Beni-Suef University Journal of Basic and Applied Sciences

REVIEW

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The application of rapid test paper technology for pesticide detection in horticulture crops: a comprehensive review

Soumya Ghosh[1*], Samar Sami AlKafaas[2], Charné Bornman[1], Wilgince Apollon[3], Aya Misbah Hussien[4], Ahmed Emad Badawy[5], Mohamed Hussein Amer[5], Manar Bakr Kamel[5], Eman Ahmed Mekawy[5] and Heba Bedair[5]

Abstract

Background: The ever increasing pests and diseases occurring during vegetable crop production is a challenge for agronomists and farmers. One of the practices to avoid or control the attack of the causal agents is the use of pesticides, including herbicides, insecticides nematicides, and molluscicides. However, the use of these products can result in the presence of harmful residues in horticultural crops, which cause several human diseases such as weakened immunity, splenomegaly, renal failure, hepatitis, respiratory diseases, and cancer. Therefore, it was necessary to find safe and effective techniques to detect these residues in horticultural crops and to monitor food security.

Main body: The review discusses the use of conventional methods to detect pesticide residues on horticultural crops, explain the sensitivity of nanoparticle markers to detect a variety of pesticides, discuss the different methods of rapid test paper technology and highlight recent research on rapid test paper detection of pesticides.

Conclusions: The methodologies discussed in the current review can be used in a certain situation, and the variety of methods enable detection of different types of pesticides in the environment. Notably, the highly sensitive immunoassay, which offers the advantages of being low cost, highly specific and sensitive, allows it to be integrated into many detection fields to accurately detect pesticides.

Keywords: Rapid detection, Nano-particle, Pesticide residue

1 Background

Pesticides are commonly employed in modern agriculture to control weeds and pests, regulate and promote plant growth, and enhance food production [90]. Crop disease management is applied to avoid destructive losses in agriculture and subsequently to satisfy the demands of a growing world population [155]. Raw and processed horticultural crops such as fruits and vegetables enrich nutritional intake and human health [20, 22, 131]. However, pesticide residues on fruit and vegetables hold serious health implications.

According to a report published in 2009, pathogens, insects, and weeds cause crop (losses of 13, 14, and 13%, respectively [143]). Regarding crop management worldwide, herbicides are used mostly (44%), followed by fungicides and bactericides (27%), insecticides (22%), and various others (7%) [113]. Excessive use or abuse of pesticides results in residues in food, which can threaten human health [66, 128, 65]. Pesticide residues contain hazardous compounds that even at extremely low concentrations have negative effects on human health and the environment. As a result, effective residue detection

*Correspondence: soumyaghosh@yahoo.com; GhoshS@ufs.ac.za

[1] Department of Genetics, Faculty of Natural and Agricultural Sciences, University of the Free State, Bloemfontein 9301, South Africa
Full list of author information is available at the end of the article

methods were designed for food security monitoring and public health safeguards [19, 25].

Instrumental detection techniques, which include high-performance liquid chromatography (HPLC), gas chromatography (GC), and chromatographic methods linked with mass spectrometry (MS) detectors, are commonly used to determine pesticide residues [6]. These techniques give precise qualitative and quantitative information about the residues. However, extensive sample pre-treatment limits the use of these techniques, because highly trained technicians and expensive equipment are needed [17]. Rapid approaches to determine pesticides are comparatively simple and include electrochemical techniques, spectroscopic analyses, and immunoassays. Although rapid methods lack the accuracy and precision of traditional analytical techniques, they can be employed as supplementary pre-screening procedures. Novel analytic methods for the quick, low cost, reliable, and selective detection of pesticides are therefore in demand [140].

The application of chemical agents not only increased agricultural productivity in short period, but also increased chemical toxicity in the air, water, and soil over time [112]. If chemicals are applied at incorrect times and products are harvested before the end of the pre-harvest interval, large concentrations of pesticides will remain in the product, which is dangerous to human health [159]. Residues on products must not exceed international regulatory maximum residue limits (MRLs) [180]. The concentration of pesticides in crops must be taken into account to maintain public health and protect the environment.

Developing and implementing pesticide alternatives must be cost-effective, environmentally safe, and produce rapid results. Thus, this review focuses on nanomaterials that are used as agricultural promoters and highlights the importance of nanomaterials in detecting pesticide residues [152]. Nanotechnology has many advantages over traditional methods, including high sensitivity and reducing energy consumption [47, 48]. Many nanomaterials such as nanoparticles, nanotubes, and nanocomposites can be utilized for the detection, degradation, and removal of pesticides [1]. This review discusses methods to detect pesticide residues on horticultural crops, explaining their advantages and disadvantages, including conventional, rapid test paper and immunoassay methods.

2 Main text

2.1 Conventional methods in pesticide detection

Hercegová et al. [77] demonstrated that there are several traditional analytical techniques for analysing pesticides and their products. These comprise flame ionization detection, diode array, electrochemical detection, gas chromatography (GC) with electron capture detection, fluorescence, and ultraviolet liquid chromatography (LC), all of which lack selectivity. The most common techniques are mass spectrometry (MS) merged with gas and/or liquid chromatography. At low detection limits, these methods have high sensitivity and selectivity, but are limited because they use sophisticated, time-consuming, and expensive equipment, which require skill to operate [155].

