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RECOGNITION AND LOCATION OF CROP SEEDLINGS BASED ON IMAGE PROCESSING

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With the development of digital image technology, we can easily obtain a large number of crop growth images. Through effective analysis of the image, the growth information of crops can be obtained, which can better direct agricultural production. The efficiency of traditional seedling growth monitoring is low, especially in large-scale farmland, which takes a lot of time. Artificial method timely restricts scientific decision-making of cultivation crops. The progress of machine vision and image processing technology provides a new way for harmlessly monitoring of crop seedling growth .The results of image analysis can help agricultural producers to understand the growth of crop seedlings quickly and accurately, so as to take effective management as soon as possible. In this paper, the images of sunflower seedling collected in farmland environment are taken as the research object. The main research content is to segment green crops from soil background. Segmentation method of sunflower seedling image based on color features and Ostu threshold segmentation is proposed. The method is simple in calculation, and can adapt to the segmentation of farmland environment images, which lays the foundation for crop recognition process. Based on the image recognition results, the algorithm locates the seedlings. Through the rapid identification of sunflower seedlings, it is possible to fill the gaps with seedlings where the seedlings are less distributed. On the contrary, if the seedlings are too dense, the number of seedlings needs to be reduced. The algorithm provides a basis for precise management. The results show that the algorithm with extra green feature can quickly and effectively identify sunflower seedlings from background, and locate the seedlings based on the image recognition results. This algorithm is not sensitive to soil moisture and light conditions, and is less affected by crop residual coverage, so it can adapt to different soil environment which realize the non-destructive monitoring of sunflower seedlings.

Key words: *image segmentation; machine vision; color features; green identification; adaptive threshold method*
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Introduction. With the development of machine vision and digital image processing technology, agricultural information management has been realized, and the development of precision agriculture is a trend (Hamuda et al., 2016; Iqbal et al. , 2018; Nguyen et al. ,2019). Farmland managers can keep abreast of the crop growth and be provided scientific guidance for the management of farmland. Various remote devices such as satellites, airplanes, or Unmanned Aerial Vehicles (UANs) are used to monitor crops on the farmland through real-time analysis and processing of aerial images (Lei et al., 2017; Zhang et al., 2019; Pena et al. ,2015; Di Gennaro et al. ,2019). Many researchers use digital image processing techniques to detect the symptoms of diseases automatically as early as they appear on the growth stage of plants. They used different methodologies for the analysis and detection of plant leaf diseases (Khirade et al., 2015; Singh et al., 2015; Pujari et al. ,2015; Oo & Htun, 2018). With the development of precision agriculture, it requires to predict the crop yield with low cost. It can be solved by image processing technology which makes a correct judgment on the plant annual yield (Filippi et al., 2020; Tedesco et al., 2020). Recent advances in technology provide new tools to solve challenging computer vision tasks such as object detection, which can be used for detecting and counting plant seedlings in the field (Samiei et al., 2020; Jiang et al., 2019; Feduck et al., 2018; Quan et al.,2019). Plant seedling detection combines the theory of graphics processing and recognition in computer science with possibility of field automatic work or reseeding and thinning of crop seedlings.

Sunflower is one of the four major oil crops in the world, it is grown on 25.4 M • ha. The area under this crop in Ukraine is 5.1M • ha. The main sunflower producing areas of China are distributed in the Northeast, Northwest and North China regions, with high production potential, and can be expanded to the Southwest, Central South and East China regions (Zhang & Gu, 2018). With the development of science and technology, new technologies have played an important role in the production and growth of sunflower. Some researchers use image processing technology to recognize and locate sunflower seedlings, then provides the theoretical basis for the robot to automatically implement sunflower seedling reseeding and thinning operations (Yin et al. , 2010).

According to different application requirements, crop recognition based on image processing is researched (Gong, 2014; Chen et al. 2019; Tian et al., 2015). Sun Ming et al. proposed an automatic recognition technology by analyzing the color images of seedlings, which can identify each radish seedling in the image (Sun & Ling, 2002). Wang Sile et al. achieved the separation of green plants from complex background elements by constructing the decision tree based on HSV and color dispersion, and better adapted to changes in the brightness of the field image (Wang et al. 2015). Ke Qiuhong et al. proposed the method for extracting green plant areas from digital images, to solve the interference of soil background in the image and the influence of different lighting conditions on it, and achieve non-destructive measurement of plants (Ke et al. , 2013). Zhang Zhibin with colleagues adopted RGB color system and proposed the fast segmentation algorithm of ridge and row structure based on color features (Zhang et al., 2010). Wang Xue and Guo Xinxin proposed the green crop image segmentation method combined with Ostu method of the largest inter-class variance based on G-R color features, it can separate green crops from complex soil background not affected by uneven outdoor light (Wang & Guo, 2018). All these studies improved the recognition effect on crop images from various aspects, but have not studied the precise position of crops. The goal of our study is to quickly identify sunflower seedlings on digital images and provide position information for precision management of farmland.

