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A Fast Detection Method for Pesticide Residues by Spectrometry Technique

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Summary: In this paper, a fast detection method for pesticide residues was proposed, and the qualitative and quantitative detection of the pesticide could be got at once by the method of solution of multiple linear regression equations which were obtained by dual wavelength absorbance and fluorescence spectrometry with least squares method. Moreover, it could detect two kinds of mixed pesticides. Four selected pesticides, aldicarb, fenitrothion, fenvalerate, and chlorothalonil were detected by the method. The results shown that there were good linear relationship in the range of 0.01-1 ppm, and $R^2 > 0.90$. And the method could 100% discriminate the four pesticide residues, the limit of detection was below 8 ppb both single one and mixed one. The recoveries of the pesticides in cabbage samples were observed 92.12%-107.50%. And the recoveries of the mixed pesticides in mineral water samples were observed 86.44%-114.10%. The preliminary study demonstrates that the proposed method has excellent potential application for the safety inspection of food.

Keyword: detection method, pesticide residues, linear regression equations, dual-wavelength spectroscopy, fluorescent spectroscopy.

Introduction

Pesticides play a very important role in increasing the yield of agricultural products [1], while pesticide residues accumulated in human body through direct and indirect ways had caused serious health problems [2]. Thus, the limit standards of pesticide residue have been established in various countries [3]. Because of the advantages in high sensitivity, high resolution, and high flux, the chromatography including gas chromatography (GC) [4], high performance liquid chromatography(HPLC) [5], gas chromatography-mass spectrometry(GC-MS) [6] and liquid chromatography-mass spectrometry(LC-MS) [7-10] are the most mature method in detecting pesticide residues. Nevertheless, they are difficult to widely use, and are not suitable for field testing owing to the disadvantages in high cost, time-consuming, expensive equipment, complex pretreatment and professional operation [11]. In order to meet the market requirements for rapid detection of pesticide residues, the methods of enzyme inhibition [12], test strip [13], molecularly imprinted polymers [14] and immunoassay [15,16] have appeared. The enzyme inhibition method is simple in operation, and suitable for field detection, but it can only be used to detect certain kinds of pesticides with low detection accuracy and only to be used for qualitative analysis. And the test strip method has low manufacturing cost and simple process. However, its detection accuracy is not high, and it can only be used for semi-quantitative detection. And the molecularly imprinted polymers are widely used for pesticide residue detection because of their high selectivity, chemical stability and simple preparation, but it can only detect certain kinds of pesticides and each pesticide needs to mate one kind of imprinting molecule. And immune analysis method including radiation immunoassay [17], enzyme-linked immunoassay [18], fluorescence polarization immunoassay [19] is detected by using the combination of antibody and antigen reaction. It needs not to do a complicated pretreatment and consume less dosage of samples and detects rapidly. However, its shortcoming also can't be ignored. For instance, it can only detect single pesticide with the reason of that a kind of antibody can only apply to detect one type of pesticide. And preparation of antibodies is complex, antibody isn't stability and needs to store in certain conditions. In recent years, spectral analysis which is easy to operate and is nondestructive detection has been more and more attention [20, 21]. And porphyrins and their derivatives, especially metal derivatives, have good optical properties [22]. These materials can identify interactions between molecules such as p-p molecular complex action, bond formation, acid–base interactions, physical adsorption, and van der Waals forces [23]. All the porphyrins and their derivatives utilized in this study were in a rigid plane conjugate

structure, which endows those excellent optical properties, including uv–v is light and fluorescence [24]. When the analyte is added, there will be an interaction between the sensing material and the analyte, which is mainly based on the physical interaction mentioned above. This will cause the charge transfer of the sensing materials, and it causes their spectra to change to varying degrees. For example, the benzene ring of chlorothalonil would interact with porphyrin mainly through p-p conjugation, which caused the charge transferred of porphyrin, accompanied by uv–vis light and fluorescence change [25]. And as a branch of absorption spectrophotometry, dual-wavelength spectrophotometry has higher sensitivity and accuracy than uv-visible absorption spectrophotometry, and can simultaneously determine multiple components and analyze high-concentration solution and turbidity solution samples [26-28]. In addition, after determining the wavelength of two monochromatic light, small laser light source can be used to replace the original large and expensive light source, and then the structure of the device can be greatly simplified.

