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Recent advances in rapid detection techniques for pesticide residue: A review

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Abstract

As an important chemical pollutant affecting the safety of agricultural products, the on-site and efficient detection of pesticide residues has become a global trend and hotspot in research. These methodologies were developed for simplicity, high sensitivity, and multiresidue detection. This review introduces the currently available technologies based on electrochemistry, optical analysis, biotechnology, and some innovative and novel technologies for the rapid detection of pesticide residues, focusing on the characteristics, research status, and application of the most innovative and novel technologies, including enzyme biosensors, immunosensors, aptamer sensors, cell and microbial sensors, surface-enhanced Raman spectroscopy, microfluidic technology, and immunoassays, in the past 10 years, and analyzes challenges and future development prospects. The current review could be a good reference for researchers to choose the appropriate research direction in pesticide residue detection.

Keywords

agricultural products; pesticide residues; rapid detection technology; recent trends

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Declaration of competing interest

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1. Introduction

Pesticides are chemical substances used for pest control, including common rodents, insects, and fungi, or to remove weeds. They are classified into rodenticides, insecticides, fungicides, and herbicides, depending on the target organism. Weeds, pests and/or diseases can seriously reduce the yield and quality of crops. Pesticides are tools for protecting crops before and after harvest. Their use may result in residues (parent and/or active substances of degradation products), which appear in the processed commodities and eventually in the food chain. [1] Pesticides are used to ensure that the agricultural output meets the needs of growing populations worldwide.[2] Over the past few decades, large amounts of pesticides have been routinely used by farmers worldwide. With this widespread use, the nonstandard use and abuse of pesticides occurs occasionally, resulting in pesticide residues that remain on or in food after they are applied, which poses a serious threat to human health and to the environment.[3] The abuse of toxic pesticides can also damage the balance of the ecosystem and, as an indirect consequence, can result in the death of the natural predators of pests and impact the food chain.[4,5] Certain pests also eventually gain resistance to pesticides.[6] The development of resistance is exacerbated by overusing and misusing pesticides.

Residual pesticides and their metabolites can be transferred to and migrated within the food chain through enrichment and bioaccumulation, thus adversely affecting the quality and safety of agricultural products, harming the environment and endangering human health.[7] The quality and safety of agricultural products are essential for health, stability and meeting sustainable development goals. To protect the health of the population, the Codex Alimentarius Commission and the EU have formulated a series of standards limiting the amount of pesticide residue in fresh produce. Careful monitoring and strict implementation are important to ensure that only permitted levels of pesticide residues and their metabolites are consumed. Conventional methods for pesticide residue and metabolite detection mainly include gas chromatography, high-performance liquid chromatography, and chromatography-mass spectrometry. These detection methods have good sensitivity, accuracy, precision, and reliability. However, their disadvantages include complex sample processing and pretreatment, high costs, the need for trained personnel, and the time taken for detection.[8] These methods fall short of meeting the practical needs of the industry: fast, real-time, and low-cost detection. It is therefore necessary to develop technologies for the rapid detection of pesticide residues.

Any method used for on-site screening should be easy to operate, high-throughput, and cost-effective, with sufficient sensitivity and a low false negative rate. Rapid pesticide residue detection technologies are quick and low-cost methods that can be used as a supplement to conventional technologies. This review examines the progress in research on rapid detection technology of pesticide residues in the past decade, focusing on the characteristics, research status, and application of the most innovative and novel technologies. It also discusses the challenges faced in the implementation of these technologies and possible research directions for the future.

2. Rapid detection technology

2.1 Rapid detection technology based on electrochemistry

Biosensors are analytical devices that combine biological source-sensing components with physical and chemical transducers and can perform quantitative or semiquantitative analyses.[9] They are highly sensitive sensors that convert biological signals into electrical signals. Examples of biosensors include colorimetric, electrochemical, fluorescent biosensors and those based on Raman spectroscopy.[10] Biosensors are used in the detection of many food and agricultural products because of their simplicity and sensitivity. Common biosensors, such as electrochemical biosensors, can determine the degree of enzyme inhibition by fluctuations in current signals generated before and after the reaction between the enzyme fixed on the electrode and the substrate. The degree of inhibition is linearly related to pesticide concentration within a certain concentration range, and this relationship is exploited to detect pesticide residues.[11] The basic principle behind biosensor application is that it can interact specifically with the target analyte to produce a signal change proportional to the intensity and concentration of the target analyte. Then, the concentration of the target analyte can be determined from the sensor measurement signal. In general, biosensors can be classified based on biomaterial or sensor usage. Examples of biosensors that use biological elements for analysis include enzyme sensors[12], immunosensors,[13] aptamer sensors[14], cell-based biosensors[15], and microbial sensors[16], and those sensors that use different sensors include electrochemical sensors[17], optical sensors[18], pressure sensors[19], and thermal sensors[20]. Different biosensors have different physical and chemical properties and can have specific effects on the target to identify it and generate signals for analysis. The principle of detection of biosensors is shown in Figure 1. Compared to traditional instruments, electrochemical biosensors have a rapid response, low detection limit and good selectivity,[21] and in recent years, there have been a large number of studies on them. Different biosensors have been combined with sensors to develop biosensors with high sensitivity, high selectivity, simple operation and low cost for the rapid detection of pesticide residues.[22,23]

2.1.1 Enzyme biosensor—Enzyme biosensors employ the principle of enzyme inhibition. These sensors determine the inhibitory effect of pesticides on enzyme activity by analyzing the rate of the catalytic reaction to determine the concentration of pesticide residue. This method is effective because many pesticides work by affecting the activity of a specific or nonspecific enzyme in the pest to produce a toxic effect. The enzyme inhibition method cannot identify specific types of pesticides, and the agricultural product itself may interfere with the detection process, resulting in false positive or negative results. To overcome the limitations of traditional enzyme inhibition methods for detecting pesticide residues, researchers have developed an enzyme-based biosensor technology. In a biosensor, the changes in enzyme activity are measured by the sensor, and the data allow the researcher to estimate the quantity of enzyme inhibitors. Electrochemical enzyme sensors typically use nanomaterials because they are biocompatible, can bind to enzymes and are capable of transferring electrons.[24]

2.1.2 Immunosensor—Immunosensors are biosensors based on immunoassay technology that detect the signal generated by the specific interaction between the antigen and antibody and transform them for quantitative detection. Compared to traditional immunoassay technology, immunosensors can perform rapid, sensitive, and specific quantitative analyses. The application of immunosensors in pesticide detection has been studied extensively and developed.[25] To meet the trace-level detection standard needed for pesticide residues, a series of new materials were used by researchers to modify the electrode and improve the detection ability. This immunosensor has strong specificity and ideally can detect the concentration of a pesticide. However, pesticide-specific antibodies are not usually commercially available, and the process of developing new pesticide antibodies is complex, making immunosensors impractical for commercial detection. In addition, the effectivity of immunosensors for the real-time detection of pesticide residues has yet to be confirmed.

2.1.3 Aptamer sensor—Aptamers are single-stranded oligonucleotide sequences that can bind specifically to target molecules, including single-stranded DNA and RNA. Aptamers can form three-dimensional structures with special conformations by base pairing, hydrogen bonding, van der Waals forces, hydrophobic interactions, and other forces in the chain and bind specifically to target molecules. For a target molecule, the selection of aptamers is made possible through the systematic evolution of ligands by exponential enrichment (SELEX). The target molecule is added to a random, synthetic, single-stranded nucleic acid library, while the uncombined nucleic acids are washed away. The nucleic acid that specifically binds to the target molecule is amplified by polymerase chain reaction (PCR) and further enriched with the target molecule until the nucleic acid fragment with the strongest binding affinity is obtained.[26] Aptamers have several advantages; they are able to bind to several types of target molecules and often have highly specific binding and strong affinity to target molecules. They are widely used in the food safety sector.[27]

2.1.4 Cell and microbial sensors—Cells can be used as target molecular recognition elements in biosensors for pesticide detection because of their diverse biological activities. Many pesticides, such as fungicides, inhibit cell activity, while some unicellular organisms, such as luminescent bacteria, can quantify changes in cell activity through changes in luminescence intensity, thus allowing for the quantitative detection of cell activity inhibitors.[28] Moreover, some bacteria contain enzymes that can degrade pesticides; the contents of these pesticides can be determined by detecting these degradation products.[29]

2.2 Rapid detection technology based on optical analysis

2.2.1 Surface-enhanced Raman spectroscopy—Raman scattering was first discovered by the Indian physicist Raman[30], who won the Nobel Prize in physics. With the improvement of laser excitation efficiency, the detection light source has become more ideal, and research on Raman scattering has entered a new era. Raman scattering is a kind of inelastic scattering of light. After monochromatic light irradiates molecules, the interaction between light and chemical bond vibrations in molecules changes the energy of some of the scattered light, thus providing information on the chemical bond vibrations in molecules.[31] The Raman spectrum can identify substances by recording the characteristic

Raman peaks of substances. The Raman scattering effect of molecules is relatively weak, so it is important to enhance the Raman signal to apply it to the quantitative detection of trace substances. Fleischmann et al. discovered the surface-enhanced Raman scattering (SERS) effect in 1974;[32] when pyridine molecules were adsorbed on the surface of a rough silver electrode, the Raman signal was enhanced approximately 10^6 times. This discovery laid a foundation for the quantitative detection of trace substances by Raman spectroscopy. Since then, the development of various new Raman signal enhancement substrates has improved the analytical ability of Raman spectroscopy and expanded its application in the field of pesticide residue detection.

The assembly process of the SERS substrate is complex. At present, metal nanomaterial substrates have been used successfully in the detection of SERS residues on the surface of fruits and vegetables. However, the manufacturing process of these substrates is complex, and the cost is high, which is not conducive to popularization and promotion. For the preparation of metal nanomaterials with high structure, distribution, and stability for SERS substrates, it is very important to improve the sensitivity and repeatability of detection. Therefore, the development of a flexible and convenient technology for the preparation of SERS substrates would be of great significance.

At present, most of the quantitative analysis of pesticide residues on the surface of fruits and vegetables by SERS detection technology is based on the linear quantification of a single characteristic peak of pesticides. However, in the actual detection process, the Raman characteristic peak of pesticide pollutants is prone to shift slightly due to the influence of nonlinear factors such as instrument and environmental noise. Thus, in practice, the quantitative accuracy of the method will be affected. This accuracy could be improved with the help of multivariable and nonlinear modeling.

2.2.2 Near-infrared spectroscopy—Near-infrared (NIR) is a kind of electromagnetic wave whose wavelength lies between visible and mid infrared light. The wavelength range is 780–2526 nm, and the corresponding wavenumber range is 12820–3959 cm^{-1}. The infrared light absorption in this region mainly comes from the frequency doubling and frequency combining effects of hydrogen-containing chemical bond vibrations such as O-H, N-H, and C-H. The identification and quantitative analysis of samples can be done by detecting the absorption of samples to different frequencies of near-infrared light and determining the change in the characteristic absorption value of samples.

2.2.3 Terahertz time domain spectroscopy—Terahertz (T*Hz*) radiation is an electromagnetic radiation region with frequencies ranging from 0.1 – 10 T*Hz* in the electromagnetic spectrum. The corresponding molecular vibration absorption mainly represents weak interactions between molecules, such as hydrogen bonds, van der Waals forces, and low-frequency vibrations of lattices, as well as the collective vibration mode of biological macromolecular configurations. These absorption effects will produce an evident response in the terahertz band, which can be used for molecular structure and configuration information. Terahertz time domain spectroscopy is a far-infrared spectral technology based on terahertz radiation. It determines molecular structure information by detecting the absorption of terahertz radiation of different frequencies. The photoelectric

detection technology used in the terahertz spectrum can measure the amplitude, phase and intensity of the terahertz electric field and is insensitive to background thermal radiation, with a signal-to-noise ratio of 10^{10}.[33]

2.2.4 Laser-induced breakdown spectroscopy—Laser-induced breakdown spectroscopy (LIBS) is a kind of atomic emission spectroscopy. After an ultrashort pulse laser beam is focused on the sample surface, the sample is gasified and excited to generate plasma. Since the excitation light of different elements has a certain characteristic frequency, the composition of the elements in the sample can be identified by recording the spectral information of the plasma emission light, and the identification of all elements can be realized theoretically.[34] LIBS technology has been widely used in the field of food analysis.[35]

2.2.5 Chemiluminescence—Chemiluminescence (CL) is a kind of light radiation effect produced in chemical reactions. When a chemical reaction produces a substance in an excited state, the energy of the substance will be released in the form of photons that produce light when it returns to the ground state.[36] Under certain chemical reaction conditions, the quantitative analysis of the substance to be measured can be carried out by measuring luminous intensity with a photomultiplier tube. Chemiluminescence has the advantages of small background signal interference, good specificity, high sensitivity, and a wide linear range.

