, contains elements of the structure, composition status, and other information. The amount of information is extremely rich, so as to near-infrared spectral analysis of quantitative samples of the physical nature and chemical composition may be provided.

There are many kinds of pesticide are widely used in China, especially organophosphorus pesticides. Chlorpyrifos is one kind of organophosphorus and it is always detected in leaf vegetable higher than national standard. The Molecular formula of chlorpyrifos is $C_9H_{11}Cl_3NO_3PS$ including hydrogen group, which provide the theoretical basis for Near Infrared Spectroscopy analysis.

3. EXPERIMENT

3.1 Sample preparation

There are three group of samples designed in the experiment listed in table 1. The background solution of first group is simulation of pesticide residues in samples of vegetables. The components are includes sugar, Vitamin C and drinking water mixed solution. The samples with different pesticide residues can be obtained by adding material standards of 1 mg/ml of chlorpyrifos according to design requirements.

To approach natural samples the background solution of the second and third group is spinage juice. The spinage purchased from the supermarket is Organic vegetables without pesticide residues. The spinage juice is prepared in the Chinese Academy of Agricultural Sciences. The samples with different pesticide residues can be obtained like the first group.

Table 1. Sample preparation

Group Label	Preparation time	Background Solution	Range of Concentration (mg/kg)	Number of Sample
1	2007-12-11	simulation vegetable juice	0.1-3	30
2	2008-03-07	spinage juice	0.1-4	35
3	2008-05-07	spinage juice	0.1-4	35

3.2 Spectral data

The spectrums of the first group are collected by fiber Optic transmission from 12500 to 4000 cm^{-1} in 8 cm^{-1} on MPA spectrometer with the liquid fiber probe of 2 m, the wavelength path of 1 mm. The spectrums of the second and third group are collected on MATRIX-F spectrometer. The other parameters are same. Spectrum acquisition and analysis software used OPUS5.0.

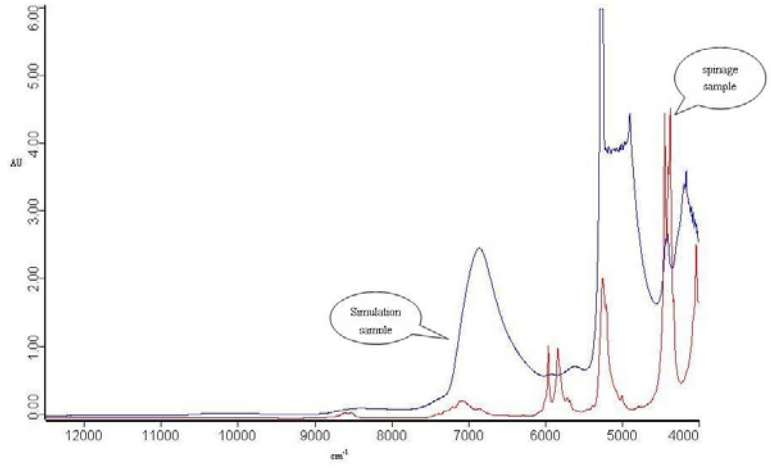

Fig.1: 2 unit spectrums

4. RESULTS AND DISCUSSION

According to the concentration difference, the sample set is divided to train set and test set. The number of the train set and test set is approximately 3. The result lists in the table 2.

From the table 2 the NIR model built by simulation samples is good. The second NIR model built on the natural spinage juice samples also has good performance. The third model is built based on the third group samples to validate the last model's reliability. The result is also satisfied.

Table 2. NIR index of 3 groups of samples

Group Label	Train set	Test set	R^2	RMSECV	RMSEP
1	23	7	0.9807	0.123	0.149
2	27	8	0.9858	0.154	0.207
3	27	8	0.9986	0.0437	0.0485

From the table 2 the NIR model built by simulation samples is good. The second NIR model built on the natural spinage juice samples also has good performance. The third model is built based on the third group samples to validate the last model's reliability. The result is also satisfied. The prediction of test sample of the second and third group list in Table 3 and Table 4.

Pesticide residues detection belongs to trace detection. It is very difficult to detect theoretically. But the result of the experiment in this paper is satisfied unexpectedly. Maybe the reason is that samples are made uniformity solution, which is conducive to collecting spectrum with strong signal, and all samples are ideal samples confected by manual in give some

condition. That reduced sample complexity. The Study on quantitative detection technology of pesticide (chlorpyrifos) residue in vegetables based on near infrared Spectroscopy should be continued deeply.

Table 3. Prediction of test sample of Group 2

Filename	True	Prediction	Difference
04.0	0.35	0.3307	0.0193
08.0	0.55	0.7266	-0.177
12.0	0.8	0.9077	-0.108
16.0	1.1	0.8374	0.263
20.0	1.5	1.644	-0.144
24.0	1.9	1.64	0.26
28.0	2.5	2.873	-0.373
32.0	3.2	3.246	-0.0456

Table 4. Prediction of test sample of Group 3

Filename	True	Prediction	Difference
04.0	0.35	0.3099	0.0401
08.0	0.55	0.4504	0.0996
12.0	0.8	0.7574	0.0426
16.0	1.1	1.149	-0.0486
20.0	1.5	1.506	-0.00582
24.0	1.9	1.933	-0.033
28.0	2.6	2.643	-0.043
32.0	3.4	3.39	0.00996

5. CONCLUSION

This paper discusses the quantitative detection technology of pesticide (chlorpyrifos) residue in vegetables based on near infrared Spectroscopy. The experimental results of three groups of samples indicate the detection technology of pesticide residue in vegetables based on NIR is feasible in the given conditions in this paper. But supposed to the natural vegetable samples that include pesticide residue, the method should to be validated more.

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