2.1.1 Gas Chromatography

Gas chromatography is one of the main analytical strategies utilized in food analysis to identify and quantify pesticide residues in complex matrices. Petsas and Vagı [142] demonstrated that GC differentiates between the pesticides based on their volatilities and thermal stability [45]. Gas chromatography can be combined with different detection methods and depends on the category of pesticides being quantified [100]. For example, methods such as mass selective detection (MSD), flame ionization detection (FID), nitrogen–phosphorous detection (NPD), and flame photometric detection (FPD) are used to determine pesticide residues in cereal samples [69]. The detectors provide selectivity and sensitivity for a particular pesticide. Electron capture detectors (ECDs) are notably used to for halogenated compounds such as organochlorine pesticides [14, 105]. The NPD is sensitive for organophosphate and nitrogenous pesticides ([105]), and the FPD for sulphur and phosphorus pesticides [14, 71]. The techniques are limited for pesticides such as N-methyl carbamate, because they are either maintained on the chromatographic column or decomposed to their phenols. Furthermore, derivatization methods can limit sensitivity and applicability of fragrant carbamates ECD, which include initial hydrolysis to the equivalent phenols or amines and reaction with halogen-rich reagents [130].

2.1.2 Liquid chromatography

Liquid chromatography (LC) is used to detect pesticide residues for limited categories of compounds or single compounds and for which there were no appropriate GC conditions. Esquinas-Requena et al. [55] demonstrated that the original detectors used for LC methods were the UV or diode array detectors (DAD). These methods are generally accurate and effective, but necessitate the use of costly instruments, specialized staff, and have lengthy procedures [61]. To develop both selectivity and sensitivity, effective coupling between LC separation can be done with MS (LC-MS and LC-MS/MS) to improve the determination pesticide residues and their transformation products in complex matrices such as food [161]. Currently, high-resolution MS (HRMS) and tandem MS (MS/MS) are widely used. Celeiro et al. [34] showed

that the usual MS analysers used in food analysis are quadrupole(Q), triple quadrupole (QqQ), time of flight (TOF), hybrid quadrupole ion trap (QTrap), and Orbitrap [34, 70].

2.1.3 High-performance LC (HPLC)

High-performance LC is widely utilized and can be combined with many detectors. It can be used with DAD and/or UV to determine organophosphorus and triazines in various matrices. The HPLC uses a pump to promote the movement of the mobile phase (s) and analyte across the column and includes a detector to allow keeping time for the analyte [175]. Many factors affect the analyte keeping time and depends on the extent to which it interacts with the stationary, the solvent composition, and the mobile phase flow rate. Reversed-phase liquid chromatography (RPLC) is a type of HPLC that is most approved, due to its capability to perform successful separation of polar to apolar pesticides with good performance and detection that cannot be directly applied to GC [79]. Table 1 summarizes conventional methods such as GC, HPLC, infrared spectroscopy, MS, and spectrophotometry, which are expensive and time-consuming, and indicates the need to develop simple and rapid methods.

2.1.4 Detection of pesticide residues through multivariate analysis and VIS /NIR spectroscopy

Using chromatographic methods has several disadvantages such as a complex evaluation procedure, long detection cycle, and lagged nature of detection results. So, it is important to develop fast, reliable techniques [53, 138, 139]. Near-infrared (NIR) spectroscopy is a convenient technique used in quantitative and qualitative analysis in fields such as medicine, agriculture, and chemistry. Ultraviolet visible–NIR spectroscopy can be used to predict soil composition and pesticide absorption [88, 103]. Near-infrared spectroscopy (12900–4000 cm^{-1}) is categorized within NIR reflectance spectroscopy and NIR transmission spectroscopy. The NIR can be non-dispersive (filter-based instrumentation) and dispersive and can use Fourier transform-based instrumentation. This method is cheap, safe, simple, environmentally friendly, avoids using organic solvents, and does not need sample preparation as does chromatographic methods [87, 156]. Models and regressions (partial least squares discriminant analysis (PLS-DA)) and models (partial least squares (PLS)) are used for quantitative determination of total nitrogen (TN) and organic carbon (OC) in soil [162]. Table 2 lists some NIR spectroscopic techniques appropriate for pesticide calculation.

3 Rapid detection technology of pesticides

3.1 Paper chromatography

Paper chromatography refers to an analytical approach that separates coloured chemicals or substances on chromatographic paper. This technique is extensively implemented to separate complex mixtures of carbohydrates, steroids, amino acids, peptides, amino acids, purines, simple organic compounds, and inorganic ions [41, 89]. It was the only technique available for the isolation and detection of pesticide residues before the development of GC and thin-layer chromatography (TLC) [58]. Currently, GC is used, because of its sensitivity and simultaneous quantitative estimation capabilities. However, paper chromatography is still implemented to validate non-specific gas chromatographic results [69]. However, TLC is increasingly replacing paper chromatography in pesticide residue research due to its enhanced resolution and shorter development time [158].

3.2 Paper chromatography in pesticide detection

Yang et al. [189] and Getz [189, 64] extensively explored various applications of paper chromatography for pesticide identification. Pesticide isolation, detection, and identification from cleaned tissue extracts have been the primary applications of paper chromatography. Pesticide residue separation depends on paper chromatography, especially insect tissue extracts to separate insecticides from their metabolites, and organophosphate residues from their lipid content. Paper chromatography has also been used to separate pesticides from plant waxes. Pesticide residues were quantified by measuring the spot size on a paper chromatogram [91].