Traditional chemiluminescence systems have poor efficiency in converting chemical energy into light energy. A catalyst, such as a natural enzyme or a nanocatalyst, with superior performance is usually needed to enhance the CL signal to improve detection sensitivity. Natural enzymes can have high catalytic activity, but they also have the disadvantages of high cost and poor stability. These limitations are increasingly being overcome with protein engineering and recombinant production.

2.3 Microfluidic technology

Microfluidics, also known as lab-on-a-chip, refers to a series of analytical chemical operations, such as purification, reaction, separation, and detection of fluids, by integrating various functional units in submillimeter microchannels. Microfluidic technology concentrates a variety of separation and analysis processes on a small chip (i.e., 1 cm^2), which can realize the automation of chemical analysis. It is capable of high integration, high throughput, and low consumption. It has wide application prospects and practical significance in the field of pollutant detection.[37]

2.4 Open mass spectrometry ion source and real-time direct analysis mass spectrometry

As a highly sensitive analytical method, mass spectrometry has been widely used in the detection of pesticide residues.[38,39] In the process of mass spectrometry detection, it is necessary to ionize the substance to be measured and determine the mass-charge ratio of ions to achieve qualitative and quantitative detection. However, conventional ion sources, such as electrospray ion sources and atmospheric pressure chemical ion sources, need to be carried out in a high vacuum environment, which is a closed structure. In conventional

mass spectrometry, extensive sample pretreatment is often required to prevent interference by the complex sample matrix. For high sensitivity, multiple technologies are being used to increase selectivity and signal-to-noise, reducing the need for extensive sample preparation.

2.5 Rapid detection of pesticide residues based on biotechnology

This paper mainly discusses the rapid detection of pesticide residues based on biotechnology, including the enzyme inhibition method and immunochemical analysis techniques. The developmental history of the rapid detection of pesticide residues based on biotechnology is shown in Figure 2.

2.5.1 Enzyme inhibition method—Enzyme inhibition methods involve quantifying the extent to which acetylcholinesterase (AChE) reduces the production of thiocholine to detect residual levels of organophosphate (OP) and carbamate pesticides. These are usually colorimetric, fluorescent or biosensor methods. Enzyme activity can be measured according to the intensity of the color. Other natural enzymes that can be used for enzyme inhibition assays include butylcholinesterase, carboxylesterase, alkaline phosphatase (ALP), and tyrosinase. OP and carbamate pesticides inhibit these enzymes, allowing the detection of residues by measuring the hydrolysis ability of enzymes. Some synthases have also been proposed for inhibition tests.[54]

2.5.2 Immunochemical analysis technique—After decades of development, immunochemical analysis has become an important research method for detection in the fields of biology, medicine, and other disciplines. The existing immunoassay methods can be divided into homogeneous immunoassays and heterogeneous immunoassays according to the physical state of the reaction system and whether it is necessary to separate the bound and free markers in the determination process. In the process of homogeneous immunoassay, the substance to be tested is directly determined after mixing with relevant detection reagents, which requires high sensitivity of the reaction. However, the reaction process does not require solid-phase participation. The reaction speed is fast, and the operation is simple. Among them, homogeneous fluorescent immunoassays are the most widely used. In contrast, heterogeneous immunoassays require that after the reaction, the substance to be tested and the reaction system need to be separated for detection. The latter is the mainstream method currently used among immunoassay methods. The technique mainly includes enzyme-linked immunosorbent assay (ELISA) and chemiluminescence immunoassay (CLIA), replacing the original radioimmunoassay technique.[55] Compared with homogeneous immunoassays, heterogeneous immunoassays involve the combination of solid carriers and cleaning and separation, which is cumbersome and time-consuming but often at least semiautomoted. However, they improve the sensitivity of the reaction and are suitable for the detection of trace substances. [56–60]

2.5.2.1 Detection technology based on ELISA: ELISA is the most commonly used heterogeneous immunoassay at present. This method has three necessary reagents: (1) antigen or antibody coated on the solid phase, namely, “immunosorbent”; (2) enzyme-labeled antigens or antibodies called “enzyme conjugates”; and (3) a chromogenic agent for enzymatic color reaction.

ELISA developed by Voller[61] was preceded by the highly sensitive radioimmunoassay (RIA) of Benson and Yallow.[55] Although more sensitive in theory and usually in practice, particularly for small molecule analyses, such as pesticides. The increasing regulatory costs and perceived health risks largely led to the replacement of RIAs to avoid handling radioactive elements. For proteins, ELISA and similar technologies have almost reached the sensitivity of RIA for proteins. Since most pesticides are small molecules, a hapten mimicking the pesticide must be coupled to a protein to raise antibodies. This often results in some recognition by the resulting antibody of the handle between the pesticide immunizing hapten and the carrier protein and sometimes even the structure of the pesticide hapten. This requires the design of a reporter hapten for the pesticide. The better the reporter hapten binds to the antibody, the more sensitive the assay until the point is reached where the free pesticide analyte cannot compete with the reporter hapten. In this case, the sensitivity drops dramatically. This situation is easily handled if one uses a radioactive tracer that is chemically identical to the target pesticide, but the use of heterologous reporter haptens often requires extensive synthesis and limits the sensitivity of the resulting ELISA. Thus, Rosylyn Yallow often pointed out this severe limitation of ELISA and similar technologies not using endogenous labels.

For RIA, decays of a radioactive element are detected with the theoretical sensitivity of the assay increasing as the square root of the specific activity of the tracer. Shan et al. used a different reporter technology based on the development of a technology called accelerator mass spectrometry (AMS) originally developed to remotely monitor nuclear weapons testing. [55] This technology was then adapted to a variety of biological questions, such as carbon dating. In RIA, energy from decomposition of radioactive elements was used for detection; in AMS, the mass of the molecule was used. Most AMS target elements are radioactive because the sensitivity of AMS depends upon the low abundance of the tracer, and natural low abundance elements are usually radioactive. Thus, with AMS, one can monitor the weight of molecules labeled with ^{14}C to obtain subattomole sensitivity. Thus, the theoretical sensitivity of AMS detection is limited by the very low abundance of the ^{14}C tracer (^{13}C is far too abundant to offer an advantage in AMS). This results in assays whose sensitivity is dependent upon the Kd of the antibody and no longer on the tracer. At the time that Shan and coworkers published their work on ‘isotope-labeled immunoassays without radiation waste’, the few AMS instruments in the world were massive and expensive. With the advent of microdosing and other uses of AMS and advances in the field, this instrumentation has reduced dramatically in cost and size. The use of endogenous labels such as ^{14}C allows running assays orders of magnitude lower than ^{14}C that can be detected by current laboratory instruments other than AMS and well below regulatory limits. Since ^{14}C labels are required by the FDA and EPA for registration of pesticides and pharmaceutical AMS technology for immunoassay is becoming more attractive with the massive advantage of using endogenous labels and avoiding hapten and linker recognition.

ELISA is a classical technology in immunology and a mature and commonly used rapid detection method. It involves the binding of a specific antigen or target antibody to a solid carrier, such as polystyrene. After the specific antigen-antibody binding reaction, an enzyme-targeted secondary antibody that recognizes the target antibody is added. After

the excess secondary antibody was washed off, the peroxidase indirectly labeled on the antibody was used for the substrate catalytic reaction. Then, the relationship between the absorbance of the product solution and the concentration of the target substance is analyzed, and qualitative judgment and quantitative detection are performed. It can be divided into indirect and direct competition modes according to whether the labeled second antibody is used. Indirect and direct competitive enzyme-linked immunoassay (ELISA) modes are shown in Figure 3. The advantage of the indirect mode is that the same enzyme-labeled secondary antibody can be used to detect different antibodies as long as the coating antigen is changed. Its disadvantage is that there are many detection steps and long detection times. The advantage of the direct mode is that it does not need a second detection step using antibodies, has fewer operation steps and has a shorter detection time. However, in the direct mode, different detection objects need to be marked or labeled before the direct mode detection method can be established. Pesticides and other small molecule chemicals are single epitope analytes, and the whole molecule can only bind to one antibody. Therefore, most of the immunoassays of pesticides and other small molecule compounds use the competitive model. The reason is that the noncompetitive mode generally requires that the antigen contains two or more nonoverlapping antigenic determinants; that is, the antibody of one antigenic determinant is fixed on the solid-phase carrier for binding to the target antigen, and the other antibody with a signal label is used to detect the amount of antigen bound by the solid-phase carrier. However, the vast majority of pesticides and other small molecular compounds will be engulfed by the binding site of the antibody after binding with the antibody, so they cannot be directly recognized by the second antibody. With a large pesticide molecule, such as rotenone or spinosad, there is the possibility of recognizing two separate faces of the pesticides by separate antibodies allowing a sandwich-type assay. Detection kits developed based on the principle of ELISA have been recognized and praised by many scientific researchers because of their strong specificity, high sensitivity, and good repeatability. They have been widely used in medical diagnosis, food safety supervision, environmental monitoring, and other fields.

2.5.2.2 Fluorescence immunoassay: Fluorescence immunoassays (FIAs) based on fluorescent tracers are one of the earliest immunoassays. FIAs use fluorescent substances as markers, and the binding reaction of antigen and antibody leads to a change in fluorescence intensity, which helps determine the quantity of the target analyte. The immunofluorescence technique has been applied to the determination of trace and ultratrace substances. According to different labeled substances and reaction systems, fluorescent immunoassay methods mainly include immunofluorescence assays (IFMA), fluorescence polarization immunoassays (FPIA), time-resolved fluorescence immunoassays (TRFIA), fluorescence resonance energy transfer immunoassays (FRETIA) and multianalyze immunoassays (MAIA).

1) Time-resolved fluoroimmunoassay: TRFIA is a promising nonradioimmunoassay method developed in the early 1980s. TRFIA uses lanthanide elements as markers to effectively eliminate the interference of the natural fluorescence background in conventional FIA analysis based on the difference in fluorescence attenuation time between TRFIA and biological samples, improve the signal-to-noise ratio, and improve the analytical sensitivity.

It is considered to be the most sensitive heterogeneous FIA at present. Because of the characteristics of the labeled substance, TRFIA has the advantages of high sensitivity and low interference. However, the high price of the TRFIA instrument limits its practical application in agricultural products and other samples with low added value to a certain extent. This technology has the advantage that it creates no radioactive contamination, has a longer validity period, has a wide range of applications, is easy to prepare and is suitable for a large number of samples and a wide range of standard curves. The research and application of this technology have developed rapidly.

2) Fluorescence polarization immunoassay: FPIA is an immunoassay method that, for example, uses fluorescein isothiocyanate, dichlorotriazinylaminofluorescein, and fluorescein as fluorescent markers. The fluorescently labeled small molecule antigen rotates rapidly in the solution, and its fluorescence polarization intensity is small. When the fluorescently labeled antigen is combined with its antibody, the rotation speed of the formed macromolecule in the solution becomes slower, and the fluorescence polarization intensity increases. According to the difference in fluorescence polarization between the antigen and its antigen antibody conjugate, FPIA directly determines the content of small molecules in the solution by a competitive method. Since the molecular weight of the antibody is much greater than that of the detected substance and the polarization fluorescence intensity produced by the free fluorescent labeled substance and the fluorescent labeled substance binding to the antibody is very different, the polarization fluorescence intensity measured in FPLA is inversely proportional to the amount of the detected substance. This method indirectly reflects the content of the target analyte by detecting the change in fluorescence polarization value before and after the binding of a fluorescently labeled small molecule antigen (tracer) with an antibody. For pesticide detection, a specific tracer can be combined with a specific monoclonal antibody (mAb), which induces a high polarization value. Once the sample containing the target pesticide competes with the mAb, the polarization value will weaken rapidly.

3) Quantum dot fluorescence immunoassay: Quantum dots (QDs) are semiconductor nanocrystals composed of II - VI or III - V group elements. It can accept excitation light to produce fluorescence. It has a wide excitation spectrum, narrow emission spectrum, adjustable color, high photochemical stability, long fluorescence life and other fluorescence characteristics. It can be used as a superior fluorescence probe. QDs have a wide excitation spectrum, narrow emission spectrum, adjustable color, high photochemical stability, long fluorescence life and other useful fluorescence characteristics that allow them to be used as superior fluorescence probes. Combined with immunoassays, QDs enhance the specificity and sensitivity of pesticide detection.