In this study, a rapid detection device for pesticide residues was established based on dual-wavelength spectrophotometry and fluorescence spectroscopy. According to the specificity of the response of various pesticides on the sensor array, the method based on solving linear equations was proposed, which could quickly qualitatively and quantitatively detect the pesticides. Moreover, based on the additivity both of dual-wavelength absorbance and fluorescence spectrum, the linear equations obtained by regression of dual-wavelength absorption spectrophotometry and fluorescence spectrum, were used to construct the groups of equations. The species of mixed pesticide and the concentration of each pesticide in the mixture were obtained by solving the algorithm of the equations.

Experimental

Pesticde and Chemicals

All the chemicals in this study were list in Table 1. The dimethylformamide(DMF) was used as the reagent to mix the selected pesticides into 10 mg/L and stored in the refrigerator at 4 ℃ for standby.

Fabrication of the sensor array

In this work, a sensor arrays was constructed for detecting dual wavelength signal and fluorescence spectra, which was shown in Fig 1(b). Five dyes including 5,10,15,20-tetraphenylporphyrinato zinc (ZnTPP), 5,10,15,20–tetraphenylporphineeuropium(III) chloride (EuTPPCl), 5,10,15,20-tetraphenylporphyrinato indium (InTPP), monosulfonate tetraphenyl porphyrin (H2TPPS1) and 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin (H2F20TPP), were served as the sensing material. And the chemical structures of these porphyrins are listed in Fig 2. Each dye has been put in a micro cuvette which is shown in Fig 1(a) in advance as one sensor of the array, thus, there are two parallel samples in each detection on the sensor array.

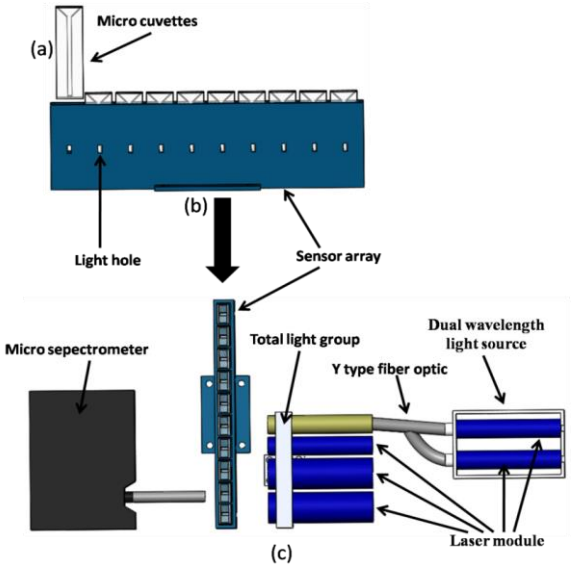

Fig. 1: Illustration of the optic cross-responsive sensor array device. (a) The structure of the micro cuvettes; (b) The structure of the sensor array that consists of 10 chemically responsive spots which are injected in micro cuvette when detecting; (c)The schematic diagram of the device.

Table-1: The list of pesticides and reagents.

Class	Active ingredient	Index parameter	Source
Organophosphate	Fenitrothion	100 mg/L	Provided by Chongqing Entry-Exit Inspection and Quarantine Bureau
Carbamates	Aldicarb	100 mg/L	
Organochlorine	Chlorothalonil	99%	
Pyrethroids	Fenvalerate	100 mg/L	
	Porphyrin and its derivative	AR	Laboratory homemade
	Dimethylformamide	99.9%(GC)	Chongqing Chuandong Chemical Co. LTD.

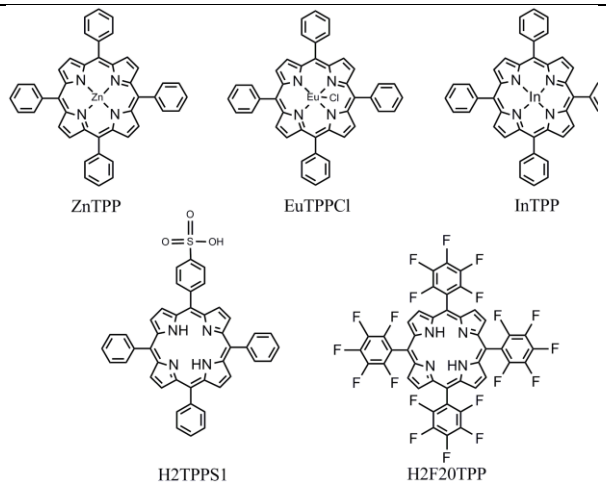

Fig. 2: The chemical structures of selected porphyrins.