3.3 Paper chromatography techniques

Paper chromatography cannot be applied to water-insoluble materials such as chlorinated hydrocarbons and organophosphate-based pesticides, which limits its scope [123, 164]. Zweig and Archer used paper chromatography to isolate and detect sevin and 1-naphthol in wine [120], and the same method has also been used to detect herbicides. For example, Mitchell used the method to determine monuron and 3-amino-1,2,4-triazole [126, 127], and Anliker et al. separated phosphamidon and its metabolites [195]. In pesticide residue studies, the most common method is reverse-phase chromatography where the paper only supports the immobile solvent. The compounds of interest are separated through the partition between the immobile solvent and the mobile solvent, which passes through it. Stationary phases are usually made of vegetable or mineral oils, silicone, propylene glycol, and dimethylformamide. This method is suitable for isolating compounds with a very low water

Table 1 Conventional methods to detect pesticides

No	Determination method	Sample	Type of pesticide detected	Advantages	Disadvantages	References
1	GC-ECD	Soil	Halogenated compound organochlorines (OC) such as DDT, DDE, Lindane, Endosulfan, Heptachlor, and Chlordane Organophosphorus pesticides (OPPs) Synthetic pyrethroids Pyrethrin Triazines	Highly sensitive, selective, sensitive for electrophilic compounds	Low detection limit, destructive, not applicable for many analytes, not environmentally safe	Amvrazi et al. [9], Ng et al. [133]
2	GC-FID	Fatty acids	Organophosphate pesticides (OP) Malathion and Parathion Diazinon and Disulfoton Hydrocarbons	Most popular, easy, rapid response, large limit of alkanes detection is 10-12g	Destructive, cannot detect inorganic substances and some are highly oxygenated, mass sensitive and not concentration sensitive	Visentainer et al. [176], Lehotay et al. [102]
3	GC-FPD	Fruits, vegetables, tomato	-Sulphur or phosphorus-containing compounds Hetero-atoms, including metallic elements Organophosphate (OP) pesticides and their OP metabolites Fenitrothion residue.	Highly sensitive detection, quick, easy, cheap, effective, rugged, safe	Filter must be exchanged between chromatographic runs	Podhorniak et al. [147], Malhat et al. [116]
4	NPD	Tomato, sweet corn, soils	-Organic compounds containing nitrogen or phosphorous Organophosphorus (OP) such as acephate, chlorpyrifos, malathion, methamidophos, and parathion-methyl residues Chlorpyrifos	Faster and less expensive, high resolution. Sufficient limits of detection. good reproducibility	Limited, destructive, not safe, not sufficiently effective	Gobo et al. [68]; Wang et al. [181]
5	GC-MS	Grape samples, cucumber	Organochlorines Organophosphorus Carbamates Pyrethroids Triazines Triazoles Pyrazoles Sulphite ester Acylalanin	Very good recovery value, quick, easy, cheap, effective, use of analyte protectants, determination of various classes of pesticide residues, simple, sensitive, selective	Clean-up performance is not good enough	Khetagoudar et al. [93], Walorczyk et al. [178], Nasiri et al. [132], Dong et al. [51]

Table 1 (continued)

No	Determination method	Sample	Type of pesticide detected	Advantages	Disadvantages	References
6	LC-MS	Zizania latifolia, fruits, vegetables	Organophosphorus pesticides (OPPs) Organophosphate pesticides (OP)	Quick, easy, cheap, effective, rugged, safe, adaptable, selective, simple, does not require a mass of toxic organic solvents, allows processing a significantly larger number of samples in a short time, identify solutes in low concentrations (which are in parts per million-PPM) in a complex mixture	Higher operational cost, more limited sample throughput and less favourable, only works with volatile buffers that are required to avoid fouling of the API interface, residual impurities being analysed should be ionized	Xu et al. [188], Alder et al. [7]
7	HPLC	Tomatoes, fruits, vegetables	Organophosphorus pesticides (OPPs) (parathion, phoxim, phorate, and chlorpyrifos) Benomyl (benzimidazol fungicide). Insecticides and acaricides Tebuthiuron and diuron (urea herbicides) Simazine, atrazine Ametryn (triazines herbicides)	High separation efficiency, good selectivity, extremely quick, high detection sensitivity	Costly, complex, requires large quantities of expensive organic compounds	Melo et al. [124], de Villiers et al. [46]
8	GC-MS/MS	Fruits, vegetables, cereal samples	Organophosphorus (OPs) pesticides include both organophosphates and organothio phosphates	Excellent sensitivity and selectivity and identification of low pesticide concentrations for non-polar (semi) volatile compounds, multi-residue method	Biological samples cannot be analysed	Chang et al. [36], Walorczyk and Drożdżyński [177], Hernández et al. [78]
9	HPLC-MS/MS	Cereal samples, Rice (Oryza sativa L)	Flutriafol Insecticide (pirimiphos-methyl).	Quick, easy, cheap, effective, rugged, safe, appropriate to assess the compliance of cereal specimens with further regulated highest residue levels of pesticides		Melo et al. [125]

GC-ECD gas chromatography with electron capture detector; *GC-FPD* gas chromatography-flame photometric detector; *GC-FID* gas chromatography-flame-ionization detector; *NPD* nitrogen–phosphorus detector; *GC-MS* gas chromatography-mass spectrometry; *LC-MS* liquid chromatography-mass spectrometry; *HPLC* high-performance liquid chromatography; *GC-MS/MS* gas chromatography-mass spectrometry/mass spectrometry; and *HPLC-MS/MS* high-performance liquid chromatography-mass spectrometry/mass spectrometry

Table 2 Near-infrared (NIR) spectroscopy applications for the determination of pesticides

No.	Instrumental technique	Determination attributes	References
1	Mid- and near-infrared	Metribuzin in agrochemicals Describes diuron sorption in soils	Khanmohammadi et al. [92]
2	NIR	Pesticide determination in commercial formulations Detecting the chlorpyrifos content (organochlorine pesticide) Determination of active ingredients of agrochemicals Detection of pesticide phoxim residues	Armenta et al. [13], Brunet et al. [31], Sun et al. [168], Shen et al. [163]
3	Fourier transform infrared spectroscopy	Propamocarb in emulsifiable pesticide concentrate formulations	Quintás et al. [150]
4	FT-IR-DRS	Classification of pesticide residues in agricultural products based on concentration	Makio et al. [115]
5	NIR/dry extracts	Resolution of acephate, dichlofluanid, and tetrachloro-isophthalonitrile	Saranwong and Kawano [159]
6	NIR–Raman	Quantitative analysis of methyl parathion pesticide	Sato-Berrú et al. [160]