2.5.2.3 Detection technology based on immunochromatography: Immunochromatography (ICA) is a detection method that combines ICA and chromatography with a chromatographic strip as the carrier. The test strip consists of four parts: a sample pad, a binding pad, a nitrocellulose membrane, and an absorption pad. Under the action of capillary chromatography, the sample solution and labeled antibody in the binding pad combine specifically with the antigen fixed on the

nitrocellulose membrane to form an immune complex. The detection line is colored by the accumulation of markers, and the results are interpreted by the naked eye or using a card reader. Depending on the markers used, ICA can be roughly divided into colloidal gold labeling technology, QD labeling technology, chemiluminescent material labeling technology, and magnetic and nanomaterial labeling technology.

2.5.2.4 Immunomagnetic bead method: Immune magnetic beads (IMB) are composed of magnetic nanoparticles (MNPs) and immune ligands. They are primarily composed of transition metal oxides, such as Fe_2O_3 and Fe_3O_4, with MNP particle sizes ranging from nano to micrometers. The external immune ligands are mainly -OH, -NH_2 and -COOH, which can covalently bind magnetic beads with bioactive substances, such as antibodies and proteins, or bind haptens to facilitate the separation of bound and free antibodies for small molecule analysis.

2.5.2.5 Bionic immunoassay: Biomimetic immunoassays use a molecular imprinting polymer (MIP) as a biomimetic antibody to label specific holes left by antigen and target substance-competitive binding MIP elution. The content of the target substance is determined by detecting the amount of probe substance bound in the holes or cavities. Compared to biological antibodies, MIPs have good physical and chemical stability, can be reused and are inexpensive and easy to prepare. At present, this technique has been widely used in the detection of sulfonylurea, organic phosphorus and plant growth regulators and has achieved good results.

2.5.2.6 Immunochromatography: Immunochromatography is a detection method that combines ICA and chromatography with a chromatographic strip as the carrier. The test strip consists of four parts: a sample pad, binding pad, nitrocellulose membrane and absorption pad. Under the action of capillary chromatography, the sample solution and the labeled antibody in the binding pad combine with the antigen fixed on the nitrocellulose membrane to form an immune complex. The detection line is colored by the accumulation of markers, and the results are interpreted by observation or using an instrument. Compared to the instrument method, the immunoassay technology based on the specificity and affinity binding reaction between antigen and antibody is widely used in the field for the screening of pesticide residues in agricultural products and the high-throughput and rapid detection of samples to be tested. The method has several advantages: it is quick, simple, inexpensive and sensitive.[62–64] Lateral flow immunochromatography (LFIA) is also widely used in food safety detection because it is quick, small in size, convenient and inexpensive. Typical LFIA uses spherical gold nanoparticles (AuNPs) as signal-marking material, but the results of this method are qualitative or semiquantitative and cannot meet the need for a highly sensitive detection method for pesticide residue detection. To enhance the detection performance of LFIA and break through the defects of traditional technology, researchers continue to improve the signal marking materials, signal enhancement methods, simultaneous detection of multiple analytes and the reading mode of LFIA detection signals. These methods improve the detection sensitivity and efficiency to a certain extent. The composition of a typical test strip is shown in Figure 4.

2.5.2.7 Biological bar code immunoassay: In 2003, biologist Paul Herbert first proposed the concept of the bar code, which is mainly aimed at short and easily amplified DNA fragments in organisms. Biological bar code immunoassay technology refers to a large number of DNA barcodes with the same sequence fixed on the surface of a carrier through chemical bonds. The analysis and detection of the target can be done directly or indirectly through the interaction between the target and the carrier or biological bar code. As early as 2003, Mirkind et al. proposed the concept of using oligonucleotide chains as biological barcodes to detect prostate-specific antigens[53]. On the one hand, the ultrahigh sensitivity of biological bar code detection methods comes from the large specific surface area of nano gold, which can mark a large number of DNA sequences. On the other hand, the released DNA sequences can be quantified by some highly sensitive signal amplification detection technologies, such as PCR, biochip silver staining, fluorescence, and colorimetry. Common methods of signal amplification and detection of BCA include the chip method,[65,66] fluorescence labeling method,[67] colorimetry,[68] biosensor method,[69–71] and immune-PCR.[72–74] DNA barcodes are amplified by a combination of technologies, for example, real-time PCR.[75]

The biological bar code immunoassay method can analyze various types of detected objects and has a wide range of applications. In this method, different sequences of DNA can be set to achieve the analysis of a variety of targets. This method does not directly detect the target, so it reduces the interference of the matrix with the targets and avoids interference. After more than ten years of development and exploration, BCA technology has been established as a simple, reliable, and efficient system for the detection of single or multiple residues of macromolecular substances, such as proteins and single residues of small molecules. Biological bar code immunoassays have been successfully applied not only to the detection of pesticide residues but also to the detection of small molecular substances such as veterinary drugs,[76] biotoxins,[77] and environmental pollutants.[78] BCA technology has the following two advantages. First, the nanomaterials used in biological bar code detection technology are safe and resistant to denaturation. In addition, their high specificity and sensitivity offer prospects for broad application. Second, BCA technology can be used to design bar code DNA with different lengths and sequences according to different targets to achieve multiresidue detection. Third, compared with chromatography and other detection methods, BCA technology has the characteristics of low cost, speed, and simplicity in the detection of a single residue of small molecules.

3. Application of rapid detection technology in pesticide residue detection

In this paper, we discuss the application and classification of biosensors for the rapid detection of pesticide residues. Table 1 lists some examples of the application of such biosensors.

3.1 Application of rapid detection technology based on electrochemistry

3.1.1 Application of enzyme biosensor—Based on the principle of specific enzyme activity inhibition, enzyme biosensor technology for the rapid detection of pesticides is an active frontier in research. Polymers are suitable as enzyme immobilization materials

because of their low cost, multifunctionality, and convenient preparation. Owing to several advantages, such as high fluorescence intensity, stable properties, and good biocompatibility, ODs can be used as fluorescent probes for optical enzyme sensors. In recent years, the combination of electrochemical enzyme biosensors and wearable devices has further expanded the ability of enzyme biosensors to detect pesticide residues. Mishra et al.[79] printed a silver electrode on a nitrile rubber glove and deposited organophosphorus hydrolase (OPH) on the electrode surface. When the glove contacts the surface of agricultural products, the OP pesticides are hydrolyzed to produce p-nitrophenol under the catalysis of OPH. The quantitative detection of OP pesticide residues thus becomes possible using a handheld electrochemical workstation connected to a smartphone. The paper-based optical enzyme sensor offers the advantage of simple operation, fast testing and low cost, which can allow for on-site and real-time detection. Research on enzyme sensors for pesticide residue detection is rapidly developing. Paper-based enzyme sensors suitable for on-site rapid detection have emerged and have broad application prospects. However, there are several challenges to address before commercialization and popularization of enzyme sensors, such as high cost, difficulty in prolonging enzyme activity, miniaturization of analytical devices, and rapid sample detection. Enzyme sensors have high sensitivity and specificity and show strong advantages in clinical disease diagnosis, food safety detection, chemical pollutant detection, and so on.

3.1.2 Application of Immunosensors—In recent years, due to the rapid development in the fields of food, medicine, and clinical diagnosis, the demand for in situ, rapid, trace, point of care, and online detection of analytes in the analysis process has also gradually increased. Electrochemical immunosensors have become a powerful tool for analytical applications. [80] The success of the immunosensor depends on the surface functionalization, antibody orientation, and antibody density on the sensor platform and the configuration of the immunosensor. With the optimization of these factors, any immunosensor can give more accurate results.[81] Immunosensors are increasingly used in the field for rapid detection because of their specificity, sensitivity, low cost, and high throughput and because they can be automatically detected in situ. They have also been used to detect trace pesticide residues in food and other environmental samples. They have become small and cost-effective devices for the on-site monitoring of environmental samples.

3.1.3 Application of the aptamer sensor—The aptamer sensor has a very low detection limit and good selectivity and is suitable for the rapid detection of pesticides. In recent years, a variety of pesticide aptamers represented by acetamiprid aptamers have been developed.[82] The development of nanomaterials has further improved the detection ability of aptamer sensors and broadened their application in the detection of food pollutants.[83] Bala et al. combined an aptamer sensor with AuNPs and the cationic polymer polydiallydimethylammonium chloride (PDDA) to detect malathion. Malathion specifically binds to the aptamer, and the PDDA originally bound to the aptamer changes into a free state, thus aggregating the gold nanoparticles in the solution and changing the color of the solution from red to blue. The aptamer sensor's detection limit for malathion was reported to be 0.06 pmol/L, and the mean recovery was 88–104%. It can be applied to the detection of malathion in environmental water and food samples.[84] Eissa et al. first prepared

carbendazim aptamers using SELEX technology and fixed highly specific aptamers on a gold electrode through mercaptan modification. Using this technique, carbendazim could be detected with high sensitivity using electrochemical impedance spectroscopy. After the aptamer molecule is combined with carbendazim, the configuration changes, which hinders electron transfer between hexacyanoferrate ions and the surface of the gold electrode and changes the impedance spectrum. The detection limit of the aptamer sensor for carbendazim was 8.2 pg/ml, and the recovery in various agricultural products was 86–95%.[85] At present, several types of aptamers have been developed, and the research space is broad. However, the selection and preparation of aptamers is relatively cumbersome, which restricts the development of aptamer sensors, and there is a lack of practical methods that could be applied in the field for the rapid detection of pesticide residues.

3.1.4 Application of cell and microbial sensors—The basic requirement of biosensors is that biological components should cause physical and chemical changes near the sensor. Immobilization technology plays a key role in biosensors. When enzymes are expressed in the periplasm and cell membrane of cells, the whole cell can be directly used for immobilization. Such systems can be used for simple biosensor applications without cofactor regeneration. It is possible to fix cells passively in the pores or on the surface of glass fibers or other synthetic membranes. As the cells adhere to them, the membrane can also be in direct contact with the liquid containing the substrate so that the biological components can cause the physical or chemical reaction needed to trigger the sensor. The advantage of this method is that cells are directly released from the substrate solution, which eliminates the problem of mass transfer usually associated with embedding and other immobilization methods. Researchers have suggested that polystyrene microplates (96 wells) be used as carriers for the immobilization of microbes and that these immobilized cells could be reused.[29] Ranjan et al. fixed *Photobacterium leiognathi* with sodium alginate to prepare a bioluminescent bead complex[86]. The concentration of 2,4-dichlorophenoxyacetic acid (2,4-D) was quantitatively detected by measuring its inhibitory effect on the bioluminescence of luciferase in bacteria. Mishra et al. proposed a new analytical method that optimized a *Sphingomonas paucimobiliz* biosensor for the detection of methyl parathion.[88] The biological composite structure of Sphingomonas- and polyethyleneimine-functionalized silicon nanoparticles was prepared, and the composite was fixed on a microplate containing an optical signal converter and reader for the direct quantitative determination of methyl parathion. Nano silicon materials have good biocompatibility, high stability, and high mechanical strength, which can improve the detection ability and stability of cell sensors. The linear range of methyl parathion detected by the biosensor was 0.1–1 μg/mL, and the properties of the assay were unchanged for 180 days.

3.2 Fast detection technology based on optical analysis

As an advanced analytical technology, spectral technology allows for the qualitative or quantitative analysis of target molecules based on the various spectral characteristics of target molecules. Spectral analysis is fast and simple, has wide applications and is relatively low cost. It has great potential in the field of rapid detection of pesticide residues. However, the sensitivity and selectivity of spectral analysis need improvement to meet the

requirements of trace pesticide residue detection. In recent years, a variety of new spectral analysis methods have been developed for the detection of pesticide residues.