Work flow of the detector

After the system is powered on, each function module is initialized automatically by micro control unit (MCU). Firstly, the micro cuvettes in which each dye has been injected respectively were put in the sensor array. Secondly, the selected pesticides which are mixed with DMF in a certain concentration are injected in the micro cuvettes respectively. After the reaction is completed, MCU will automatically select appropriate light source and control the light source to turn on and off in sequence. The fluorescent excitation light source contains three laser lights whose wavelengths are, respectively, 420 nm, 450 nm, and 530 nm, so it can ensure each dye is excited with appropriate excitation wavelength. And the dual wavelength light source contains two laser lights whose wavelengths are 420 nm, 450 nm. When detecting, the dual wavelength light source are turn on and off in sequence and fastly. And it can ensure the absorbance of the analytes is big enough, and each of the absorbance of the analytes is different. After the analyte in the first micro cuvette is detected by both fluorescence and dual wavelength spectroscopy, the sensor array is moved to the position of the next micro cuvette by the stepper motor. Then the second analyte is detected by the same way. And so on, until all the analtes are detected and after that the sensor array is moved to the initial station by the stepper motor.

Data analysis methods

In order to discriminate the type of the pesticide and concentration, it is necessary to analyze the fluorescence spectra data and dual wavelength absorbance data through a series of processing, mainly including preprocessing and linear regression analysis. And there are 10 chemically responsive dyes in the sensor array that has five kinds of elements, each of which is repeated two times as parallel samples. For each kind of element, the final data is the average value of the two parallel samples. That means there are five fluorescence spectra and five absorbance data in each analyte. Thus, each of the analytes has 10 feature points in total.

Results and discussion

Linear regression analysis

In order to obtain the linear regression equations, the least square method was used. And the result was shown in Fig 3, taking chlorothalonil for example.

Pesticide residues results

Four selected pesticides were used for analysis of samples by the method at five different concentrations: 0.01 ppm, 0.05 ppm, 0.2 ppm, 0.5 ppm and 1ppm. In this research, the equilibrium time of reaction was 20 minutes. Take detection of chlorothalonil, for example, Fig 4 exhibits the data obtained from the system and data analysis methods mentioned above. It can be seen apparently ten fixed data, P1 (EuTPPCl), P2 (InTPP), P3 (H2F20TPP), P4 (H2TPPS1), and P5 (ZnTPP). It was shown good linear relationship in the range of 0.01-1 ppm, and $R^2 > 0.90$, and the response characteristics of the pesticides with different dyes were shown in Table 2 and Table 3.

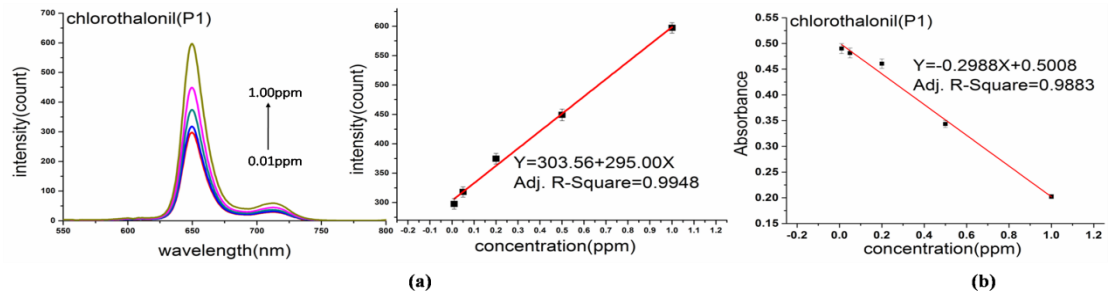

Fig. 3: The result of the linear regression of chlorothalonil. (a) Fluorescence spectra. (b) Dual wavelength

absorbance.