NIR Near-infrared reflectance spectroscopy; and *FT-IR-DRS* Fourier transform infrared diffuse reflectance spectroscopy

solubility, such as chlorinated hydrocarbons and organophosphorus (OP) pesticides [28, 179]. Paper chromatography is used to separate pesticide residues without chemically altering the chromatographic paper. However, fibreglass papers have been used for reverse-phase chromatography of OP compounds [91]. McKinley, Colovic and their colleagues have also used acetylated papers to separate organophosphorus pesticides in reverse-phase chromatography [42].

3.4 Advantages of paper chromatography

The ease of the procedure, low cost, and the ease of altering conditions are all advantages of paper chromatography. In paper chromatography, many characteristics, including the paper, immobile phase, developing solvents, development direction, duration, and detection method, can be changed quickly and effortlessly [24]. This aspect is vital when developing procedures for samples under specific circumstances. If the sample is processed after chromatographic separation, but before quantitative analysis, then paper chromatography has a significant advantage over TLC, because the paper can be processed along with the sample [24]. It is occasionally necessary to elute the separate parts from the thin-layer chromatogram in TLC before processing. As paper chromatography has been used in pesticide studies for several years, it is more familiar than newer chromatographic techniques. Due to this familiarity, interpreting paper chromatographic findings is more straightforward and done with more confidence [24, 43].

3.5 Mechanism of rapid test paper technology in pesticide detection

An enzyme inhibitor is a molecule that binds to an enzyme's active site, thereby reducing its activity and preventing the substrate from binding. This prevents the development of enzyme–substrate complexes, the catalysis of reactions and reduces product formation. Enzyme inhibition-based methods have been used to detect organophosphates and carbamates [21, 32]. Guo et al. created a rapid test strip for visual pesticide identification by inactivating the enzyme, its substrate, and a chromogenic agent on a paper matrix [73]. This method is portable, fast, easy to use, and inexpensive. It has a shelf life of 2 months when stored at four degrees Celsius; however, the enzyme activity is lower if stored at room temperature for 2 months [73]. Increasing colour resolution improves visual pesticide residue identification accuracy, because human optic cells are especially sensitive to wavelengths on the blue-green spectrum. Sun et al. [169] developed a dual-film screening strip made of fibreglass and polyester fibre-containing acetylcholinesterase (AChE) and indoxyl acetate. The strip was able to soak up and liberate all of the AChE or indoxyl acetate (Fig. 1).

4 Colorimetric analysis

Colorimetric analysis is a commonly used technique in paper-based analysis. Colorimetric analysis has several advantages, including high effectivity, operation ease, and increased stability [149]. Screening tools that are rapid, simple, inexpensive, and detectable by the naked eye are designed for the high-throughput screening of pesticides [39]. In colorimetric analysis, the sample solution is inserted into a test zone via capillary action. The sample then reacts with a colour reagent, and the colour changes. The colour formation or colour change is used to perform qualitative and quantitative studies of the pesticide from the test result [149].

4.1 Colour signals

Colour signals can be collected in two ways: (1) Smartphones, single-lens reflex cameras, and inexpensive desktop scanners can be used to directly image the result, after which quantitative analysis can be performed by