3.2.1 Application of Surface-enhanced Raman spectroscopy—Surface-enhanced Raman spectroscopy (SERS) is an analytical technique based on the Raman scattering effect, which can enhance the Raman scattering signal of organic substances by adsorbing the target organic substances on the metal surface. This technique has high detection precision, simple pretreatment, good selectivity, fast and nondestructive testing, and several advantages in the determination of trace pollutants. At present, it has been applied in many fields, such as food safety, life sciences, environmental monitoring, and the chemical industry, and can potentially be used in the field of rapid detection of pesticide residues. Wang et al. first proposed a nanoantenna surface-enhanced Raman spectroscopy (G-SERS) platform inspired by gecko, which can simultaneously detect thiamine, methyl p-thiophosphatide, malachite green and many other components through a simple and intuitive "stripping" method.[88] The development of a lower cost and more stable Raman signal enhancement substrate suitable for the detection of more kinds of pesticide residues is the key to promoting the application of Raman spectroscopy in the field of pesticide residue detection. Combining Raman spectroscopy with other detection techniques can further improve the detection ability. Alami et al. combined Raman spectroscopy with an enzyme inhibition method.[89] Nie et al took the aptamer pesticide structure as the detection target of Raman spectroscopy, which can selectively detect malathion.[90] Therefore, the development of Raman signal enhancement substrates suitable for the detection of more kinds of pesticide residues with lower cost and more stability is the key to promoting the application of Raman spectroscopy in the field of pesticide residue detection.

3.2.2 Application of chemiluminescence in pesticide residue detection—Zhang et al. developed an ultrasonic-assisted CL device that can detect pyridaben residues in fruit peels.[91] The general principle of detection is to use the high-energy hydroxyl radical generated by water under the action of ultrasound to excite the pyridaben molecule. The energy released by the excited pyridaben molecule when it returns to the ground state can excite 3-aminophthalate (3-AP), a CL product of the reaction of luminol with potassium permanganate. The content of pyridaben in the sample can be detected by measuring the change in 3-AP luminous intensity, and the detection limit of the pyridaben residue in peels is 0.351 mg/kg. Khataee et al. developed an analytical technique based on suppressed CL for the detection of cypermethrin.[92] In this method, the introduction of graphene QDs (GQDs) and cetyltrimethylammonium bromide (CTAB) enhances the CL effect of morin potassium permanganate, while cypermethrin affects the CL enhancement system and reduces CL intensity through the interaction of GQDs and CTAB. The detection limit of cypermethrin in this method was 0.08 mg/L. Chemiluminescence technology can be combined with other analytical techniques to meet the needs of rapid detection of pesticide residues. Liu et al. combined CL with paper chromatography technology to prepare a test paper for a rapid detection test of dichlorvos residues.[93] The detection limit of this test was, at most, 3.6 ng/mL, signifying that it has application potential. New nanomaterials can help enhance the performance of CL in the detection of pesticide residues.[94] Metal organic framework (MOF) materials were used as catalysts for CL reactions, which greatly enhanced luminous

efficiency. Combined with AChE and choline oxidase (ChOx), based on the inhibition of AChE by OP pesticides, they realized the detection of diazinon, an OP pesticide, with a detection limit as low as 0.045 nmol/L.

3.3 Application of microfluidic technology in the rapid detection of pesticide residues

Tahirbegi et al. prepared a glass-based algal microfluidic device to detect a variety of pesticides.[95] Using a pH sensor, an oxygen sensor and a fluorescence detector integrated in the microfluidic device, the effects of pesticides on the photosynthesis, respiration and luminescence of *Chlamydomonas reinhardtii* were detected to realize the quantitative detection of pesticides. Wang et al. combined microfluidic technology with an enzyme inhibition method and used a microelectrode array to detect the inhibition of OP pesticides on AChE.[96] The size of the microfluidic chip was only 3 cm^2, and the miniaturization of the detection device reduced the consumption of AChE and saved costs. The method can be used for on-site, real-time detection of OP pesticide residues. Huang et al.[97] synthesized a molecular imprinted polymer (MIP) in a microfluidic chip and visualized methylphosphonic acid, a metabolite of OP pesticides.

3.4 Application of open mass spectrometry ion source and real-time direct analysis mass spectrometry

In recent years, a variety of scientific research teams have focused on creating the appropriate combination of direct analysis in real-time mass spectrometry (DART-MS) and pretreatment technology. Guo et al. combined QuEChERS technology, paper spray ionization technology and DART-MS analysis and developed a method for simultaneous extraction and DART-MS multiresidue analysis of 36 pesticides.[98] This method takes less time (3 min) and has high sensitivity (detection limit as low as 0.1 ng/mL). Wang et al.[99] combined DART-MS technology with solid phase microextraction technology to directly extract pesticides from 50 ml environmental water samples without using organic solvents for mass spectrometry analysis and realized high-throughput mass spectrometry detection of pesticide residues. Pereira et al. combined DART-MS technology with MIP to synthesize MIP on the surface of cellulose membranes using pesticides (such as diuron and 2,4-D) as templates for adsorption and direct ionization of pesticides to be tested in simply treated fruit extracts. The method can specifically adsorb and detect target pesticides, and the detection limit was reported to be as low as 0.31 ng/mL.

3.5 Application of a rapid detection method for pesticide residues based on biotechnology

3.5.1 Application of enzyme inhibition techniques in pesticide residue detection—Enzyme inhibition technology is an analytical method based on the inhibition of enzymes when they interact with certain substrates. This technique usually employs enzymes such as cholinesterase and carboxylesterase and is generally applied to the detection of OP and carbamate pesticide residues in agricultural products. Enzyme inhibition methods are simple, quick, and sensitive, have low requirements for instruments and equipment and have a wide application range. Yang et al. established an enzyme inhibition reaction system for the rapid determination of OP and carbamate pesticide residues in

milk.[100] The detection limit of pesticides was 0.5–1.0 mg/kg. Although rapid detection methods based on enzyme inhibition technology have some limitations, such as low accuracy, poor selectivity, and occasional interference, they are still the mainstream method for the rapid detection of OP and carbamate pesticide residues. Researchers are also trying to use a variety of ways to optimize enzyme inhibition technology to improve the performance of related products. Jin et al. improved the AChE inhibition analysis method and developed a paper-based microfluidic analysis system by organic solvent extraction combined with spontaneous in situ solvent evaporation, which significantly improved its analytical performance.[101] Wu et al. organically combined enzyme inhibition technology with gold nanomaterials to develop a colorimetric method that uses different colors of gold particles in different valence forms to indicate the concentration of OP pesticides.[102,103] Under the best conditions, the minimum colorimetric concentration observed was 0.7 mg/L, greatly improving the detection sensitivity. Triazophos was used as a model pesticide for verification. Qing et al.[104] also adopted enzyme inhibition technology based on gold nanomaterials to establish a method for the rapid detection of OP pesticides. Under optimal conditions, the detection limit of triazophos was 4.69 nmol/L owing to the high sensitivity of gold nanomaterials. The improved and optimized pretreatment method of enzyme inhibition technology has broad application prospects in the field of rapid detection of OP pesticide residues in the future.[105] Enzyme inhibition analysis has a wide range of applications, but there are also various problems. For some fruits and vegetables, this analytical method easily produces false positive reactions with pesticide residues, which directly affects the final inspection results, thus increasing the difficulty of food detection.

3.5.2 Application of immunoassay in pesticide residue detection

3.5.2.1 Application of ELISA in pesticide residue detection: Detection methods involving ELISA may use a double antibody sandwich method, a capture method–both of which are noncompetitive– or a competitive method. In this mode, the antibody and the target analyte form a complex, and the detection signal is positively correlated with the content of the target analyte, which is generally applicable to the detection of macromolecular antigens.[106] However, pesticides, as a class of small molecular compounds with single antigenic determinants, can only bind to one antibody, so the competitive detection mode is usually used. Here, the detection signal is negatively correlated with the content of the target analyte. Lan et al. prepared a novel monoclonal antibody against spinosad and constructed an indirect competitive ELISA (ic-ELISA) to monitor spinosad residues in milk, fruits and vegetables.[107] The IC_{50} and limit of detection (LOD) of the method were 4.11 ng/mL and 0.63 ng/mL, respectively. Moreover, Fang et al. developed a sensitive biotinylated ic-ELISA method to detect acetamiprid residues in pollen.[108] Through biotinylation of the anti-acetamiprid monoclonal antibody, the sensitivity of the immune response was further improved. The LOD was 0.17 ng/mL, and the recovery rate was 81.1–108.0%. For the detection of isocarbophos residue, Xiang et al. proposed an aptamer-based ELISA (apt-ELISA) method.[109] Aptamers are easily synthesized and stored. The rapid determination of isocarbophos in water using an aptamer-stimulated antibody shows good selectivity and high sensitivity.

3.5.2.2 Application of fluorescence immunoassay in pesticide residue detection

1) Application of time-resolved fluoroimmunoassay in the detection of pesticide residues: Xu et al. developed a monoclonal antibody-based direct competitive TRFIA method with wide specificity for a class of OP pesticides.[110] The detection limit was less than 10 ng/mL. The spiked recovery of OP pesticides in environmental water samples was 74.8–121.3%, with a relative standard deviation (RSD) of 6.4–15.1%. The method is sensitive, simple and rapid. Liu et al. used an Eu^{+3}-labeled antibody as a tracer to establish a rapid and sensitive TRFIA method for the determination of thiazoline.[111] Under optimal conditions, the IC_{50} of the TRFIA method was 2 μg/L, the LOD was 1.9 ng/l, and the recovery rate spike in water, soil, pear, and tomato was 83.4–121%. Due to the different emission wavelengths of different lanthanide fluorescent chelates, TRFIA can simultaneously determine two or more analytes. Shi et al. established a double-labeled TRFIA method to simultaneously detect parathion and IMI in food and environmental matrices.[112] Eu^{3+} and SM^{3+} were used as fluorescent markers to couple with anti-IMI and anti-parathion polyclonal antibodies, respectively. The IC_{50} values of parathion and IMI were 10.87 μg/L and 7.08 μg/L, respectively, and the detection limits (IC_{10}) were 0.025 μg/L and 0.028 μg/L, respectively. Although the cost of TRFIA is slightly higher than that of ELISA, its lower background interference and higher sensitivity enable it to monitor pesticide residues at trace levels.

2) Application of Fluorescence Polarization Immunoassay in the detection of pesticide residues: Liu et al. developed a fast, uniform and high-throughput FPIA method for triazophos detection based on a specific anti-triazophos monoclonal antibody and a fluorescein isothiocyanate ethylenediamine fluorescent tracer.[113] The reaction time was less than 10 minutes, the detection limit was 0.29 μg/L, the IC_{50} was 3.62 μg/L, and the average spiked recoveries in water, brown rice, cabbage and apple samples were 72.07–104.35%. Boroduleva et al. established an FPIA method for thiabendazole and fluetherazole in wheat.[114] Xu et al. developed a simple, rapid and high-throughput FPIA method for the simultaneous determination of five OP pesticides using broad-spectrum monoclonal antibodies (mAbs).[115] The detection limit was less than 10 ng/mL, and the recovery of spiked vegetables was 71.3–126.8%.

3) Application of quantum dot fluorescence immunoassay in the detection of pesticide residues: Li et al. established a QD fluorescence immunoassay method based on a polyclonal antibody that can simultaneously detect clothianidin and thiacloprid in agricultural products and environmental samples.[116] The IC_{50} of the method was less than 12.5 ng/mL. Tan et al. embedded $CsPbBr_3$ QDs into an MIP to synthesize an MIP/QD composite, which has excellent selectivity for phoxim with an LOD of 1.45 ng/mL.[117] The method was used for the detection of Phoxim in potato and soil, and the recovery was 86.8–98.2%. Liao et al. used CdSe/ZnS QDs as probes to label mAbs and established a rapid and sensitive fluorescence immunoassay for the recognition of triazophos.[118] The determination method was within 10 – 25 μg/L. It had good linearity in the concentration range of g/L, the IC_{10} was 0.508 ng/L, and the recovery observed in fruit samples was 82.6–96.6%. Owing to their wide excitation and narrow emission spectrum, the same excitation light source can be

used for the synchronous detection of QDs with different particle sizes and for the detection of multiple pesticides. Fe_3O_4@SiO_2@MIP was used as a biomimetic antibody by Jiang et al.,[119] and CdSe/ZnS QDs with different emission wavelengths were used as markers to simultaneously detect methyl parathion, chlorpyrifos and trichlorfon in fruits. Similarly, based on the different emission wavelengths of CdSe/ZnS QDs, Liu et al. established a direct competitive bionic immunoassay method for the simultaneous determination of trichlorfon and chlorpyrifos in fruits and vegetables.[120] Wang et al. combined double QDs with highly active porphyrins to create double nanosignal amplification and established a paper sensor based on fluorescence visualization for three OP pesticides to produce different color change responses.[121] The FIA method has a wide linear range and good reproducibility, but it is susceptible to external factors, such as temperature, solvent and scattered light, and sensitive to environmental factors.