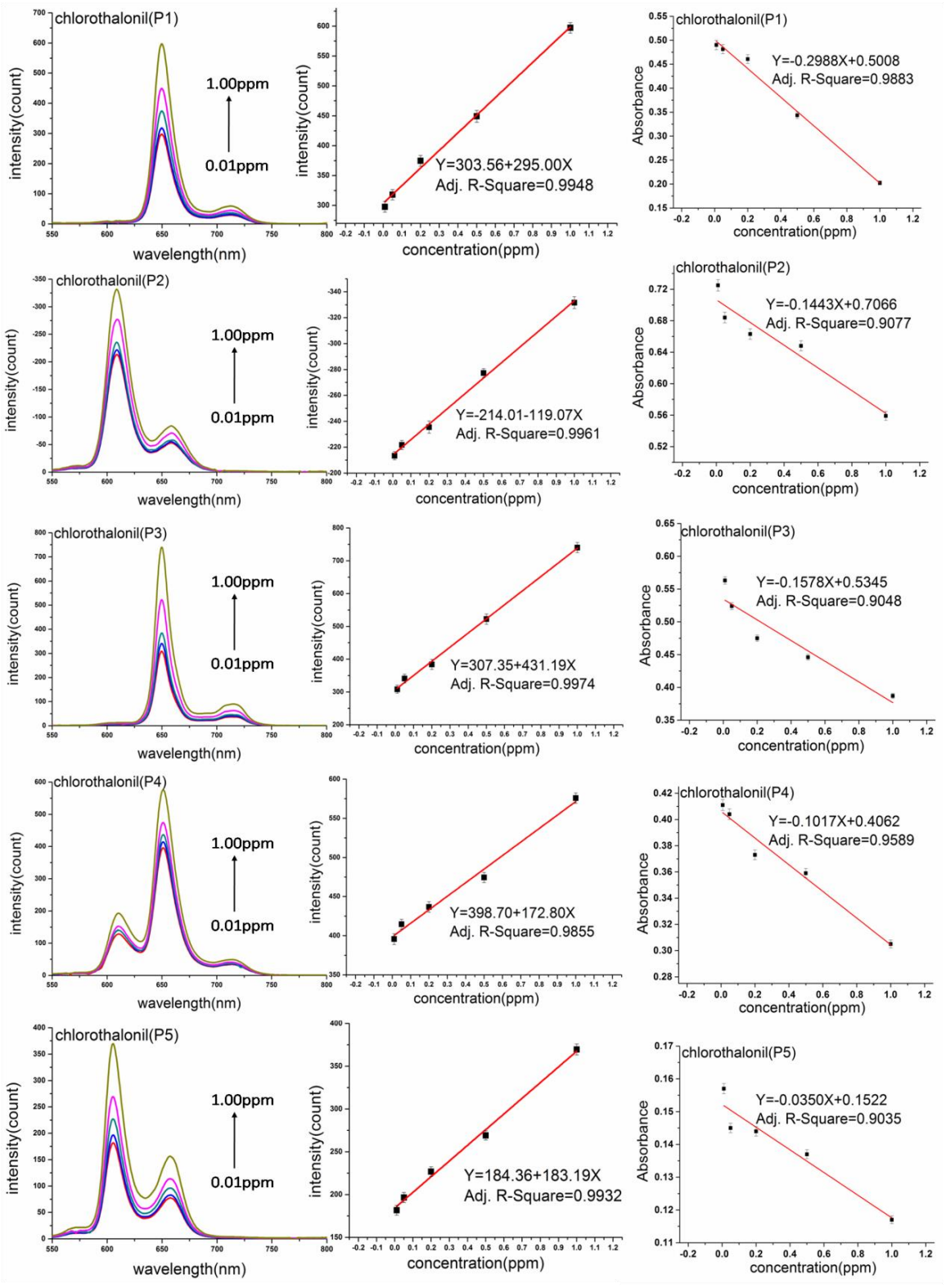

Fig. 4: The results of the linear regression of chlorothalonil. (a) Fluorescence spectra. (b) Dual wavelength absorbance.

Table-2: The regression equations and the detection limit of the four pesticides based on dual wavelength absorbance method