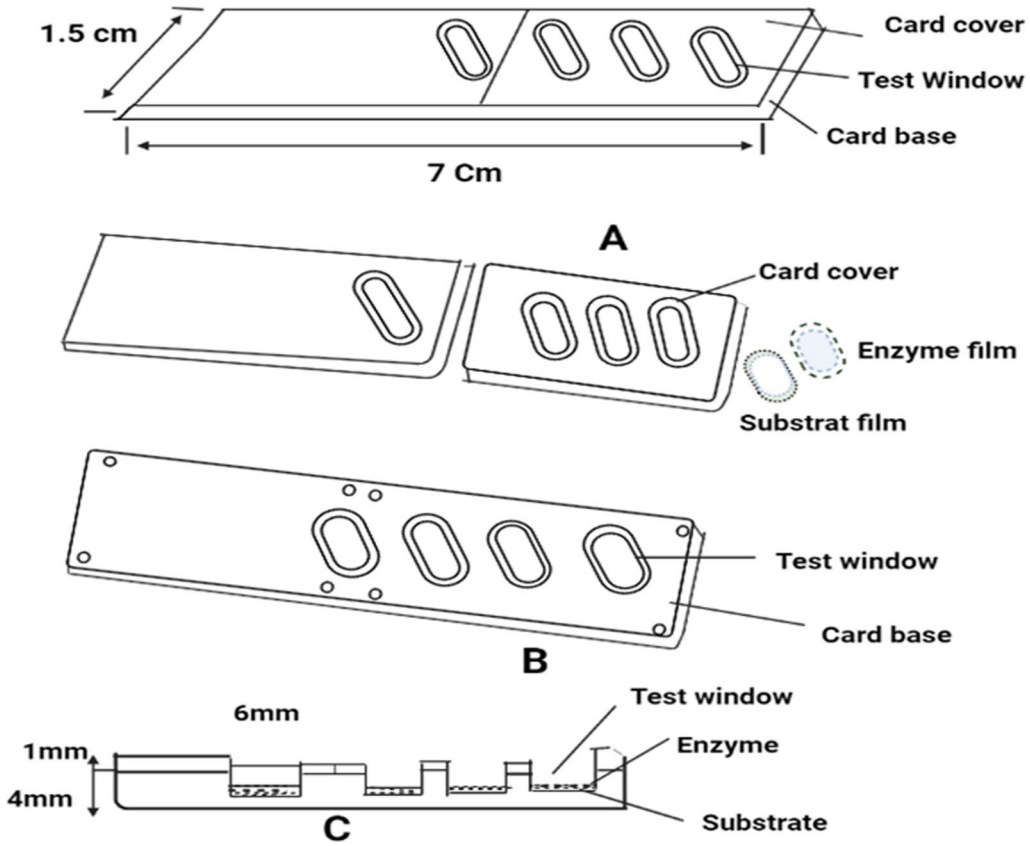

Fig. 1 Schematic illustration of the dual-film visual screening card: **A** panorama, **B** decomposition schematic, and **C** longitudinal section

specific software. (2) A spectrophotometer can be used to measure the absorbance at a specific wavelength, giving an accurate quantitative result [149].

A paper-based microfluidic chip can measure de-oxynivalenol (DON-Chip) in animal feed and food rapidly and at a low cost. The DON-Chip combines a colorimetric immunoassay with gold nanoparticles (AuNPs) and a paper microfluidic apparatus. The AuNPs act as signal indicators. As shown in Fig. 2, a new ratiometric analysis technique proposed for the analysis of DON performed well and successfully detected compounds in 12 minutes [149].

4.2 Surface-enhanced Raman spectroscopy (SERS) swabs to detect pesticides in vegetables and fruits on-site

The feasibility of using silver nanoparticles–graphene oxide (Ag NP/GO) surface-enhanced Raman spectroscopy (SERS) swabs was tested on-site in fruits and vegetables with and without spiked pesticide [112]. The peels of vegetables and fruits were cut into 1 cm^2 squares. Following this, 10 mL of pesticide solutions of varying concentrations was added to the peels [112]. Ten mL ethanol was added onto the AgNP/GO paper before applying Raman measurements to improve contact with the area of analysis and pesticide adsorption [112]. The square-shaped peel was blotted with the paper for 3 seconds. The Ag NP/GO paper was placed on a glass slide for SERS analysis after the strips dried out [112] (Fig. 3).

4.3 Examples of rapid paper use in pesticide detection

Blažková et al. developed a strip-based immunoassay that quickly detects thiabendazole in fruit juice. The immunoassay depends on the interactions between thiabendazole–ovalbumin and thiabendazole. C-nanoparticles are combined with anti-thiabendazole to create a detection complex after which thiabendazole can be visualized [27]. If thiabendazole is absent, the detection complex will bind to thiabendazole–ovalbumin to produce a black band [27]. If thiabendazole is present, a portion of the detection complex will be neutralized. The test line's colour intensity is inversely correlated with the thiabendazole concentration [27]. There is a similar test card similar, which can detect carbaryl [80]. The test card relies on the capture of carbon NPs by inactivated antibodies on the test zone, giving a black band.