Materials and methods.

1.1. Sowing method

Sunflower varieties are mainly divided into two types: edible and oil. Sowing methods differ for them. Sunflower of the oil type have 70 cm row space and 40 cm plant space. There are 30,000–37,500 seedlings per hectare for ordinary varieties. Digging holes are used for sowing, the depth of the holes is 3 cm–4 cm, and 1–2 seeds are placed on each acupuncture point. After emergence of plants, seedlings should be checked and supplemented timely. When the seedling reaches 2–3 pairs of leaves, it is necessary to carry out thinning in time.

1.2. Analysis of crop color characteristics

The object color is determined by the reflected light characteristics, and the color of an opaque object depends on the light color it reflects. The characteristic of the reflection spectrum of green plants is different from the inanimate soil background, and this characteristic can be used to distinguish them (Liu et al. 2013).

The current color models used for image processing are RGB, HIS, YCbCr, etc (Liu et al., 2012). The RGB color space is composed of three colors – red, green, blue as the primary ones (Fig. 1). The other colors are formed by mixing of three primary colors. The HIS color space is composed of hue, saturation, and brightness, and it is beneficial for human perception. The YCbCr color space is a relative value of a luminance signal Y and two-color difference signals: blue relative luminance B-Y and red relative luminance R-Y.

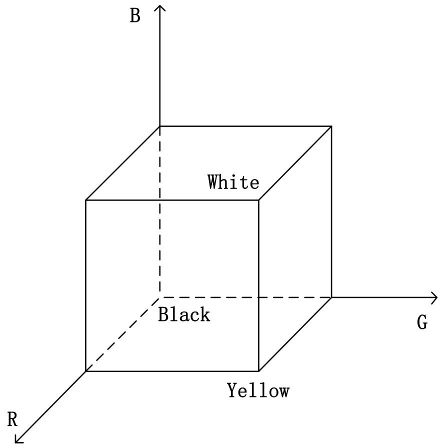

Fig. 1. Model of RGB color system.

1.3. Method of image segmentation

Segmenting the seedlings from the background is a key step in image processing, and the segmentation effect will affect the acquisition of location information by seedling recognition system (Zhou et al., 2013). The background segmentation of color image is generally achieved by grayscale and binarization. The green plants and the background soil have different characteristics in the three-color components of R, G, and B (Su et al., 2018). By separating the original image into three independent primary color dimensions, and then selecting different combinations of color features, each pixel in the image is converted, that can achieve the purpose of enhancing the contrast between the target crop and the background soil in the image. Since the original colored image is transformed into a grayscale image in this process, the combination of color features applied in the conversion is called the grayscale factor. According to the color characteristics, the most commonly used method is the extra green one, which makes use of characteristics that the twice of G value is greater than the sum of R and B values. The extra green method extracts the green plant image better. The shadow, withered grass and soil in the images can be more obviously suppressed, and the sunflower seedling is more visible in the images. In my research, two images of sunflower seedlings were selected. First image was taken in the dark outside environment (Fig. 2, A), and the second one was taken in the outside environment with strong sunlight (Fig. 2, B), so there were some shadows in the images. There were impurities in the soil background in the two images.

(A) Sunflower seedling 1 (B) Sunflower seedling 2

Fig. 2. Sunflower seedlings.

According to the characteristics of the Color eigenvalue of green crops in farmland, method of weighting grayscale image is adopted. The calculation formula is as follow (1) :

$$Gray(x,y) = w_1R(x,y) + w_2G(x,y) + w_3B(x,y) \quad (1)$$

$Gray(x,y)$ represents the gray value of pixels of (x,y) ; $R(x,y)$ 、 $G(x,y)$ 、 $B(x,y)$ are the three color components of the input RGB color images. w_1 , w_2 , w_3 denotes the coefficients of each component, their values are $w_1 = -1$, $w_2 = 2$, $w_3 = -1$, so the formula is showed as (2).

$$Gray(x,y) = 2G(x,y) - R(x,y) - B(x,y) \quad (2)$$

Using formula (2) to gray the image, the gray image is shown on Fig. 3.

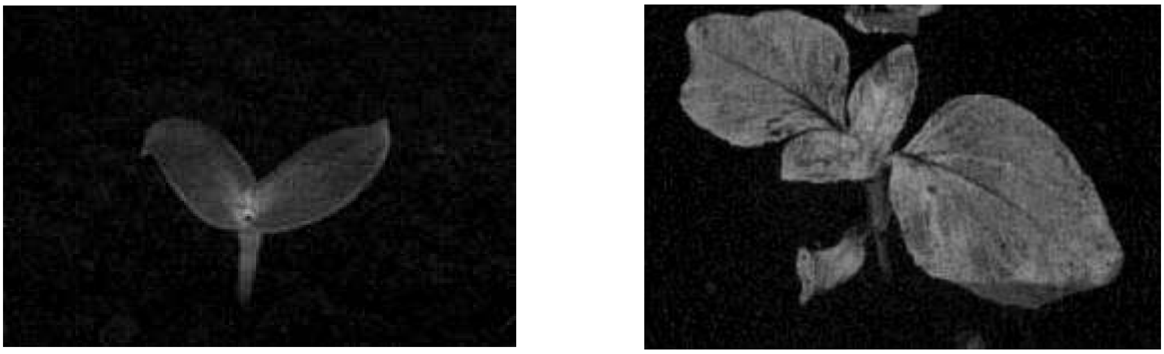

Fig. 3. Grayscale images.