3.5.2.3 Application of detection technology based on immunochromatography in pesticide residues: Lan et al. combined colloidal gold with broad-spectrum mAbs to prepare immunochromatographic test strips for the detection of carbofuran and 3-hydroxycarbofuran in water samples.[122] The method does not require complex sample pretreatment, and the whole process can be completed within 5 minutes, with an LOD of 7–10 ng/mL. Wu et al.[123] used a sidestream chromatography strip based on CdSe/ZnS QDs to detect residual benzothiazole quickly and intuitively in strawberries. The multiconcentration detection of spiked samples thus becomes possible, and the results can be visualized under a UV lamp. The detection limit was 25 μg/L. Yang et al. designed a new CL immunochromatographic technique with a double reading signal probe to detect parathion methyl and fenpropathrin, and the LODs were 0.17 ng/mL and 0.10 ng/mL, respectively.[124] Li et al. proposed an immunochromatographic method based on SERS for the dual detection of two pyrethroid pesticides, cypermethrin and fenvalerate.[125] Gold nanoparticles coupled with antibodies (AuNPs) were used as SERS substrates. By fixing two test lines designed to detect two pesticides, simultaneous dual detection was achieved. The ICA method is fast and intuitive, and the test strip is portable. These advantages make it suitable for on-field rapid pesticide residue detection. When agricultural products pass the primary screening of the test strip, the samples close to or exceeding the residue limit can be further determined with more accurate instruments and methods. Therefore, ICA accelerates the detection process and improves the detection efficiency.

3.5.2.4 Application of immunomagnetic beads in pesticide residues: Du et al. developed an immunomagnetic-bead-based ELISA (imb-ELISA) in which carboxyl-functionalized magnetic Fe_3O_4 nanoparticles were used to detect triazophos.[126] compared to classical ELISA, the sensitivity of this method was considerably higher, the detection limit was 0.10 ng/mL, the average recovery in fruits, vegetables and cereals was 83.1–115.9%, and the RSD was less than 10%. Immunomagnetic beads provide a solid-phase carrier immune reaction site with appropriate size, good dispersion, and high magnetization, but there are also some bottlenecks in the preparation process, such as low yield and easy agglomeration. Therefore, in future research work, we can address new methods for the synthesis of magnetic beads, improve their surface functionalization and biocompatibility and improve the enrichment efficiency of ligands to expand the scope of application.

3.5.2.5 Application of bionic immunoassay in pesticide residues: Zhang et al. deposited CdTe on a microfluidic paper chip to obtain paper@QDs@MIPs.[127] Through the fluorescence quenching mechanism induced by electron transfer, they specifically recognized and sensitively detected 2,4-D. The combination of 2,4-D significantly reduced the fluorescence intensity in less than 18 min and had good linearity in the range of 0.83–100 μm. The recovery rate of standard addition in bean sprouts was 94.2–107.0%. Li et al. established a capillary electrophoresis biomimetic immunoassay for the detection of trichlorfon, with an IC_{50} of 0.16 mg/L and an IC_{15} of 0.13 μg/L.[128] Tang et al. developed a new and rapid direct competitive biomimetic ELISA (cb-dc-ELISA) based on an MIP membrane as an antibody simulant for the determination of the N-methyl carbamate insecticide methomyl.[129] The MIP synthesized by the template molecule not only has good stability under conditions of high temperature, high pressure, acidity and basicity but can also be synthesized and used repeatedly. Compared to traditional immune methods, the matrix effect is small, and the anti-interference is strong. It shows positive prospects in many fields, such as trace pesticide residue analysis. However, the molecular recognition and mechanism of action require further study. At the same time, the application of MIPs in aqueous solutions or polar solvents, as well as innovations in functional monomers, types of crosslinking agents and polymerization methods, can be expanded.

3.5.2.6 Application of immunochromatography in pesticide residues: As an alternative method of instrument detection, immunochromatographic strips are fast, sensitive, simple, and low-cost. They have shown great potential in the field of environmental monitoring and maintenance of food safety. Conventional LFIA uses spherical gold nanomaterials with a diameter of 20–30 nm, but the luminescence intensity of this material is weak, which affects the detection sensitivity.[130] At the same time, once impurities appear in the process of preparation and storage, they easily accumulate and precipitate, which affects the use of AuNPs. To improve the signal marking materials of LFIA, an increasing number of nanomaterials have been applied to immunochromatographic strips in recent years. The research progress of colloidal gold immunochromatographic strips for the rapid detection of pesticide residues is shown in Table 2. The research progress of fluorescent signal immunochromatographic strips in the rapid detection of pesticide residues is shown in Table 3. The research progress of other signal immunochromatographic strips in the rapid detection of pesticide residues is shown in Table 4. The application examples of immunochromatography in the detection of conventional pesticide residues are shown in Table 5. Liu et al. used dopamine nanospheres (PDA NPs) with outstanding covalent connectivity to effectively improve the stability and LFIA sensitivity of the probe.[131] The LOD of furazolidone in food samples by LFIA labeled with the antibody-PDA NP probe was 3.5 ng/mL. Similarly, Wang et al. developed a fluorescent immunochromatographic strip assay (QBs–FITSA) based on QD beads for the rapid and sensitive detection of tebuconazole in agricultural products.[132] The linear detection range of the method was 0.02 – 1.25 ng/mL, and the LOD was 0.02 ng/mL. Cheng et al. developed a two-dimensional Pt-$Ni(OH)_2$ nanosheet (NSS)-amplified two-way lateral flow immunoassay with smartphone-based reading, which can simultaneously detect acetochlor and fenpropathrin.[133] The LOD of acetochlor was 0.63 ng/mL, and the LOD of fenpropathrin was 0.24 ng/mL. In traditional LFIA, chromogenic nano labeling materials are mainly used to label mAbs by electrostatic

adsorption and covalent binding methods. However, the electrostatic adsorption method is easily affected by factors such as the isoelectric point, temperature and pH of antibodies, and the covalent binding method will inevitably block some antigen binding sites of mAbs, resulting in a decline in the detection performance of LFIA. To overcome the adverse effects of nanomaterials on the antibody labeling process, researchers have developed alternate methods in which nanomaterials are not labeled with mAbs. Although nanomaterials are widely used in LFIA, the synthesis process of nanomaterials is relatively complex and time-consuming. The coupling between nanomaterials and antibodies will affect the activity of antibodies. Nanomaterials synthesized in different batches may have certain differences, which may affect the detection performance of LFIA. At the same time, the synthesized nanoprobes are prone to aggregation and precipitation under colloidal force and need to be stored at 4 ℃. Therefore, in recent years, researchers have explored the development of LFIA without nanomaterial labeling. Xu et al. developed a new type of test strip using the protein dye Coomassie brilliant blue (CBB).[134] By using the mAb of CBB against the metabolite of furazolidinone (AOZ), the dyed mAb can be used as a color signal label to replace the colored nanomaterials. The detection limit of AOZ in this method is 2 ng/mL, and the production cost of the test strip is 300 times lower than that of other methods.

Traditional LFIA can only be used to detect one kind of target analyte, and its detection efficiency is low, which cannot meet the simultaneous detection requirements of multiple target analytes. To improve the detection performance of test strips, researchers have developed a test strip capable of simultaneously detecting multiple targets. Shu et al. used hybrid cell technology to prepare a bifunctional antibody with two antigen recognition sites, which can be used to recognize methyl parathion and IMI simultaneously.[135] The antibody is fixed on the test line of the test strip, and combined with time-resolved CL technology, the detection of two substances can be completed on a T-line. The detection signal results of methyl parathion and IMI can be collected at 2.5 s and 300 s, respectively.

In recent years, to realize the high-throughput detection of LFIA, different test strip structures have been designed, such as a three-channel 120-degree crossing[136], dendritic, flower, disc, four-channel vertical crossing, parallel arrangement at one end of the channel, parallel arrangement at both ends of the channel,[137] multichannel test cylinder for simultaneous detection of four target analytes,[138,] etc. Traditional LFIA detection results mainly analyze the color signal of the strip on the test strip and carry out qualitative and quantitative detection of substances through colorimetric methods. However, when the color difference of the test paper is not obvious or the sample background color is dark, the readout results will be inaccurate. In recent years, to improve the accuracy of the test paper results, researchers have explored other signal readout methods. Sheng et al. synthesized silver core and gold shell nanomaterials and encapsulated the Raman signal molecule 4-nitrothiophene (4-NTP) in the middle of the core-shell materials to form Ag4-NTP@Au.[139] As a Raman signal tag, it is used to detect chlorothalonil (CHL), IMI and oxyfluorfen (OXY).

Traditional LFIA detection can provide only “yes” or “no” qualitative results through the color development of the detection line (T line) and the control line (C line) or rely on the naked eye to judge the results according to their relative strength. Due to the influence of

subjective factors, it is possible for researchers to report false positive or negative results. In addition, because the LFIA has different detection modes for different targets, such as the competition method, indirect method, double antibody sandwich method, etc., the determination methods of test strips from different manufacturers, types and batches are usually different, which is inconvenient for the user. In recent years, quantitative and precise test strip readers have solved the drawbacks of visual judgment and can also realize the quantitative interpretation of the target object. However, the widespread application of the product is limited by the high cost of the commercialized instrument and because the card reader may only match the test strip of the same manufacturer. Therefore, there is a dire need for the development of economical, portable, and universal rapid detection equipment to make the interpretation of test strip test results more convenient and accurate. Detection technology based on highly sensitive immunochromatographic strips and smartphone photo interpretation has become an active frontier in research in recent years.[140] In these cases, photos taken with smartphone cameras and an image recognition algorithm are used to render the optical signal of the test strip into a digital signal.

At present, there are few reports on the application of such rapid detection technology based on smartphones and immunochromatographic strips for the detection of pesticide residues in agricultural products. In 2018, Xu et al. used the fluorescence quenching effect of a gold nanostar (AuNSs) on fluorescent QDs to develop a three-channel lateral flow immunochromatographic test strip. The fluorescently labeled aptamer was used to replace the antibody of the traditional test strip, and a device based on smartphone photography, ImageJ and origin image analysis software was developed to read the fluorescence intensity of the strip, allowing for the detection of chlorpyrifos poisoning in agricultural products. The LODs of the three target compounds were 0.73, 6.7, and 0.74 ng/mL, respectively.[141] In 2019, the research group reported a two-way platinum nickel hydroxide tablet (PT $Ni(OH)_2$NSs) side flow immunochromatographic test strip combined with mobile phone photography to analyze the color intensity of the T-line. Acetochlor and fenpropathrin could be detected using this method under ambient light conditions. The addition recovery rate of this method was 97.12–111.46%, and the LODs of acetochlor and fenpropathrin were 0.63 and 0.24 ng/mL, respectively. The detection results were consistent with the verification results of gas chromatography–mass spectrometry, indicating the high sensitivity and accuracy of this method.[142] It, however, requires the software to manually intercept the color developing part of the test strip, which is prone to subjective error, and the influence of different light source intensities on the experimental results is not investigated.

The development of pesticide antibodies is difficult. Many pesticide residues are usually present in the same agricultural product matrix, and the maximum residue limits are different. Therefore, the wide application of ICA in the detection of pesticide residues is limited. In addition, the pigments in fruits, vegetables, tea, and other samples greatly interfered with the color development of the test strips in some cases. When using image recognition technology combined with side flow ICA to quantitatively detect pesticide residues, it is also necessary to investigate the influence of substrate background color on the color development results. Smartphone technology and LFIA are combined to realize quantitative detection, which is based on visible-light colorimetric and fluorescence analysis. The fluorescence signal is generally more sensitive than traditional colloidal gold signals. To

enhance the colloidal gold colorimetric signal, AuNFs,[143] AuNSs,[141] or materials with an enhanced signal can be used on the colloidal gold probe. There are many modes of detection that can be used to achieve multitarget and high-throughput detection. Multiple T-lines can be set on the same test strip, different color marking materials can be used for different targets, separate color channels can be selected for image analysis, or multiple test strips can be designed such that they can be scanned at the same time.