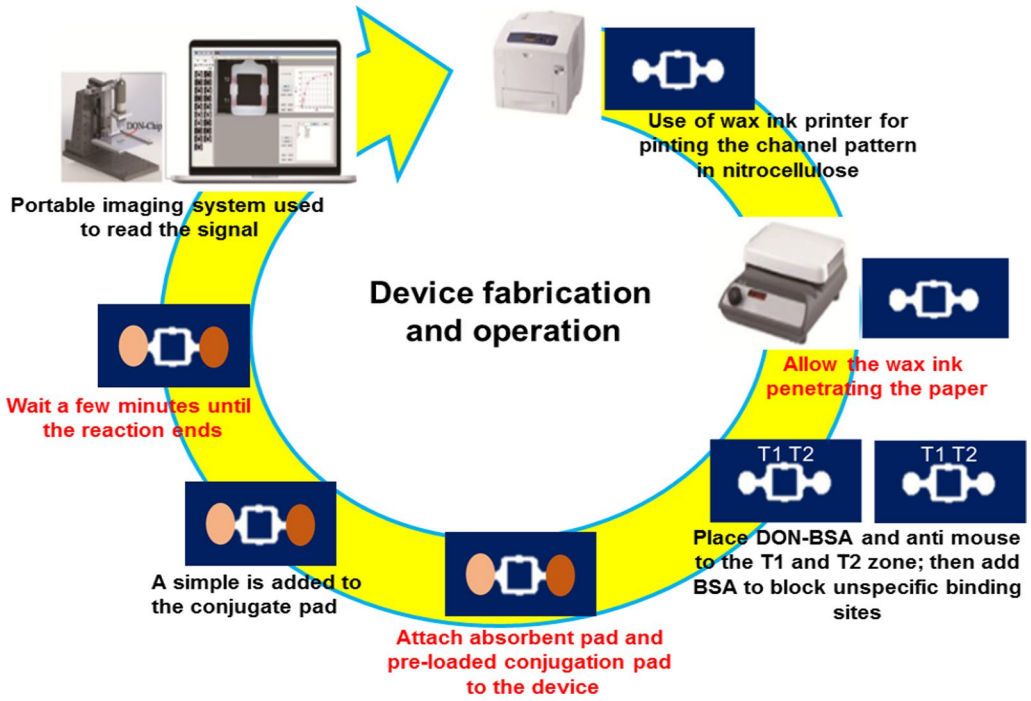

Fig. 2 Schematic illustration of DON-Chip production and operation

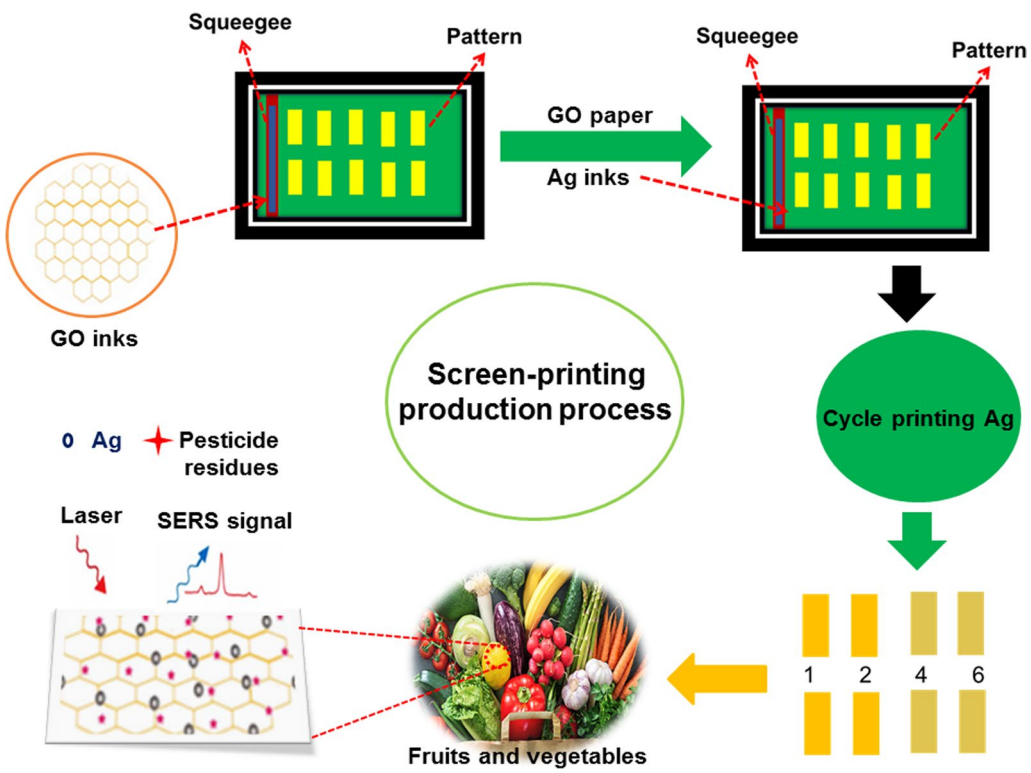

Fig. 3 Illustration of the screen-printing production process for SERS swabs its application to detect pesticides in fruits and vegetables

Free carbaryl binds to immobilized antibodies, which stops the interaction of carbon NPs with the inactivated antibodies. The colour intensity of the test band is inversely proportional to the sample's carbaryl concentration [80]. A competitive immunoassay dipstick based on AuNPs was developed as a rapid test for dichlorodiphenyltrichloroethane (DDT). The DDT pesticide is harmful, because it does not break down easily in the environment, and causes nervous system damage and complications in animal reproduction [106]. The gold nanoparticles are coupled with anti-DDT antibodies, after that the immune-complex solution is added to nitrocellulose membrane cards, which contain free DDT and the antigen. The free DDT then competitively inhibits the antigen at the AuNPs binding site. In the absence of free DDT, the card will show the red colour of the AuNPs. The red colour intensity decreases with an increase in free DDT concentration [106].

4.4 A Highly sensitive immunoassay of pesticide

The previous methods have disadvantages such as costly apparatuses needed, the long time needed for analysis, and the necessity of professional staff and not being safe to the environment. As a result, using of immunoassay-based antigen-antibody is widely used. [44] demonstrated that the immunoassay is an analytical method for detecting different substances using antigen-antibody specific binding reactions. There are two types of immunoassay: *(i)* labelled immunoassays and *(ii)* unlabelled immunoassays. For example, labelled immunoassays involve the bio-barcode immunoassay, enzyme-linked immunoassay (ELISA), fluorescence immunoassay (FIA), etc., while unlabelled immunoassays comprise immunoelectrophoresis and immunodiffusion. Advantages of immunoassay include simplicity, low cost, high sensitivity, and its ability to identify multiple types of pesticides (veterinary drugs, bio-toxins, heavy metals, etc.) or different types of small molecules at the same time. Cui et al. [44] demonstrated the main method of multiple residual detections which includes bio-barcode assay immunoassay, ELISA, FIA, etc. There are pesticides such as fenpropathrin, decamethrin, λ-cyhalothrin parathion, methyl parathion, fenitrothion organothiophosphate pesticides, organophosphate pesticides, and chlorpyrifos fenthion analysed and detected by ELISA and CLIA [44], 170.

5 Types of test paper technology utilized in rapid detection of pesticides

5.1 Nanoparticle markers

Nanoparticle markers have recently been developed and are known as ultrafine particles or nano-dust. The particles have a diameter of less than one nanometre (typically between 1 and 100 nm) [47]. Concerning light, heat, and susceptibility to magnetic fields, the particles are different from ordinary particles and have a broad specific surface region [23]. Nanoparticles are analytically important with various applications [47, 48]. Chemical nanoparticles, colloidal gold, lanthanides, quantum dots, magnetic nanoparticles, and carbon nanotubes are only a few of the nanoparticle markers that have been included in test strip processes [194].