The color image has been converted into a gray image after being processed by the grayscale factor. In this image, the difference between the gray value of the green plant and the gray value of the background soil is obvious. Therefore, the image threshold segmentation method can be used to achieve the recognition of green plants. Threshold segmentation methods include fixed threshold method and adaptive threshold method. The gray histogram of the two images are showed on Fig. 4.

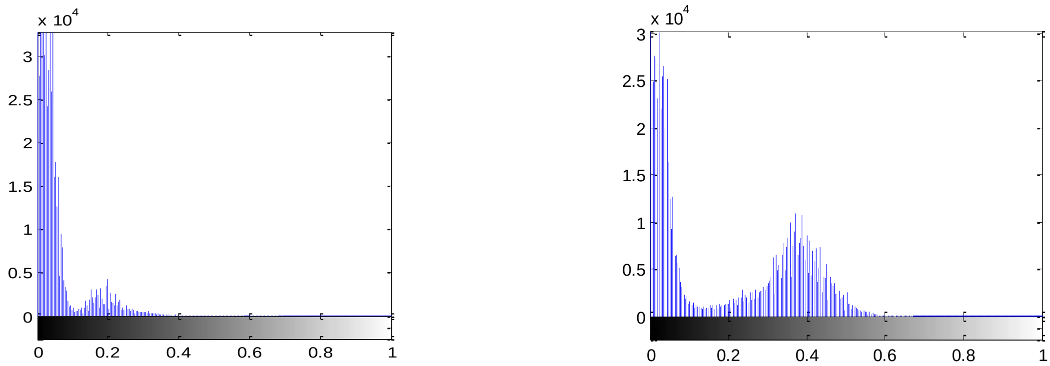

Fig. 4. Gray histogram of image.

The grayscale histogram has obvious bimodality and is suitable for thresholding, as long as the threshold is taken at the valley directly between the two peaks. Due to the influence of outdoor sunlight, the value at the trough is variable for each image, and a fixed threshold cannot be determined to segment the image. Therefore, in order to automatically identify sunflower seedlings, this study uses the maximum variance automatic threshold method. This method is an adaptive threshold method. Its calculation is simple and stable. The basic idea is to divide all the pixels in the image into two categories. The pixels less than the threshold T are called background pixels, and the pixels larger than the threshold T are called the target pixels. n_1 represents the number of background pixels, n_2 represents the number of target pixels, $m \times n$ represents the size of an image, θ_1 represents the proportion of the number of background pixels, θ_2 represents the number of target pixels after segmentation by threshold T. T represents the optimal segmentation threshold. The calculation formula is as follows:

$$\theta_1 = \frac{n_1}{m \times n}$$

$$\theta_2 = \frac{n_2}{m \times n}$$

$$n_1 + n_2 = m \times n \quad (3)$$

The gray value t is sequentially taken within the range of the minimum gray value to the maximum gray value, and the variance σ^2 is obtained, when the gray value $t = T$. The value of t at this time is the optimal segmentation threshold T. The formula for calculating the variance is as follows:

$$\sigma^2 = \theta_1 \times \left(\mu_1(t) - \mu_T(t)\right)^2 - \theta_2 \times \left(\mu_2(t) - \mu_T(t)\right)^2 = \theta_1\theta_2\left(\mu_1(t) - \mu_2(t)\right)^2 \quad (4)$$

$\mu_T(t)$ represents the total average gray level of the whole image, $\mu_1(t)$ represents the average gray level of background pixels, $\mu_2(t)$ represents the total average gray level of target pixels.

1.4. Algorithm design

According to the above analysis, this paper proposes a fast segmentation method based on farmland green crop image, the steps are follows:

(a) The image is divided into small pieces of a region; each sub region corresponds to a crop seedling.

(b) Pre-process each sub-piece, using the super green method ExG to get gray scale image.

(c) In order to reduce the influence of noise points on image segmentation accuracy, median filtering method is used to decrease noise in gray image.

(d) Automatic calculation of optimal threshold T by Ostu method. The gray value of each pixel is compared with the threshold value, and the pixel is divided into plant or background according to the comparison results.