Pesticide	dye	Regression equation	R^2	Detection limit (ppb)
Fenvalerate	P1	$Y = 0.5934 - 0.3487X$	0.9191	6.18
	P2	$Y = 0.6528 - 0.1575X$	0.9499	5.94
	P3	$Y = 0.5213 - 0.497X$	0.9394	7.06
	P4	$Y = 0.3761 - 0.1188X$	0.9308	5.83
	P5	$Y = 0.1775 - 0.0333X$	0.9001	7.43
Aldicarb	P1	$Y = 0.2601 - 0.1452X$	0.9755	6.72
	P2	$Y = 0.7242 - 0.1593X$	0.9436	7.65
	P3	$Y = 0.4013 - 0.1398X$	0.9853	6.29
	P4	$Y = 0.6398 - 0.1104X$	0.9795	6.89
	P5	$Y = 0.3783 - 0.0724X$	0.9886	7.66
Fenitrothion	P1	$Y = 0.2912 - 0.0931X$	0.9848	6.25
	P2	$Y = 0.4603 - 0.0885X$	0.9837	6.56
	P3	$Y = 0.4247 - 0.1056X$	0.9556	5.25
	P4	$Y = 0.5629 - 0.1564X$	0.9875	7.74
	P5	$Y = 0.2935 - 0.1196X$	0.9594	6.93
Chlorothalonil	P1	$Y = 0.5008 - 0.2988X$	0.9883	6.47
	P2	$Y = 0.7066 - 0.1443X$	0.9077	5.67
	P3	$Y = 0.5345 - 0.1578X$	0.9048	6.36
	P4	$Y = 0.4062 - 0.1017X$	0.9589	5.13
	P5	$Y = 0.1522 - 0.0350X$	0.9035	5.42

According to the results in the Table 2, the linear correlation coefficient between the dual wavelength absorbance and concentration of each pesticide in the sensor array are greater than 0.90, which is indicated that it has a good linear correlation. And the detection limit is below 8 ppb.

Table-3: The regression equations and the detection limit of the four pesticides based on differential fluorescence spectrometry method

Kind	dye	Regression equation	R^2	Detection limit(ppb)
Fenvalerate	P1	$Y = 404.68 + 365.10X$	0.9974	4.02
	P2	$Y = -97.11 - 55.14X$	0.9750	7.53
	P3	$Y = 114.57 + 393.32X$	0.9951	3.21
	P4	$Y = 253.77 + 313.72X$	0.9927	3.91
	P5	$Y = 106.90 + 160.72X$	0.9959	7.13
Aldicarb	P1	$Y = 471.99 + 349.05X$	0.9874	3.49
	P2	$Y = -147.76 - 151.75X$	0.9891	5.71
	P3	$Y = 201.09 + 300.88X$	0.9947	5.22
	P4	$Y = 243.34 + 217.85X$	0.9863	6.81
	P5	$Y = 440.31 + 90.39X$	0.9621	3.53
Fenitrothion	P1	$Y = 227.95 + 659.59X$	0.9923	5.59
	P2	$Y = -144.53 - 163.50X$	0.9828	4.41
	P3	$Y = 326.11 + 140.93X$	0.9764	5.46
	P4	$Y = 412.51 + 460.52X$	0.9956	4.34
	P5	$Y = 94.92 + 134.35X$	0.9937	6.38
Chlorothalonil	P1	$Y = 303.56 + 295.00X$	0.9948	5.77
	P2	$Y = -214.01 - 119.07X$	0.9961	5.24
	P3	$Y = 307.35 + 431.19X$	0.9974	4.36
	P4	$Y = 398.70 + 172.80X$	0.9855	6.66
	P5	$Y = 184.36 + 183.19X$	0.9932	2.69

According to the results in the Table 3, the linear correlation coefficient between the fluorescence

intensity and concentration of each pesticide in the sensor array are greater than 0.96, which is indicated that it has a good linear correlation. And the detection limit is below 8 ppb.

The linear equations of each pesticide in different dyes indicated that only one set of absorbance values and spectral peaks corresponds to a pesticide at a certain concentration. If not, it was assumed that two of these pesticides had the same data at some concentration, then Eq. 1 was gained:

$$k_{1i}x_{1i} + b_{1i} = k_{2i}x_{2i} + b_{2i}$$

$$x_{1i} = \frac{k_{2i}}{k_{1i}}x_{2i} + \frac{b_{2i} - b_{1i}}{k_{1i}} \quad , i=1,2,3,\ldots,10 \qquad (1)$$

k_{1i} and b_{1i} were the coefficients of linear equations under a pesticide in different dyes, and k_{2i} and b_{2i} were the other one in Eq. 1. Took the fenitrothion and chlorothalonil as an example, Eq. 2 was acquired.