Organic nanoparticles with strong optical properties, such as fluorescein isothiocyanate (FITC) nanoparticles, were one of the first to be used in the test strip process [8]. The primary amines of proteins are provided by the FITC nanoparticles, resulting in the ideal dye-protein conjugate [121]. The addition of fluorescein in the compound can be used to determine the presence of proteins. However, this approach has low sensitivity and photochemical stability since it relies too heavily on the chemiluminescent properties and lacks the effect of inorganic nanoparticles, which may regulate wavelength. As a result, new markers are increasingly being developed.

Colloidal gold, called a gold sol, is a multiphase uneven system created by the electrostatic repulsion between gold particles in water [118]. A system will ingest biological macromolecules without disrupting biological function and emit colours varying from green to red to purple. This allows for use as markers to differentiate between macromolecules such as proteins, polysaccharides, nucleic acids, and hormones. The test strip colloidal gold marker is the oldest and most thoroughly researched technique [140]. It has been used to test for aflatoxins in food. Many compounds such as the gold marker test strips, which are used for the identification of veterinary drug residues and pesticides, have been commercialized and include vibrio parahaemolyticus, Sudan red, and MicroRNA [182]. The gold colloidal-based immuno-dip strip was used to detect Sudan red I residue in tomato sauce and chilli powder samples quickly, with a limit of detection of 10 ng/g [72].

Lanthanide elements are a group of intermediate elements with atomic numbers ranging from 57 to 71 in the periodic table. A group of fluorescent up-conversion phosphor particles are produced by combining two related lanthanide ions as "light absorber" and "emitter" and incorporating them into ceramic particles that serve as "primary substrates". Hong et al. [81] produced a strip that is stable for 10 days at 37 degrees Celsius with 10.3 per cent using up-conversion phosphor particles as markers. Its sensitivity and quantitative findings are equivalent to those of a traditional immunology assay. The traditional enzyme-linked immunosorbent assay (ELISA) is used for antibody detection with a linearity fitting coefficient of determination (R^2) between 0.93 and 0.99. As a result, using lanthanide elements in

test strips provides ideal detection limit and stability [81], resulting in rapid application development.

Quantum dots, also classified as fluorescence semiconductor nanoparticles, have compounds and nanoparticles of Si and related elements, as well as primary groups II-IV (e.g. CdSe) and III-V (e.g. InP). Particle diameters range from 1 to 10 nanometres. Since they mimic tiny dots, they are named after quantum dot. A core–shell standardized quantum dot is currently the most widely used since it not only has strong photochemical stability, but also a high luminescence quantum yield (30–50%). Quantum dot application in test strip markers is still under investigation, but its viability has been documented. With a minimal test line of 1–2 nm, Petryayeva and Algar [141] were able to complete the quantitative detection of protease in 5 minutes.

Nano-magnetic particles, also known as super-paramagnetic particles, are a relatively new kind of nanomaterial. Their super-paramagnetic feature, large specific surface area, and compact particle size incorporate the aspects of magnetic particles and nanomaterials. Magnetic materials (e.g. iron oxide) that act as a stable phase carrier are common markers. When active groups are added to the layers of magnetic substances, a coupled reaction between the magnetic materials and biological molecules including enzymes and antibodies occurs. The research material can be detected easily and quantitatively in this manner [63]. Fisher et al. [57] developed an immunomagnetic lateral flow system that allowed the identification of *Bacillus anthracis* spores in 10 mL dairy samples (n = 38) at a concentration of 5×10^5 CFU mL^{-1}, resulting in a 60-fold increase in sensitivity over standard strip methods. However, since magnetic particles are vulnerable to aggregation during the chromatographic process, few records of nano-magnetic particles used in test strip markers exist.

Carbon nanotubes, called buckytubes, are quantum substances with a topological shape resembling a twisted hexagonal grid structure of graphite. Carbon nanotubes have quantum effects similar to ordinary nanoparticles, have a large surface area, and have high conductivity and high mechanical power. Its distinct black colour makes it easier to identify qualitatively or semi-quantitatively with the naked eye. A nucleic material lateral flow method was defined for detecting listeria infection [136], with a low visual level of 0.1 ng of the labelled amplicon. The PCR solution is specifically applied to the strip, and the presence of clear amplicons is shown by the appearance of a grey/black line mediated by carbon nanoparticles (maximum time of 15 min). However, removing the carbon graphite and amorphous carbon debris mixed in the carbon nanotubes is technically challenging.

5.2 Paper in microfluidics

As described by Whiteside in 2006 [26], microfluidics is the modern science of devices that manage and control small quantities of fluid (10^{-9} L). Fluidic channels of hundreds to tens of micrometres in diameter are used. Because of variation in length, use of small amounts of samples and reagents, and rapid isolation and detection with high resolution and sensitivity [2], microfluidics experienced exponential growth with significant impacts in analytical chemistry. Glass, silicon, and polymers such as polydimethylsiloxane (PDMS) were used in early microfluidic studies. Even though microfluidic systems miniaturize traditional approaches for precise isolation and identification, they have disadvantages such as the cost of substrate materials and the need for power and fluid transfer instruments [157].

Paper is an attractive substrate medium to synthesize microfluidic devices [122]. Paper has many benefits as a low-cost diagnostic tool, which has been extensively explored: It can be printed quickly, coated, and impregnated; the cellulose structure is consistent with proteins and biomolecules, widely available and environmentally friendly since it can be disposed of by incineration [99]. The cellulose membrane network of microfluidic paper-based analytical devices (μPADs) uses paper as the primary substrate to provide instrument-free liquid transport through capillary action. Paper has a large surface area, a volume ratio that improves detection limits for colorimetric assays, and has the capacity to store chemical components in their active state within the paper fibre network. While μPADs lack the high resolution and sensitivity of silicon, glass, or plastic-based instruments, their implementation is suitable for point-of-need monitoring. The μPADs can be used in inexpensive research for constant testing, especially in less developed countries where complex instrumentation, analytical laboratories, and experts are scarce. As a result, μPADs have emerged as an appealing alternative to highly sophisticated instrumentation in analytical applications for food and water monitoring [137]. Much research studies have been conducted on the construction and deployment of μPADs for water and food protection and quality control and include fabrication techniques of μPADs and appropriate detection methods for quantitative and qualitative analyses [137].