(e) The white connected area of the identified plants is analyzed and located, ignore the scattered white areas. Using the method of regional feature extraction, calculate the centroid position of the largest polygon composed of plant regions, and mark the centroid position with small red circle in the image.

(f) If there are other sub-pictures untreated, skip to (b) to continue.

Results. In this experiment, sunflower images collected under different illumination conditions were used as materials (as shown in Fig. 1). The algorithm proposed in this paper was tested and verified. The identification and location of sunflower seedling images in farmland was solved.

The algorithm was implemented by MATLAB, and its version is r2014a. The operating system of the computer was Windows 10, the computer processor was Intel Core i5, and the memory capacity was 4G.

This method was used to recognize the sunflower seedling image (Fig. 2). The binarization segmentation result is shown on Fig. 5.

Fig. 5. Image segmentation results.

The results show that the sunflower seedlings in the image can be identified correctly by using the method of this paper, regardless of the illumination intensity and the interference of impurities in the soil background. After obtaining the integral binary image of sunflower seedling plant area, the centroid position of the largest polygon composed of plant area was calculated by region feature extraction method, and marked with small red circle. The marking result is shown on Fig. 6.

Fig. 6. Centroid of the crop image.

Discussion. 100 sunflower seedling images were taken for recognition, in order to verify the effectiveness of the algorithm, and compared with Cr color difference method in YCbCr color space. 10 representative images were extracted from 100 images for processing and analysis (Reference to table 1). The relative error rate was calculated by comparing the segmented seedling area with the actual area (Reference to table 2).

Tabel 1

Segmentation results of seedling area (Pixel)

Num	Extra Green	Cr	Manual caculation
1	2862	2792	2812
2	2571	2490	2550
3	1753	1660	1745
4	2855	2693	2812
5	1832	1776	1816
6	2800	2605	2720
7	2495	2346	2486
8	2865	2690	2800
9	2280	2170	2273
10	2250	2170	2240

Tabel 2

Relative error of segmentation (%)

Num	Extra Green	Cr
1	1.78	0.71
2	0.82	2.35
3	0.46	4.87
4	1.53	4.23
5	0.88	2.20
6	2.94	4.23
7	0.36	5.63
8	2.32	3.93
9	0.31	4.53
10	0.45	3.13

It can be seen from the result of table 2 that the segmentation effect of Extra Green with Ostu threshold segmentation method is better than that of color difference Cr with Ostu threshold one. It can eliminate the disturbance of soil background and light change to some extent, and can adapt to the growth environment of crop seedlings.

Conclusions. In our study, the identification and location of sunflower seedlings in farmland were researched. A fast segmentation method based on green crop image was proposed. It used color characteristics of green crops and background soil, and carried out gray scale and binarization of images. The segmentation and location of green crops from farmland images were realized, which provides scientific basis for the next step of seedling management.

The rate of emergence of a certain area in the farmland can be obtained and provide scientific guidance for supplementing and thinning seedlings. The experimental results showed that the algorithm can effectively extract and locate the green crop seedlings from the image, and realized the non-destructive measurement of crops.

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РОЗПІЗНАВАННЯ ТА ЛОКАЛІЗАЦІЯ СХОДІВ СІЛЬСЬКОГОСПОДАРСЬКИХ КУЛЬТУР НА ОСНОВІ АНАЛІЗУ ЦИФРОВИХ ЗОБРАЖЕНЬ

З розвитком цифрових технологій можна з легкістю отримати велику кількість зображень сільськогосподарських угідь. Завдяки ефективному аналізу таких цифрових зображень, ми отримуємо інформацію стосовно темпів росту сільськогосподарських культур, що може покращити сільськогосподарське виробництво. Ефективність традиційного моніторингу росту культур невисока, особливо на великих сільськогосподарських угіддях, оскільки такий моніторинг займає багато часу. Штучний метод обмежує своєчасність прийняття наукових рішень щодо необхідності обробки сільськогосподарських угідь. Прогресивні цифрові технології та технології обробки зображень відкривають новий спосіб моніторингу, який не завдає шкоди сільськогосподарським культурам. Результати аналізу зображень можуть допомогти агровиробникам швидко і точно оцінювати темпи росту культур, що сприятиме прийнятю швидких та ефективних управлінських рішень. Об'єктом дослідження є отримані зображення сходів соняшнику на сільськогосподарських угіддях. Основний зміст дослідження полягає у розпізнавані зелених сходів на ґрунтовому фоні. Запропоновано метод розпізнавання сходів соняшнику на основі зонації ділянок за кольором і методу Оцу для обчислення порогового зображення. Цей метод простий у застосуванні та може бути пристосований для сегментації зображень сільськогосподарських угідь, що закладає основу для процесу локалізації таких культур. Ґрунтуючись на результатах розпізнавання зображень, завдяки алгоритму сходи культур можуть бути локалізовані. Завдяки швидкій ідентифікації сходів соняшнику, можна визначити ділянки із прогалинами, де зійшли не усі саджанці. Або навпаки, визначити ділянки із ущільненими сходами, де кількість сходів потрібно зменшити. Алгоритм забезпечує основу для точного управління. Отримані результати показують, що алгоритм із компонентом визначення зеленого кольору може швидко та ефективно ідентифікувати сходи соняшнику на ґрунтовому фоні та на основі розпізнавання зображень локалізувати такі сходи. Цей алгоритм не чутливий до вологості ґрунту та умов освітлення, а також менше схильний до впливу залишкового покриву угідь, тому він може застосовуватися до різних типів ґрунту. Окрім цього, такий метод є прикладом неруйнівного моніторингу сходів соняшнику.