$$\begin{aligned}
x_{11} &= 3.2095x_{21} - 2.2513 \\
x_{12} &= 1.6305x_{22} - 2.7831 \\
x_{13} &= 1.4943x_{23} - 1.0398 \\
x_{14} &= 0.6503x_{24} + 1.0019 \\
x_{15} &= 0.2926x_{25} + 1.1814 \\
x_{16} &= 1.3317x_{26} - 1.5994 \\
x_{17} &= 1.4807x_{27} - 0.3074 \\
x_{18} &= 0.9425x_{28} + 0.8901 \\
x_{19} &= 0.9665x_{29} - 0.6975 \\
x_{110} &= 1.9423x_{210} + 0.5145
\end{aligned} \qquad (2)$$

According to the suppose , x_{11}, x_{12}, x_{13}, x_{14} ,x_{15} , x_{16} , x_{17} , x_{18} , x_{19} and x_{110} should be closed to each other, and so as x_{21}, x_{22}, x_{23}, x_{24}, x_{25}, x_{26}, x_{27}, x_{28}, x_{29},and x_{210}. However, there is a significant difference between x_{18} and x_{19}, with at least 1.5876 difference between them, it is obviously contradicted to the assume from Eq. 2. Similarly, there were no two or more pesticides, whose solutions with the same concentration were obtained by solving linear equations. Thus, while getting aseries of absorbance values and spectral peaks, set them substituted into the corresponding equations of each pesticide, if the difference among the solutions of the equations of some pesticide were small, it can be determined that the pesticide detected was this one, and its concentration was Figd out.

In this study, 30 samples from each kind of selected pesticides at each concentration were tested by the detector repeatedly. For the premise that each kind of pesticide can be selected, 20 specimens were randomly selected for recognition in accordance with the method above, and these were repeated 100 times. The results were shown in Table 4.

The results showed that the qualitative recognition accuracy was 100%, and the RSD of each kind of pesticide was less than 5%. Obviously, the method has a good stability and repeatability.

Analysis of those pesticides in spiked samples

In order to verify the feasibility of this method in actual samples, the experiment of labeling cabbage was carried out. Specifically, we prepared pesticides-spiked mineral water samples in multiple concentrations, and then analyzed the samples with the method. And the detection results were listed in Table-5.

Table-4: The statistics of recognition results.

Kind	Concentration (ppm)	Selected (number)	Relative standard error(%)	Error of kind discrimination
	0.01	**50**	**4.79**	
	0.05	**38**	**4.16**	
Fenvalerate	**0.20**	**50**	**4.01**	**0%**
	0.50	**57**	**3.77**	
	1.00	**52**	**3.79**	
	0.01	**53**	**4.96**	
	0.05	**54**	**4.61**	
Aldicarb	**0.20**	**56**	**3.95**	**0%**
	0.50	**53**	**3.69**	
	1.00	**56**	**3.58**	
	0.01	**43**	**4.67**	
	0.05	**44**	**4.25**	
Fenitrothion	**0.20**	**41**	**3.98**	**0%**
	0.50	**47**	**3.73**	
	1.00	**53**	**3.38**	
	0.01	**43**	**4.74**	
Chlorothalonil	**0.05**	**61**	**4.61**	
	0.20	**53**	**3.91**	**0%**
	0.50	**53**	**3.29**	
	1.00	**47**	**3.44**	

Table-5: The recovery experiment results of real samples.

Sample	Spiked concentration (ppb)	Measured concentration (ppb)	Rate of recovery (%)
fenvalerate1	100	97.52	97.52
fenvalerate2	400	427.13	106.78
fenvalerate3	700	718.62	102.66
aldicarb1	100	107.50	107.50
aldicarb2	400	374.28	93.57
aldicarb3	700	723.24	103.32
fenitrothion1	100	95.07	95.07
fenitrothion2	400	417.96	104.49
fenitrothion3	700	661.22	94.46
chlorothalonil1	100	92.12	92.12
chlorothalonil2	400	423.76	105.94
chlorothalonil3	700	684.88	97.84

The results showed that the recoveries of the four pesticides in cabbage samples were observed in the range of 92.12% - 107.50%. It indicated that the method was highly reliable.