3.5.2.7 Application of BCA technology in pesticide residues: Pesticides and other small molecules have only one epitope, which is not suitable for sandwich detection. Few synthetic chemical pesticides are large enough to allow binding to separate antibodies. Du et al. introduced fluorescent quantitative PCR technology into biological bar code immunoassays to detect triazophos pesticides.[144] This method overcomes the obstacle that biological bar code analysis cannot be used for small molecule detection. The detection linear range was 0.04–ng/mL, and the minimum LOD was 0.02 ng/mL, which was 10–20 times lower than that of ELISA. On this basis, Zhang et al. used fluorescent markers instead of horseradish peroxidase and biological bar code immunoassays to detect triazophos pesticides.[145] Gold nanoparticles (AuNPs) were modified with triazophos monoclonal antibody and 6-carboxyfluorescein-labeled single chain mercaptan oligonucleotides (6-FAM-SH-ssDNAs). The fluorescence of 6-FAM was quenched by AuNPs. The ovalbumin-linked hapten was coated on the bottom of the microplate to compete with triazophos in the sample and bind to the antibody on the AuNP probe. The fluorescence intensity is inversely proportional to the analyte concentration. The linear range of this method was 0.01–20 μg/L, and the lowest LOD was 6 ng/L. Cui et al. established a biological bar code immunoassay method based on digital PCR.[146] Three AuNPs and magnetic nanoparticle (MNP) probes were prepared to combine the antibodies of triazophos, parathion and chlorpyrifos with the three pesticides. To ensure the method to design three primers, probes and templates under the best conditions, the minimum detection limits (IC_{10}) of triazophos, parathion and chlorpyrifos were 0.22, 0.45 and 4.49 ng/mL, respectively. The linear ranges were 0.01–20, 0.1–100 and 0.1–500 ng/mL, and the correlation coefficients (R^2) were 0.9661, 0.9834 and 0.9612, respectively. However, because the above methods require PCR equipment, it is difficult for ordinary laboratories to apply them well. To improve the practicality of the method, Zhang et al. detected trace quantities of triazophos using RNA/DNA hybridization technology.[147] The monoclonal antibody (mAb) connected to AuNPs was encapsulated by DNA oligonucleotides, which were used as a signal generator, and complementary fluorescent RNA was used for signal amplification. The system generates detection signals through DNA–RNA hybridization and subsequent ribonuclease H (RNase H) dissociation of fluorophores. RNase H can only decompose RNA within a DNA–RNA complex but cannot denature single-stranded or double-stranded DNA. Therefore, through the iterative cycle of DNA–RNA hybridization, a strong enough signal can be obtained to reliably detect residues. The method can quantitatively detect triazophos residue by fluorescence intensity measurement; the LOD is 0.0032 ng/mL. To explore the multiresidue immunoassay method for pesticides, Xu et al. further developed a method established by Zhang for the detection of traizophos.[148] This novel technique allowed for the simultaneous detection of triazophos, chlorpyrifos and parathion. The method showed satisfactory linear ranges of 0.01 – 25, 0.01 – 50, and 0.1 – 50 ng/mL for triazophos, parathion, and chlorpyrifos, respectively,

and the lowest LODs were 0.014, 0.011, and 0.126 ng/mL, respectively. Zhang et al. further selected 6-FAM, Cy3 and Texas Red, which have high fluorescence intensity and no obvious cross reaction, as the markers of the oligonucleotide chain. Zhang et al. constructed AuNP probes for three analytes by simultaneously modifying the corresponding antibodies and fluorescently labeled oligonucleotides on the probe surface. Three fluorophores (6-FAM, Cy3 and Texas Red) with high fluorescence intensity and little excitation/emission wavelength overlap were selected. The method showed satisfactory linear ranges of 0.01 – 20, 0.05 – 50 and 0.5 – 1000 μg/L for triazophos, parathion and chlorpyrifos, respectively, and the lowest LODs were 0.007, 0.009 and 0.087 μg/L, respectively.[149] Chen et al. added a platinum nanoparticle probe to the reaction mixture for the detection of parathion on the basis of a biological bar code immune competitive reaction mode. The LOD was 0.002 μg/L, and a multiresidue detection method was established for OP pesticides. [150]

4. Summary and Outlook

In recent years, there has been significant progress in the development of rapid pesticide detection technology, and various new methods have emerged. Rapid detection technologies offer significant advantages over conventional technologies. Most importantly, they are less time-consuming and lower cost. The main challenges in rapid detection technologies are sensitivity, selectivity and stability of detection and the development of testing methods suitable for commercialization. Future research progress should be aimed at combining rapid detection technologies with other novel technologies to achieve high sensitivity, rapidity, integration and miniaturization.

1. At present, rapid detection cards and rapid detection based on enzyme inhibition are mature and commercialized options. However, these methods have certain disadvantages, such as their lack of specificity in identifying the type of pesticide residues, poor sensitivity, difficulty in conducting quantitative analysis, and false positive results.

2. Biosensors have improved the quantitative analysis ability of traditional rapid detection methods for pesticide detection to a certain extent, but certain inherent defects still need to be addressed. Enzyme sensors are only suitable for a specific class or for certain types of pesticides, and it is difficult to determine which pesticide might have been used in the produce under evaluation. In addition, the activity and stability of the enzyme may be disturbed by the environment, and detection repeatability is poor. An immunosensor can only specifically detect pesticide residues that it is designed to detect. It cannot detect unknown pesticide residues in the sample, and hence, broad-spectrum detection is difficult to achieve. Furthermore, the process of preparing antibodies is complex, and the degree of commercial production is low, which affects the practical application value of immunosensors. The preparation process of aptamers designed to target pesticides is also complex, and only a few aptamers have been developed yet.

3. Spectral analysis usually requires specific instruments, but the popularity of new spectral instruments suitable for the rapid detection of pesticide residues is

relatively low. There are still technical difficulties in using spectral technology for multiresidue detection, and complex modeling and calculation are needed.

4. After years of continuous improvement and development, the LFIA has provided a convenient, fast, and sensitive technical platform for food safety detection. The technology is relatively mature, and the detection of some analytes has been commercialized. At present, the main challenges and development trends are summarized as follows: Test papers based on nanollabeled materials require cumbersome material synthesis steps, extreme conditions, significant time and energy and have poor stability and monodispersity. The development of signal-labeled materials with excellent performance is still a major goal for the future. In recent years, most test papers have used mAbs to specifically identify target analytes. However, the preparation process of mAbs takes a long time and requires considerable manpower, material and financial resources, and there may be considerable differences between different batches. In the future, LFIA should develop specific recognition probes that can replace mAbs, such as full-length recombinant antibodies, aptamers, phages and their cytolysins. Detection sensitivity is an important parameter to check whether the performance of the test strip is good. Traditional signal enhancement methods rely on additional operating steps that prolong the detection time of the test strip. The development of a convenient and time-saving one-step signal enhancement method will go a long way in improving the detection performance of the test strip. Although the simultaneous detection of multiple target substances improves detection efficiency, mutual interference reduces detection sensitivity. Therefore, progress will also depend on the development of high specificity identification probe technology.

5. In the future, fast detection products based on side flow immunochromatographic test strips and smartphone photos could be used in practical detection applications to achieve the goal of “fast detection, accurate detection, high throughput, and more detection”. To make progress in this direction, the following issues should be addressed: (1) The layout and location of cameras of different mobile phone brands varies greatly, and the use of a cassette similar to a mobile phone camera to collect images limits the versatility of the technology. In the future, to realize sensitive and accurate photodetection under ambient light conditions without cassettes, it is necessary to explore the objective laws of system interpretation results using different types of mobile phones and varying light intensities. This will help us establish models, optimize background deduction and system correction algorithms, and make the detection results accurate and reliable. (2) For fluorescent LFIA, photos must be taken in the cassette with a built-in excitation light source, so researchers need to work on the miniaturization, portability and economy of the detection device. (3) All existing mobile phone built-in cameras use CMOS sensors, but different brands of mobile phones have different processing algorithms for raw image data. Photos are then processed on the basis of the phone’s algorithm. Therefore, the compatibility and stability of image recognition algorithms on different mobile phone brands needs

to be investigated. (4) When multiple test strips are used for the simultaneous detection of multiple targets, to clearly obtain the detection results of different test strips, the identification information of each test strip must be given, and different kinds of test strips can be marked with corresponding bar codes or two-dimensional codes to distinguish them. (5) It is necessary to develop targeted algorithms, depending on the types of detection signals, so that the image processing algorithm model can more accurately reflect the relationship between signal strength and the concentration of the substance to be measured. (6) To improve the sensitivity and accuracy of the method, it is necessary to develop marker materials with more stable and enhanced colorimetric signals. (7) The design of the test strip and multichannel detection may also be developed to allow for automatic processing image recognition algorithms to achieve multiobjective and high-throughput detection.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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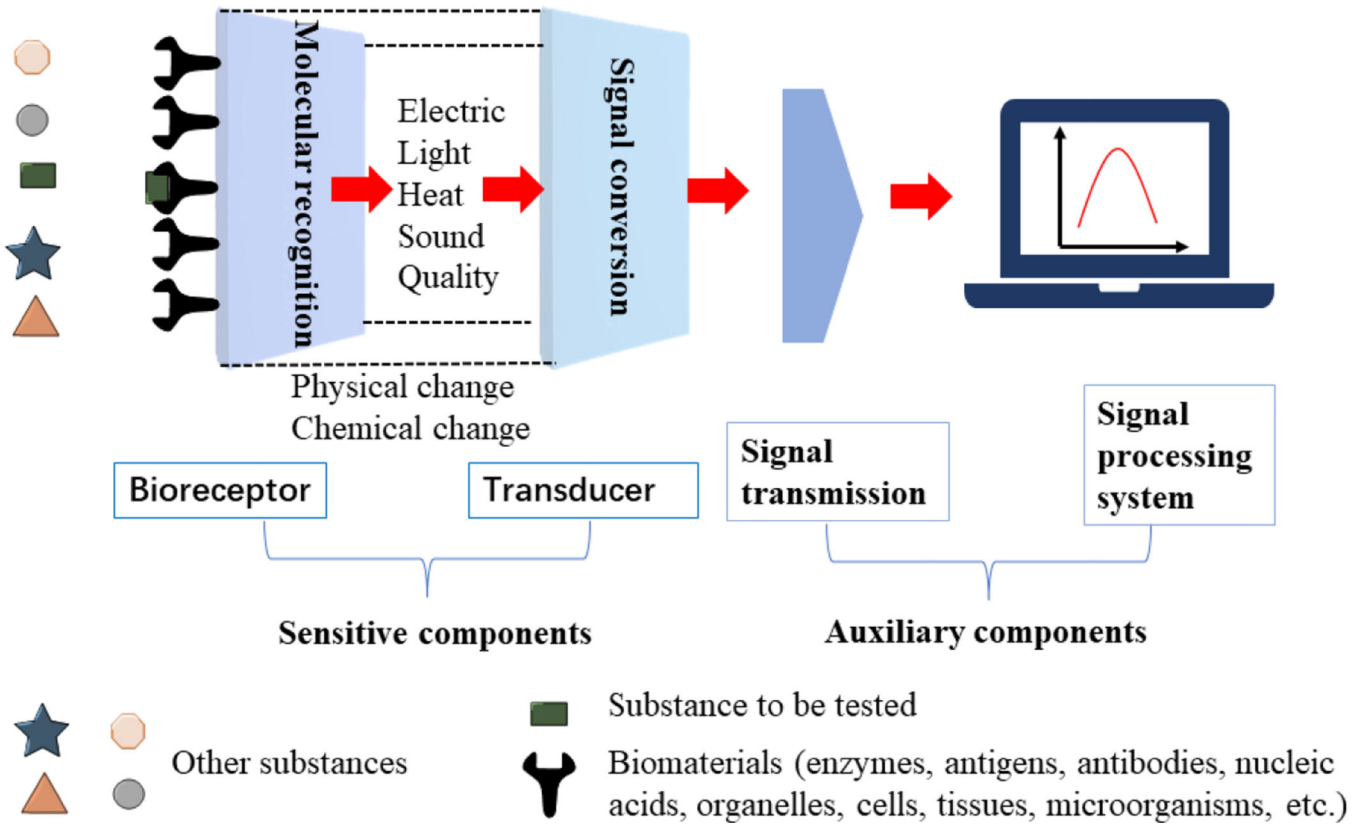

Figure 1.
Operating principles of biosensors.