***Ключові слова:** сегментація зображення; машинний зір; колірні ознаки; визначення зеленого кольору; адаптивний метод порогової обробки зображень.*

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A REVIEW OF RAPID PESTICIDE RESIDUES DETERMINATION IN VEGETABLES AND FRUITS

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With the increasing demand of production, pesticides have been widely used in fruit and vegetable yield. Pesticides are used to kill insects, fungi and other organisms that harm the growth of crops in order to ensure and promote the growth of crops. In particular, pesticides are used to control diseases and insects and regulate plant growth and weeding. From the point at this stage, the use of pesticides in agricultural production is inevitable, and the corresponding, also in rapid increase in the amount of pesticide, pesticide residue problem is along with the production and extensive use of pesticides, pesticide, especially the organic pesticide used in great quantities, cause serious problems of pesticide pollution, a serious threat to human health. That is the abuse of pesticides does harm for environment and human health, particularly in the bioaccumulation effect of pesticide residues on human body, attracting more and more attention from scientists. Therefore, it's imperative to develop high sensitivity, high selectivity, simple, rapid and low-cost methods for pesticide residues detection and analysis. The traditional methods of pesticide residue analysis mainly include gas chromatography high performance liquid chromatography, chromatography-mass spectrometry, etc. These methods have been widely used in pesticide residue detection, and a series of important achievements have been made. Although with high detection sensitivity, these methods have some problems such as complicated sample pretreatment, expensive equipment, time-consuming analysis, and the need for specialized instrument operators and so on, which cannot meet the requirements of rapid and real-time field detection of pesticide residues. Therefore, researchers in various fields have carried out and strengthened the research on rapid detection technology of pesticide residues, seeking to develop convenient, sensitive, accurate and stable new pesticide residue detection technology. In this paper, we mainly reviewed the rapid detection technologies of pesticide in fresh fruits and vegetables in recent years, including new chromatographic analysis, enzyme inhibition, fluorescence sensor, spectrophotometric and biosensor detection technology, and analyzed the development status, advantages, and disadvantages of each method, as well as the development prospect of rapid detection technology in the future.

***Key words**: pesticide residues, rapid detection techniques, cross-fusion technology, fruits and vegetables.*
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Introduction. Modern agricultural production is inseparable from the usage of pesticides to prevent and control all kinds of crop diseases, insect pests and weeds, following by severe food safety problems due to pesticide residues (Caria et al., 2021; Loganathan & Murugan, 2017). There are many kinds of pesticide, including organophosphorus pesticides, organic nitrogen pesticides (carbamate, triazine and its derivatives). Among them, organophosphorus and organic nitrogen pesticides have occupied the vast majority of the market because of their short half-life in the environment, relatively low toxicity to mammals, wide range of application and low price. As is known to all, residual pesticides are toxic, which can cause various chronic or acute poisoning, leading to physiological diseases such as rashes, asthma, chronic diseases, and neurological diseases (Calaf et al., 2021; Freire & Koifman, 2012; Li et al., 2021; Steenland et al., 1994; Upadhayay et al., 2020; Yu et al., 2021). Therefore, to ensure the quality and safety of agricultural products, efficient and rapid pesticide residue detection methods are researched (Wu et al., 2021). Traditional detection methods include chromatography, chromatography-tandem mass spectrometry and high-performance liquid chromatography and so on (Golge, 2021). They can be the preferred detection methods in the formulation of national standards for pesticide detection in many countries because of the high repeatability and stable test results. However, these methods need large detection equipment and specific operating environment, which are not suitable for the practical production requirements for the rapid field test.

In recent decades, a variety of low time-consuming, convenient and rapid detection methods developed, including but not limited to new chromatographic analysis, enzyme inhibition, fluorescence sensor, spectrophotometric and biosensor detection technology (Ninga et al., 2021; Rojas et al., 2021; Saegusa et al., 2021). What's more, these technologies have made great breakthroughs on the basis of each one, and various rapid detection technologies tend to be more and more cross-fusion, mutual penetration and advantages superposition (Hao & Wang, 2016). With the rapid development of nanomaterials, multi-cross rapid detection technologies based on nanomaterials have a great breakthrough in sensor technology improvement, and biosensor technology has a huge development advantage in rapid detection technology (He et al., 2019; Lei et al., 2018; Lu et al., 2018; Wu et al. 2017).