Moreover, in case of that these four pesticides were independent of each other between dyes in the reaction, it could detect two kinds of mixed pesticides by the improved method which mentioned above. According to that the optical signal can be added, the Eq. 3 was obtained:

$$\begin{aligned} Y_{1i} + Y_{2i} &= Y_i \\ K_{1i}X_{1i} + b_{1i} + K_{2i}X_{2i} + b_{2i} &= Y_i \end{aligned} \quad (3)$$

In this equation, Y_i was the value of the optical signal in the mixed system, Y_{1i} was the value of the optical signal of one of the mixed pesticides, and Y_{2i} was the other one's. And each group of mixed pesticide has ten equations which were obtained from Table 1 and Table 2. If there were two groups of mixed pesticides could get consistent solutions, the Eq. 4 was acquired:

$$K_{1i}X_{1i} + b_{1i} + K_{2i}X_{2i} + b_{2i} = K_{3i}X_{3i} + b_{3i} + K_{4i}X_{4i} + b_{4i} = Y_i \quad (4)$$

While i=1,2,3,…,10, and it represented the equation under each of dyes, and K_{1i}, K_{2i},K_{3i},K_{4i} were the coefficients of corresponding to the equations, and b_{1i}, b_{2i}, b_{3i}, b_{4i} were the constants of corresponding to the equations, and X_{1i}, X_{2i}, X_{3i}, X_{4i} were the concentrations of the mixed pesticides. Similarly, each concentration of the same pesticide should be closed. Therefore, it could be assumed that $X_{1i}=X_1$, $X_{2i}=X_2$, $X_{3i}=X_3$, $X_{4i}=X_4+e_i$. And $\sum_{i=1}^{10}|e_i|$ was the overall error in this system, and $|e_i|$ should be smaller than $0.05(X_1+X_2+X_3+X_4) < 0.05*4*1=0.2$. Then the Eq. 5 was gained.

$$\frac{K_{1i}}{K_{4i}}X_1 + \frac{K_{2i}}{K_{4i}}X_2 - \frac{K_{3i}}{K_{4i}}X_3 - X_4 = \frac{b_{3i} + b_{4i} - b_{1i} - b_{2i}}{K_{4i}} + e_i \quad (5)$$

If that was the same kind of pesticide in the two groups of mixed pesticides, it could be obviously detected based on the method by which the single pesticide was detected. Thus, took the group of mixed pesticides with fenitrothion and chlorothalonil and the group of mixed pesticides with fenvalerate and aldicarb for example, Eq. 6 was acquired.

$$\begin{aligned}
0.6412X_1 + 2.0579X_2 - 2.4015X_3 - X_4 &= e_1 - 0.4236 \\
0.5556X_1 + 0.9058X_2 - 0.9887X_3 - X_4 &= e_2 - 1.3189 \\
0.7554X_1 + 1.1288X_2 - 3.5551X_3 - X_4 &= e_3 + 0.2618 \\
1.4167X_1 + 0.9212X_2 - 1.0761X_3 - X_4 &= e_4 - 0.4239 \\
1.6519X_1 + 0.4834X_2 - 0.4599X_3 - X_4 &= e_5 - 1.5207 \\
0.4830X_1 + 0.6431X_2 - 0.8574X_3 - X_4 &= e_6 - 0.5094 \\
0.9781X_1 + 1.4484X_2 - 0.6572X_3 - X_4 &= e_7 - 1.2585 \\
1.6217X_1 + 1.5284X_2 - 0.5697X_3 - X_4 &= e_8 - 0.7791 \\
1.6217X_1 + 1.6348X_2 - 1.0429X_3 - X_4 &= e_9 - 0.4181 \\
0.2156X_1 + 0.4187X_2 - 0.2428X_3 - X_4 &= e_{10} - 0.1509
\end{aligned} \quad (6)$$

Obviously, it contradicted to the original assumption because of that e_7-e_6 was greater than 0.7491, and in the same way, the else groups of mixed pesticides were the same situation. Therefore, the method could be used in the detection of two kinds of mixed pesticides which were independent of each other in the reaction between dyes. There are four pesticides belonged to four categories, and there are six kinds of mixed group in total. And the concentrations of each group were shown in Table 6

Table-6: The selected detection object and the concentration of each pesticide in mixed group.

Mixed group	Concentration of the first one in the mixed group (ppb)	Concentration of the other one in the mixed group (ppb)
Fenitrothion + Aldicarb (A+B)	50	200
Fenitrothion + Chlorothalonil (A+C)	10	50
Fenitrothion + Fenvalerate (A+D)	500	200
Aldicarb + Chlorothalonil (B+C)	200	10
Aldicarb + Fenvalerate (B+D)	50	50
Chlorothalonil + Fenvalerate (C+D)	10	50

Table-7: The detection results of the mixed solutions.