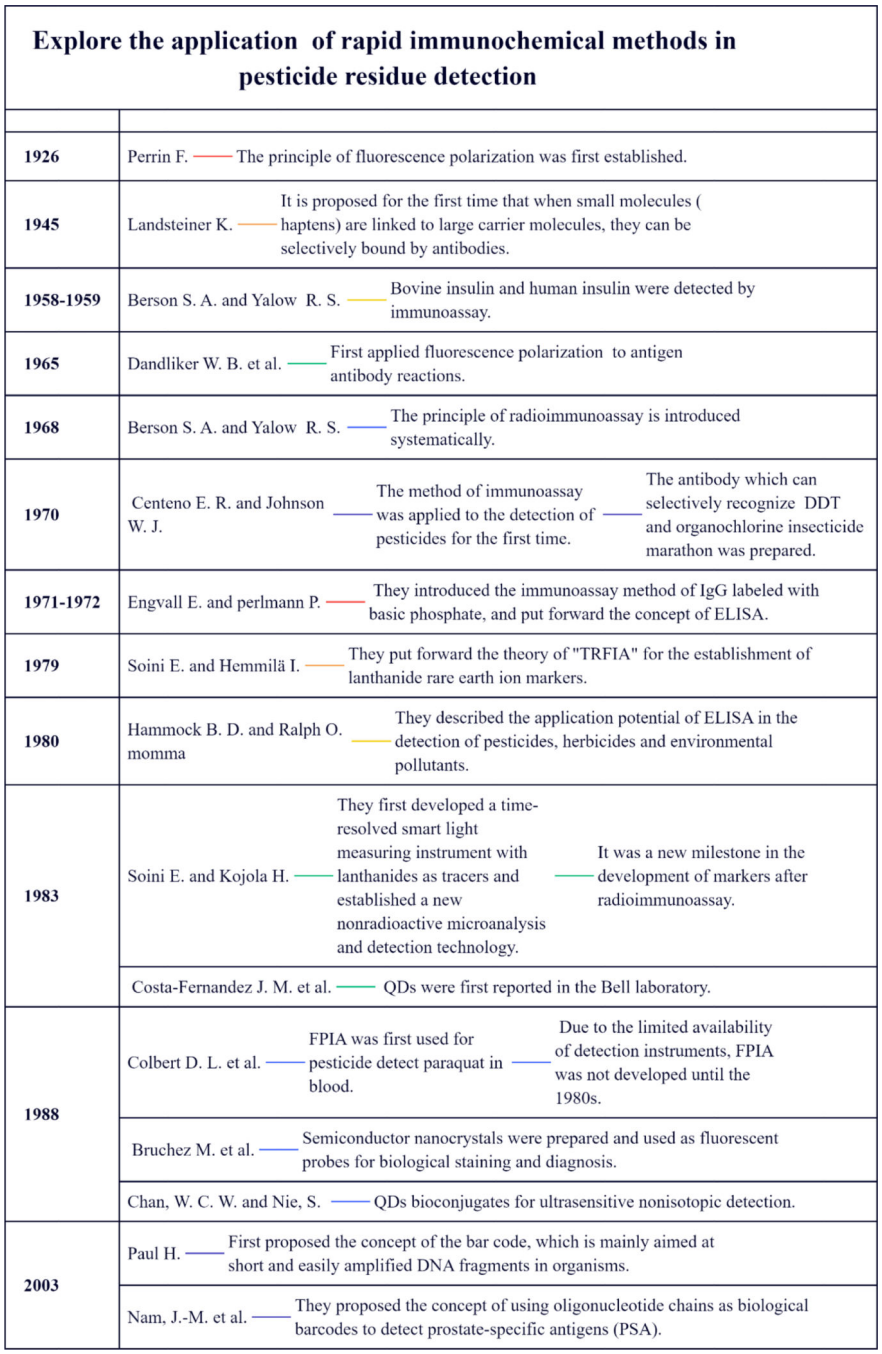

Figure 2.

The application of immunochemical methods in pesticide residue detection based on biotechnology. [40–53]

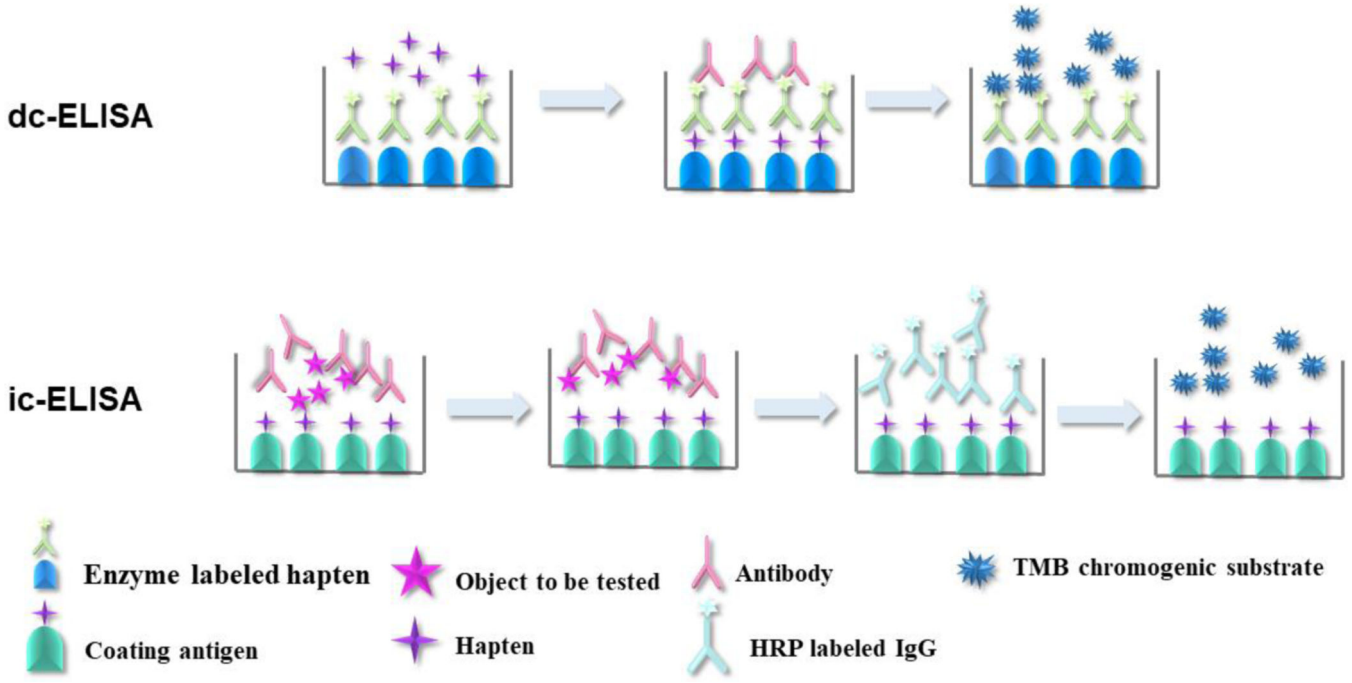

Figure 3.
Indirect and direct competitive enzyme-linked immunoassay (ELISA) mode.

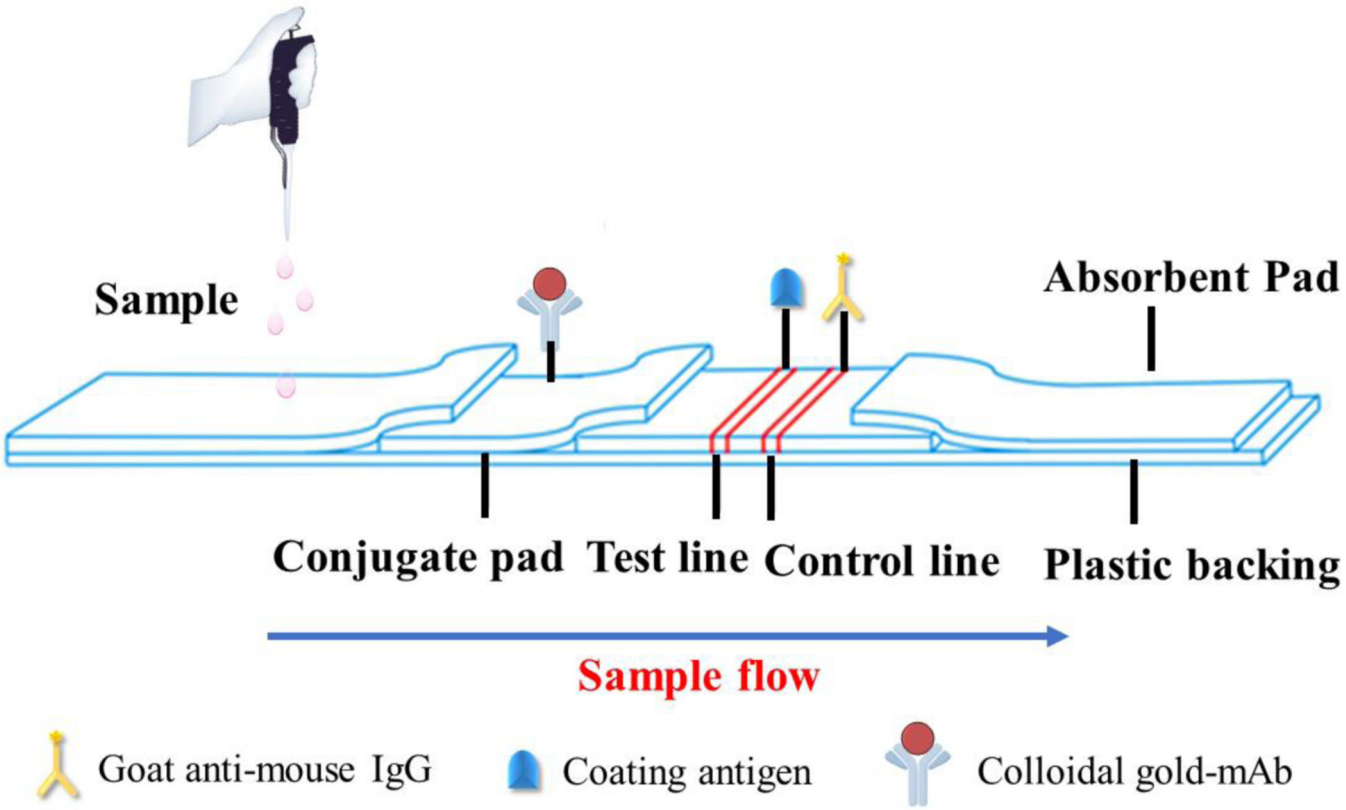

Figure 4.
Composition of the lateral flow immunochromatography (LFIA) test strip.

Table 1.

Some examples of the application of biosensors in the rapid detection of pesticide residues.

Biosensor Type	Name of sensor	Pesticide	Linear range	LOD	Reference
Enzyme biosensor	NF/AChE-CS/SNSNF/GCE	Chlorpyrifos Carbofuran	10^{-12}–10^{-10} mol/L 10^{-10}–10^{-8} mol/L	5.0×10^{-13} mol/L	151
	PPy-AChE-Geltn-Glut/Pt biosensor	Paraoxon carbofuran	0.1–12.5, 12.5–150 ppb 0.025–2, 5–60	1.1 ppb 0.12 ppb	152
	tyrosinase/ZnO NPs/spce biosensor	chlortoluron	1~100 nM	0.47 nM (~0.1 ppb)	153
	ACh/CNT/NH_2	Paraoxon	0.2–1 nmol/L	0.08 nmol/L	154
	AChE-FH-A-GNPs	Carbofuran Oxamyl Methomyl Carbaryl	–	2 nmol/L 21 nmol/L 113 nmol/L 236 nmol/L	155
	paper-based fluorescent sensor (PFS)	Diazinon	–	0.5 ng/mL	156
	hydroxyphenylpyruvate dioxygenase (HPPD) electrochemistry biosensor	sulcotrione	5.10^{-10} M −5.10^{-6} M	$1.4.10^{-10}$ M	157
	N-GQDs-AChE biosensor	fenoxycarb	–	3.15 μM	79
	AChE/e-pGON/GCE	Carbaryl	0.3–6.1 ng/mL	0.15 ng/mL	158
	GCE/P-ABSA/DAR /AuNPs/DAR/AChE	Malathion Parathion-methyl	0.003–30 pmol/L 0.0038–38 pmol/L	0.0016 pmol/L 0.0022 pmol/L	159
	AChE/Ce-UiO-66 /MWCNTs/GCE	Paraoxon	0.01–150 nmol/L	0.004 nmol/L	160
	AChE/AuPt/PDA	Paraoxon	0.5–1000 ng/L	0.185 ng/L	161
Immunosensor	A novel multianalyte electrochemical immunosensor	endosulfan paraoxon	0.05–100 ppb 2–2500 ppb	0.05 ppb 2 ppb	162
	Gold nanoparticles/cdte quantum dot immunosensor.	methamidophos	0.06–0.78 mg/mL	2 μg/kg	163
	Coulombimetric Immunosensor	Paraquat	3.08–67.76 μg/kg	1.4 μg/kg	164
	Organophosphorus Hydrolase-Based Biosensor	Paraoxon	-	5×10^{6}μmol/L	165
	Portable Potentiometric Biosensor.	chlorpyrifos	0.25 ng/mL- 37.5μg/mL	-	166
	Graphene modified screen printed immunosensor	parathion	-	0.052 ng/L	167
	a direct surface plasmon resonance (SPR) biosensor	triazophos	0.98–8.29 ng/mL	0.096 ng/mL	168
Aptamer sensor	Ultrasensitive aptamer biosensor	malathion	_	0.06 pmol/L	84
	DNA aptamer electrochemical biosensor	carbendazim	_	8.2 pg/mL	85

Biosensor Type	Name of sensor	Pesticide	Linear range	LOD	Reference
Cell and microbial sensors	Photobacterium leiognathid biosensor	2,4-D	100–600 ppm	100 ppm	[86]
	a biohybrid of Sphingomonas sp. cells-silica nanoparticles	methyl parathion	0.1–1 ppm	0.1 ppm	[169]

–: no data.