Current rapid detection technology of pesticides

1. Chromatographic detection techniques

Chromatography, which is highly sensitive and mature, mainly include gas chromatography, gas chromatography-mass spectrometry, high performance liquid chromatography and other technologies (Hao et al, 2010; Tong et al., 2014; Wu et al., 2009). Although their disadvantage like expensive equipment requirement, high technical personnel, complex pretreatment and testing time, cross-fusion of rapid detection technologies make these methods showing great potential in the market for rapid detection recently. Khan (Khan et al., 2018) proposed a pressurized liquid extraction by ethyl acetate based method for simultaneous analysis of different pesticide residues in tuber crops, and then selectively identified and quantified the residuals by GC-MS selected reaction monitoring. They got the limits of quantification with 0.1–10 ng/g, and recovery rate from 70 % to 120 %.

Chromatographic detection technique is mainly used in laboratory precision detection. This technology shows high selectivity for organophosphorus pesticides, but its scope of action is relatively limited. The current research directions are mostly focused on improving pretreatment technology, enrichment methods and extraction methods. In other aspects, the method for rapid detection in the market needs to be further improved.

2. Enzyme inhibition detection techniques

Enzyme inhibition rapid detection method is based on the inhibitory effect of pesticide residues in food on enzyme. This technology has the advantages of simple and quick operation and simple pretreatment, and a variety of simple instruments have been developed for rapid detection in the market currently. However, this method has great limitations, and with poor stability due to many factors to be controlled (Gumpu et al., 2017; Li et al., 2019). So, there are a large room for improvement in sensitivity and accuracy. Through the effective combination with the biosensor technology, the sensitivity and accuracy of the enzyme inhibition technology have been greatly improved. After the fusion, the enzyme inhibition method with the biosensor technology is more suitable for rapid detection (Badawy, 2021; Singh et al., 2020). The rapid detection principle of enzyme inhibition method is relatively simple. By organophosphorus pesticides inhibiting the activity of acetylcholinesterase, the catalytic process can produce less H_2O_2, and the oxidation ability can be reduced, resulting in visible discoloration reaction of the substrate (Albendin et al., 2021; Lin et al., 2021). The intensity of colorimetric signal is an important factor in the research of enzyme inhibition method to realize the real visual detection. Yang (Yang et al., 2019) proposed an enzyme inhibition method to detect the pesticide residues of the milk. He established a system to study the inhibitory reactions of organic phosphorus and aminoformate residues in milk. The analysis of color reactions of milk showed a good correlation between color intensity and content of tolclofos-methyl, methamidophos and isoprocarb 1-naphthalenyl methyl carbamate, and the detection range of four kinds of pesticides is 0.5 ~ 1.0 mg/kg.

By combining with the biological sensing technology, the application scope of the enzyme inhibition method is expanded, and the enzyme sensitivity is enhanced. Enzyme inhibition sensor is one of the most widely used rapid detection technique in the current rapid detection market, but there are still many problems with its own (Wu et al., 2019). Recently, many researchers study the selective purification of enzyme, effective oxidation pretreatment, colorimetric signal enhancement and false positives elimination. The sensitivity of enzyme inhibition method is influenced by the purity of the enzyme, the concentration of substrate and environmental factors, etc., and the stability and sensitivity of the enzyme suppression method are need to be higher (Arduini et al., 2019; Pundir et al., 2019; Sgobbi & Machado, 2018).

3. Fluorescence detection techniques

Fluorescence detection method is based on the different material molecules, the different absorption and reaction of light wavelength. This technology has high sensitivity, but it is limited to the luminous pesticide, and the non-luminous pesticide still needs to be added with fluorescent agent, and is susceptible to the interference of external factors, with poor adaptability (Ouyang et al., 2021; Wang et al., 2021). In recent years, through the fusion of biosensors, this detection technology has also made great progress (Chen et al, 2021; Han et al., 2021; Liang et al., 2021; Lin et al., 2021). The fluorescence sensor has the advantages of simple operation, quick response, high sensitivity and good reproducibility. The fluorescence sensor consists of two parts: the fluorescence signal element and the recognition element. Enzymes, antibodies, aptamers and molecularly imprinted polymers (MIP) are combined with nanomaterials to further enrich the types of fluorescence sensors (Zhou et al., 2018). Carbon Quantum Dots (CQDs) have been proposed as the photo-sensitizer for this purpose, however the optical properties of pure CQDs restrict the detection limit of such an approach. Doping is an effective strategy to introduce novel electronic structure into the CQDs to solve this problem. using ionic liquids as a single source, H. Li (Li et al., 2016) proposed a novel N and S co-doped CQDs by a simple ultrasonic method. The doping in the structure introduces localized states which can trap photo-excited electrons and enhance their PL lifetime. These quantum dots are successfully used as the basis of a simple, efficient sensor for ultrasensitive pesticide detection (Limit of Detection = 5 ppb). J. Hou (Hou et al., 2015) used tyrosinase to catalyze the oxidation of tyrosine methyl ester on the surface of carbon dots to corresponding quinone products, which can quench the fluorescence of carbon dots, and the enzyme inhibition rate is proportional to the logarithm of the methyl parathion concentration in the range 1.0×10^{-10}–1.0×10^{-4} M with the detection limit (S/N = 3) of 4.8×10^{-11} M.