Group of mixed pesticide	Measured concentration of the first one in the mixed group (ppb)	Measured concentration of the other one (ppb)	Relative standard error of the first one (%)	Relative standard error of the other one (%)
A+B	45.63	213.78	8.75	6.89
A+C	11.36	46.89	13.57	6.21
A+D	534.17	215.37	6.83	7.68
B+C	187.45	8.86	6.28	11.38
B+D	55.17	44.96	10.35	10.08
C+D	9.09	54.76	9.91	9.53

Table-8: The recovery experiment results of real samples.

Group of mixed pesticide	Spiked concentration of the first one (ppb)	Spiked concentration of the other one (ppb)	Measured concentration of the first one (ppb)	Rate of recovery of the first one (%)	Measured concentration of the other one (ppb)	Recovery of the other one (%)
A+B	20	50	17.89	89.45	53.66	107.32
	150	100	162.4	108.27	108.13	108.13
	300	400	287.37	95.79	424.19	106.05
A+C	20	450	22.82	114.10	473.82	105.29
	150	80	141.38	94.25	74.49	93.11
	300	250	290.29	96.76	231.18	92.47
A+D	20	100	18.28	91.40	95.82	95.82
	150	500	159.24	106.16	528.35	105.67
	300	50	323.27	107.76	46.64	93.28
B+C	50	450	54.59	109.18	475.56	105.68
	100	80	109.79	109.79	87.3	109.13
	400	250	385.46	96.37	229.41	91.76
B+D	50	100	54.62	109.24	93.67	93.67
	100	500	91.64	91.64	532.43	106.49
	400	50	417.85	104.46	43.22	86.44
C+D	450	100	439.49	97.66	106.55	106.55
	80	500	83.76	104.70	521.94	104.39
	250	50	233.91	93.56	44.81	89.62

However, because of the influence of the error, it could not be obtained the concentration directly through ten equations of each group, therefore, it was selected two equations randomly constitutes a binary systems from ten equations of one of the groups which was mentioned in Eq.3. And the concentrations of the two pesticides were calculated separately, then the other two equations were selected randomly constitutes a binary systems from the same group, and the concentrations of the two pesticides were calculated separately again, and repeated the above steps, that got five sets of results. If each set of the results was approximate, it was the group of the mixed pesticide. Otherwise, it was repeated the same way until got a similar set of results, and the group of the mixed pesticide which was selected to calculate was the tested solution. Thus, the kind of the pesticide in mixed group was determined, and their concentrations were calculated respective. And the results of statistics were shown in Table 7.

The results showed that the method could be used to detect two kinds of mixed pesticides, and the relative standard error was less than 14% which was bigger than the single one's, one of the reason is that the method is based on solving system of linear equations which have certain deviation, and the detection error is cumulative in the calculation. Considering the interaction between each pesticide in mixed group, especially between the acid and alkaline pesticide, it can cause bigger impact to the result. Fortunately, the pesticides involved in this paper are all slightly acidic and independent of each other, so they can be detected and identified by this method.

Analysis of these mixed pesticides in spiked samples

It was prepared the samples which were mixed two kinds of pesticides in mineral water, and each group of mixed pesticides had three different combinations of concentrations and 10 groups of parallel samples, and the qualitative and quantitative detection of each pesticide was detected by the method mentioned above, and the results of statistics were shown in Table 8.

The results showed that the recoveries of the ten groups of mixed pesticides in mineral water samples were observed in the range of 86.44%-114.10%, the developed detector was highly precise and reliable. And it indicated that the method displayed great potential real application in mixed pesticides analysis.

Conclusions

In this work, a fast detection method based on solution of multiple linear regression equations which were obtained by dual wavelength absorbance and fluorescence spectrometry with least square method for pesticide residues has been proposed. And four selected pesticides, aldicarb, fenitrothion, fenvalerate and chlorothalonil were detected by the method. The results showed that the method could 100% discriminate the four pesticide residues and the limit of detection was below 8 ppb, and the testing time is about 20 minutes on average, and the recoveries of the four pesticides in cabbage samples were observed in the range of 92.12%-107.50%. Moreover, based on the additivity of optical signal, two kinds of mixed pesticides were detected by the method. The results showed that the method could 100% discriminate the six groups of the mixed pesticide, and the recoveries of the six groups of mixed pesticides in mineral water samples were observed in the range of 86.44%-114.10%. It indicate that the method has great potential in the actual detection of pesticide residues and has excellent potential application for the safety inspection of food.

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