Table 2.

Research progress on colloidal gold immunochromatographic strips for the rapid detection of pesticide residues

Test types	Test object	Types of pesticides	Stroma	LOD	Reference
Single residue	Chlorothalonil	Organochlorine	Drinking water	5 ng/mL	[170]
	Chlorothalonil	Organochlorine	Cucumber	100 ng/mL	[171]
	Triazophos	Organophosphate	Cucumber	250 ng/mL	[172]
	Imidacloprid	Neonicotine	Leek, sweet potato, and potato	0.02 ng/mL	[173]
	3-phenoxybenzoic acid	Pyrethroid	River water	1 μg/mL	[174]
	Pyrimethanil	Aniline pyrimidines	Grape, strawberry, peach, tomato, apple, and cucumber	0.9 ng/mL	[175]
	Dicamba	Benzoic acids	Environmental water sample	0.1 ng/mL	[176]
	Pyridaben	Pyridazinones	Cucumber and apple	25 ng/g 50 ng/g	[177]
	spirotetramat spirotetramat-enol	Tetronic acid	Alcohol	1000 ng/mL	[178]
Multiresidue	Chlorpyrifos methyl Isocarbophos	Organophosphate	Cabbage and soil	100 ng/mL 100 ng/mL	[179]
	Parathion Triazophos	Organophosphate	Rice, cabbage, and apple	50 ng/mL; 100 ng/mL	[180]
	Carbofuran and 3-hydroxy-carbofuran	Carbamates	Environmental water sample	7–10 ng/mL	[181]
	Fipronil and its metabolites	Phenyl pyrazole	Egg and cucumber	0.25 ng/mL	[182]
	Clomazone	—	Potato and pumpkin	5 μg/kg	[183]

Table 3

Research progress of fluorescent signal immunochromatographic strips in the rapid detection of pesticide residues

Marking material	Test type	Test object	Types of pesticides	Stroma	LOD	Reference
Fluorescent quantum dot	Single residue	Parathion	Organophosphate	Rice, cabbage, and apple	6.25 ng/mL 0.411 ng/mL	[184]
		Tebuconazole	Triazole	Wheat, cabbage, and cucumber	0.02 ng/mL	[132]
		Pyrimethanil	Aniline pyrimidines	Tomato and cucumber	4.98 ng/mL	[185]
		Benzothiazole ester	Methoxy acrylate	Strawberry	10 ng/mL	[186]
	Multiresidue	Chlorpyrifos Diazinon Marathon	organophosphate	Corn, long beans, broccoli, eggplant, Pleurotus ostreatus, Lentinus edodes, apples, oranges, tomatoes, blueberries, spinach, lettuce, and cabbage	0.73 ng/mL, 6.7 ng/mL, 0.74 ng/mL	[141]
		Imidacloprid Chlorothialine Thiamethoxam	Neonicotinoid	Green tea, black tea, and oolong tea	0.104–0.33 ng/mL	[187]
Upconversion luminescent material	Multiresidue	Parathion Methyl- parathion Fenitrothion	Organophosphate	Cucumber, tomato, orange, and environmental water sample	3.44, 3.98, 12.49 ng/mL	[188]
Phage free fluorescent peptide	Single residue	Imidaclothiz	Neonicotinoid	Soil and wheat	10.1 ng/mL	[189]
Fluorescent mesoporous materials	Multiresidue	Pyrethroid type I	Pyrethroid	Aircraft interior environment sample	1 ng/mL	[190]
Time resolved fluorescent microsphere	Single residue	Imidacloprid	Neonicotinoid	Leeks, sweet potatoes, and potatoes	0.02 ng/mL	[191]

Table 4

Research progress of immunochromatographic strips for other signals in the rapid detection of pesticide residues.

Marking material	Test type	Test object	Types of pesticides	Stroma	LOD	Reference
Visible light colorimetric signal of magnetic nanoparticles	Single residue	Methyl paraoxon	Organophosphate	Buffer	1.7 ng/mL	[192]
Visible light colorimetric signal of nano carbon material		Forchlorfenuron	Pyridines	Kiwi fruit and grape	33.4 μg/kg	[193]
Chemiluminescence signal		Parathion-Methyl	Organophosphate	Traditional Chinese medicine	0.058 ng/mL	[194]
Chemiluminescence signal		Acetochlor	Organochlorine	Corn, sorghum, soybean, apple, orange, peach, cabbage, cauliflower, tomato, and drinking water	0.63 ng/mL	[142]
Chemiluminescence signal		Imidacloprid	Neonicotinoid	Traditional Chinese medicine	0.058 ng/mL	[194]
Electrochemical signal	Multiresidue	Acetochlor Atrazine	Organochlorine	Environmental water sample	3.2 ng/mL, 0.24 ng/mL	[195]
SERS signal		Cypermethrin Beta cypermethrin	Pyrethroid	Tap water, river water, and milk	2.3×10^{-4} ng/mL, 2.6×10^{-5} ng/mL	[196]

Table 5

Application examples of immunochromatography in the detection of conventional pesticide residues.

Pesticide category	Target object	Stroma	Detection signal	Testing equipment and analysis software	LOD	Reference
organophosphorous	Triazophos	Cucumber	Colloidal gold visible light colorimetric signal	Visual judgment	250 ng/mL	[172]
	Chlorpyrifos methyl	Cabbage and soil	Colloidal gold visible light colorimetric signal	Visual judgment	100 ng/mL	[179]
	Diazinon and malathion	12 fruits and vegetables	Quantum dot fluorescence signal	Smartphones and ImageJ software	6.7, 0.74 ng/mL	[197]
	Methyl paraoxon	Buffer	Visible light colorimetric signal of magnetic nanoparticles	Camera and ImageJ software	1.7 ng/mL	[192]
	Dual biomarkers from exposure to organophosphorus pesticides	Serum	Visible light colorimetric signal	Smartphone and illuminometer app	0.025, 0.028 nM	[198]
	Triazophos	Rice cabbage and apple	Colloidal gold visible light colorimetric signal	Visual judgment	100 ng/mL	[180]
	Parathion	Rice, Cabbage, and apple	Quantum dot fluorescence signal	Visual judgment and test strip card reader	6.25, 0.411 ng/mL	[184]
	Fenitrothion	Cucumber, tomato, orange, and environmental water sample	Up-Converting of fluorescent signals of luminescent materials	Test strip reader	12.49 ng/mL	[188]
Organochlorine	Chlorothalonil	Cucumber	Colloidal gold visible light colorimetric signal	Test strip reader	100 ng/mL	[171]
	Acetochlor	10 food samples	Chemiluminescence signal	Smartphone and data analysis app	0.63 ng/mL	[142]
	Acetochlor and atrazine	Environmental water sample	Electrochemical signal	Electrochemical analyzer	3.2, 0.24 ng/mL	[195]
	Chlorothalonil	Drinking water	Colloidal gold visible light colorimetric signal	Test strip reader	5 ng/mL	[170]
Carbamates	Propamocarb	Tomato and cucumber	Colloidal gold visible light colorimetric signal	Test strip reader	1.43, 0.44 ng/g	[199]
	Isoprocarb, propoxur, and carbaryl	Environmental water sample	Colloidal gold visible light colorimetric signal	Visual judgment	0.08–3.37 ng/mL	[200]
	Carbaryl	Rice, oats, carrots, and green pepper	Colloidal gold visible light colorimetric signal	Visual judgment	100 ng/mL	[201]
	Carbaryl	Cabbage, rice, and barley	Colloidal gold visible light colorimetric signal	Visual judgment	100 ng/mL	[202]

Pesticide category	Target object	Stroma	Detection signal	Testing equipment and analysis software	LOD	Reference
Pyrethroid	Cypermethrin and fenvalerate	Tap water, river water and milk	SERS signal	Raman spectrometer	2.3×10^{-4}, 2.6×10^{-5} ng/mL	196
	All pyrethroids type I	Aircraft interior environment	Fluorescent signal	Smartphones and ImageJ software	1 ng/mL	190
	Pyrethroid pesticide metabolite 3-phenoxybenzoic acid	Urine and lake water	Colloidal gold visible light colorimetric signal	Visual judgment	0.1 ng/mL	203
Neonicotine	Acetamiprid	Pear, apple, tomato, and cucumber	Visible light colorimetric signal	Test strip reader	4.68 pg/mL	204
	Imidacloprid, chlorothialine, and thiamethoxam	Green tea, black tea, and oolong tea	Quantum dot fluorescence signal	Fluorescent strip reader	0.104–0.33 ng/mL	187
	Imidacloprid	Leek	Colloidal gold visible colorimetric signal and quantum dot fluorescence signal	Test strip reader	0.02, 0.02 ng/mL	173
	Imidacloprid	Cabbage and soil	Colloidal gold visible light colorimetric signal	Visual judgment	50 ng/mL	179
	Imidacloprid	Traditional Chinese medicine	Chemiluminescence signal	Chemiluminescence analyzer	0.058 ng/mL	194
	Imidaclothiz	Soil and wheat	Colloidal gold visible light colorimetric signal and fluorescence signal	Camera and ImageJ software	9.62, 10.1 ng/mL	189
Other structure categories	Tebuconazole (triazole)	Wheat, cabbage, and cucumber	Quantum dot fluorescence signal	Fluorescent strip reader	0.02 ng/mL	205
	Propiconazole (triazole)	Cabbage, lettuce, leek, cucumber, and cowpea	Colloidal gold visible light colorimetric signal	Test strip reader	0.13 ng/g	206
	Fipronil and its metabolites(phenylpyrazole)	Egg and cucumber	Colloidal gold visible light colorimetric signal	Visual judgment	0.25 ng/mL	182
	Pyrimethanil (aniline pyrimidine)	Grape, strawberry, peach, tomato, apple, and cucumber	Colloidal gold visible light colorimetric signal	Test strip reader	0.9 ng/mL	207
	Pyrimethanil (aniline pyrimidine)	Tomato and cucumber	Quantum dot fluorescence signal	Fluorescent strip reader	4.98 ng/mL	208
	Chlorphenamine (triazine)	Food of animal origin	Colloidal gold visible light colorimetric signal	Test strip reader	0.22 ng/mL	209
	Clopidourea (pyridine)	Kiwi fruit and grape	Visible light colorimetric signal of carbon material	Camera and totallab software	33.4 μg/kg	193
	Benzothiazole ester (methoxy acrylate)	Strawberry	Quantum dot fluorescence signal	Gel imager	10 ng/mL	186
	Dicamba (benzoic acid)	Environmental water sample	Colloidal gold visible light colorimetric signal	Smartphone and data analysis app	0.1 ng/mL	176

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Pesticide category	Target object	Stroma	Detection signal	Testing equipment and analysis software	LOD	Reference
	Pyridaben	Cucumber and apple	Colloidal gold visible light colorimetric signal	Visual judgment	25, 50 ng/g	177
	Spirulina ethyl ester, spirulina ethyl enol (quaternary ketonic acid)	Alcohol	Colloidal gold visible light colorimetric signal	Visual judgment	1000 ng/mL	178
	Clomazone	Potato and pumpkin	Colloidal gold visible light colorimetric signal	Visual judgment	5 pg/kg	183