The combination of fluorescence detection method and biosensor method has greatly promoted the rapid detection of pesticide residues (Hou et al., 2015; Long et al, 2015; Meng et al., 2013; Upadhyayula, 2012). Q. Luo (Luo et al., 2018) proposed a simple method for the preparation of highly selective and sensitive fluorescent probes based on Rhodamine B (RB) modified silver/gold bimetal nanoparticles (RB-Ag/Au NPs). Because that the coordination ability of Ag/Au NPs and organophosphorus pesticides (Ops) is stronger than that of Ag/Au NPs and RB, RB will be displaced from the Ag/Au NPs surface, accompanied by the fluorescence recovery of RB. It can be applied to the determination of OPs in real fruit and water samples with the limit of detection (LOD) as low as 0.0018 ng/mL.

4. Spectrophotometric colorimetry techniques

Colorimetry determines the content of components to be measured by measuring the color depth of colored substance solution (Kostelnik & Pohanka, 2018; Liu et al., 2012). This method has high sensitivity and selectivity, and the reaction product is stable. In recent years, more and more researchers have combined spectrophotometric colorimetry with new sensors, and the newly emerging sensing materials have greatly improved the detection sensitivity of spectrophotometric technology. A. Kodir (Kodir et al., 2016) developed a novel pesticide colorimetric sensor based on L-cysteine-modified silver nanoparticles (L-cys-AgNPs). By reducing the silver nitrate solution in the presence of Diospyros blancoi leaf infusion, and then mixing with the l-cysteine solution, the colorimetric sensor was prepared. In the presence of cypermethrin, the color of l-cys-agnps was obvious, and the peak absorbance decreased from 1.15 to 0.17.

The optical colorimetric sensor synthesized from gold nanoparticles has high sensitivity (Li, et al., 2018). Moreover, the gold nanoparticles are stable, and the reaction with pesticides can make the gold nanoparticles aggregate and produce visible color changes (Bettazzi et al., 2021; Hua et al., 2021; Ma et al., 2021; Vilian et al., 2021; Wang et al., 2021). Using this principle, Bala (Bala et al., 2016) built a colorimetric apparatus based on gold nanoparticles to measure the phosphorous in a mixture. The results showed that the linear relationship was good within the concentration range of the uv-vis wavelength from 0.01 nm to 1.3 mm, and the detection limit was 1.3 mm, indicating a high sensitivity. Recently, biosensors based on nanomaterials have developed rapidly in pesticide detection, and more and more new nanomaterials have been used to prepare electrochemical biosensors. By Introduction of nanomaterials It greatly promoted the development of the biosensor technology, and with the progress of material science, all kinds of polymer and nano materials combine to form nanocomposites are also solved the traditional biological sensing technology stability and sensitivity is not high question, nanometer materials to make biological sensing technology has entered a new period of development.

5. Biosensor techniques

Biosensor techniques generally use enzymes, antigens, antibodies, cells and other active sensitive materials as recognition elements (Silva et al., 2020; Tang et al., 2020). The change in concentration will be converted into electrical signals after recognition and then displayed and recorded by amplification. Recently, biosensors based on nanomaterials have developed rapidly in pesticide detection, and more and more new nanomaterials have been used to prepare electrochemical biosensors, which greatly promoted the development of the biosensor technology (Akdag et al., 2020; Ayat et al., 2021; Chouichit et al., 2020; Jain et al., 2021; Lah et al., 2021). Although the stability and sensitivity of traditional biosensors technology is not high, all kinds of polymer and nanomaterials combine to form nanocomposites have solved these questions.

The electrochemical biosensor based on the inhibition of acetylcholinesterase is a promising method for the detection of organophosphorus. The irreversible oxidation peak of the active product thiocholine is an important marker for the detection of organophosphorus (Alex & Mukherjee, 2021; Cao et al., 2020; Caratelli et al., 2020; Davletshina et al., 2020; Silva et al., 2020; Singh et al., 2020). Different from traditional organophosphorus detection methods, this method does not need expensive experimental equipment and well-trained technicians, and the detection cost is low and efficient. To improve sensor sensitivity and reduce detection limits, the researchers used different nanomaterials in the sensor, such as Au nanoparticles (Li & He, 2021; Lipinska et al., 2021; Rashed et al., 2021; Yang et al., 2021), carbon nanotubes (Kathiresan et al., 2021; Li et al., 2021; Qian et al. 2021; Rashid et al., 2021; Siew et al. 2021), graphene (Gan et al., 2021; Rashid et al., 2021; Siew et al., 2021; Sun et al., 2021; Zhou et al., 2021) and magnetic nanomaterials (Da Silva & Brett, 2020; Lu et al., 2020; Shen et al., 2021). The large specific surface area and easy modification characteristics of nanomaterials provide more active sites on the electrode surface, which is more conducive to full contact with the reactants, thus providing detectable electrical signals. Zhao (Zhao et al., 2015) constructed an ultra-sensitive current sensor by using Au nanoparticles (AuNPs)-β-cyclodextrin (β-CD) and Prussian blue-chitosan (PB-CS) and acetylcholinesterase(AChE), and realized the high sensitivity detection of malathion and carbaryl through the synergic action of multiple components, with detection limit as low as 4.14 pg/mL and 1.15 pg/mL, respectively. By cross-linking acetylcholinesterase onto the IL-GR/Co3O4 / CHI electrode constructed from ionic liquid modified graphene (IL-GR) and Co3O4 nanoparticles, Y. Zheng (Zheng et al., 2016) was able to effectively reduce the loss of enzyme activity and improve the detection sensitivity. A linear relationship between the inhibition percentage (I%) and logarithm of the concentration of dimethoate was found in the range from 5.0×10^{-12} to 1.0×10^{-7} M, with a detection limit of 1.0×10^{-13} M (S/N = 3).

In order to further enhance the stability of the biosensors, a nanocomposite material which can significantly enhance the mechanical strength of each component is formed by introducing a polymer into the nanometer material (Bagheri et al., 2017; Cinti et al., 2016; Guler et al., 2017; Huang et al., 2010; Huo et al., 2014; Jeyapragasam & Saraswathi, 2014; Wei & Wang, 2015; Zheng et al., 2015). New biosensors have developed rapidly, and the stability and sensitivity of all kinds of biosensors have been greatly improved, but they are only used for single pesticide and the detection range still is very small. So, they can't be widely used for the rapid detection of a variety of organophosphorus pesticides on the market. The development of nanometer materials made great progress for biological sensor technology in sensitivity and stability, which has significantly outpaced the development of other rapid detection technologies (Jiang et al., 2020; Wang et al., 2016). Therefore, the cross-fusion detection methods combining with biosensor and other rapid detection technologies retain the development advantages, and overcome many limiting factors in the rapid detection technology, making the rapid detection technology develop rapidly and become perfect.

Conclusions. In recent years, with the improvement of market requirements for the rapid detection technology of pesticides, organophosphorus pesticides, as an important part of the pesticide market, whose development speed of the rapid detection technology is very rapid. There are a wide variety of traditional detection technologies for pesticide, and each of them have own pros and cons, with development difficulties (Chen et al., 2021; C. J. Li et al., 2021; J. J. Li et al., 2021; Liang et al., 2021; Lin et al., 2021; Teysseire et al., 2021). At present, the rapid detection methods in the pesticide market tend to be more and more cross-fusion with various detection technologies. With the progress of science and technology, the development of new nanomaterials also makes great contributions to the improvement of rapid detection technology. Especially for the biosensor technology, who highly require for new material, the development of nanomaterials directly promotes the progress of this technology (Burratti et al., 2021; Du et al., 2021; M. Li et al., 2021; Ren et al., 2021; X. Y. Zhou et al., 2021). As the cross-fusion of a variety of rapid detection technologies, biosensor technology shows strong combination, and is suitable for a variety of rapid detection method of combining. Through the combination of biosensor detection technology and other rapid detection technologies, many difficulties in the development of rapid detection technology have been overcome. The advantages of rapid detection technology, such as enzyme inhibition detection technology, fluorescence detection and spectrophotometric detection technology, have been amplified, therefore the rapid detection techniques become more extensive and faster (Badawy, 2021; Cao et al., 2020; Singh et al., 2020; Q. S. Wei et al., 2020; N. Yang et al., 2020).

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ДОСЛІДЖЕННЯ ПРОЦЕСУ ШВИДКОГО ВИЗНАЧЕННЯ ЗАЛИШКІВ ПЕСТИЦИДІВ В ОВОЧАХ ТА ФРУКТАХ

Зі збільшенням попиту на виробництво сільськогосподарської продукції, збільшується використання пестицидів, які на сьогоднішній день забезпечують збереження врожаю фруктів та овочів. Пестициди використовують для контролю чисельності шкідливих організмів, забезпечуючи тим самим оптимальні умови для росту та розвитку сільськогосподарських культур. Сучасне виробництво сільськогосподарської продукції неможливе без застосування пестицидів. Але зловживання під час використання пестицидів завдає шкоди навколишньому середовищу та здоров'ю людей, особливо внаслідок