5.3 Molecular imprinted polymer grafted paper-based multi-disc micro-disc plate (MIP method)

Pesticides have been used in agriculture for many years and have made a major contribution to food safety and productivity. However, these compounds harm human well-being [33]. Wang et al. [183] created a paper-based molecular imprinted polymer-grafted multi-disc

micro-disc plate (MIP) for 2,4-dichlorophenoxyacetic acid CL detection (2,4-D).The MIP method had been considered as an option for immunoassay, which depends on antibodies. There are, however, significant disadvantages such as antibody hydrolysis and instability during manufacture and transport.

Tobacco peroxidase (TOP)-labelled 2,4-D molecularly imprinted on a polymer-grafted unit was used in an indirect comparative assay. The luminol–TOP–H_2O_2 CL system produced enzyme-catalysed chemiluminescence emission with a limit of detection of 1.0 pM [182, 183]. Liu et al. [111] created a simple paper-based luminol–H_2O_2 chemiluminescence for the identification of dichlorvos (DDV). Gilbert-López et al. [67] formalized a μPAD chemiluminescence assay to detect DDV in fruits and vegetables using paper chromatography, and the separation was completed in 12 minutes using 100 mL of developing reagent. The technique was successfully applied to identify trace DDV on cucumber, onion, and cabbage using a spiking method (3.6 ng mL^{-1} detection maximum). Liu et al. [111] proposed another MIP method for chemiluminescence detection of DDV using a paper-based instrument with a molecularly imprinted polymer. The detection limit was 0.8 ng mL^{-1}, and the procedure worked well on cucumber and tomato. A paper-based colorimetric technique for identifying organophosphate and carbamate pollutants has also been demonstrated. Wang et al. [183] created a system based on the inhibition of organophosphate (methomyl) and carbamate (profenophos) pesticides and used acetylcholinesterase (AChE) to degrade acetylcholine molecules into choline and acetic acid. The degree of AChE inhibition suggested pesticide toxicity, making AChE a typical bioevaluator for the presence of organophosphates and carbamates [111].

5.4 Smartphone-based detection

The use of smartphones is growing, along with the number of μPAD techniques that combine tablets or smartphones for measurements [166]. Chaiyo et al. [35] established a μPAD sensor and a mobile application for on-site colorimetric identification of organophosphate pesticides (paraoxon and malathion) based on the pesticides' inhibition of immobilized AChE. The enzyme AChE hydrolyses the substrate in the absence of pesticides, and the colourless indoxyl acetate substrate is converted to an indigo-coloured substance. The colour strength decreases with rising pesticide concentration due to AChE inhibition. The colour intensity is evaluated using an image analysis algorithm on a smartphone, resulting in real-time monitoring and mapping of water quality. The tool can detect pesticide concentrations as low as 10 nM, as demonstrated by a colour shift in the μPAD [134]. Zhang et al. [191] focused on the use of nanoceria-coated μPAD for colorimetric organophosphate pesticide detection using enzyme inhibition assay with AChE and choline oxidase. In the existence of pesticides, AChE activity is prevented, resulting in no or limited H_2O_2 production and, as a result, less yellow colour formation of the nanoceria. (The colour production process is depicted in Fig. 4.) The assay could detect methyl-paraoxon and chlorpyrifos-oxon with detection limits of 18 ng mL^{-1} and 5.3 ng mL^{-1}, respectively. The procedure was applied successfully for methyl-paraoxon identification on spiked cabbage and dried green mussel, with 95% recovery values for both samples.

5.5 Paper-based visual detection

The design of a mobile (CdTe) paper-based sensor for identifying carbamate pesticides was continued. The nano-ZnTPyP concentration on the paper chip was increased to ensure the high sensitivity of the sensor. The same concentration (10 g L^{-1}) of metolcarb was tested using a CdTe-based paper sensor with different concentrations of nano-ZnTPyP (17.04, 17.85, 18.75, 19.73, and 20.83 mol L^{-1}). A low concentration of nano-ZnTPyP was not beneficial to visual identification, whereas a high concentration of nano-ZnTPyP was detrimental to eventual fluorescence recovery. The nano-ZnTPyP concentration of 17.85 mol L^{-1} had the most noticeable variations in colour change between quenching and regeneration, which was useful for visual recognition. As a result, the nano-ZnTPyP concentration for the paper-based sensor was determined to be 17.85 mol/L. The paper chips were then used thereafter to identify carbamate pesticides. As shown in Fig. 5**,** various concentrations of metolcarb (1–20 g L^{-1}) were applied to the paper chips. As the metolcarb concentrations rose, the colour of the paper changed from dark green to yellow-green, then to pale green, and eventually to green, allowing for the quick visual identification of pesticides. Images were taken with a camera under 365 nm ultraviolet analyser, and the colour RGB values were collected and simulated by a computer programme, revealing the same pattern of colour shifts on the paper. Carbofuran and carbaryl were detected visually and quantitatively by the paper-based sensor under the same conditions. It was stated that the production of a novel nano-zinc 5, 10, 15, 20-tetra(4-pyridyl)-21H-23H-porphine (nano-ZnTPyP)-CdTe-based paper sensor could successfully detect carbamate pesticides in a quick, highly sensitive, highly precise, and on-site manner [148].

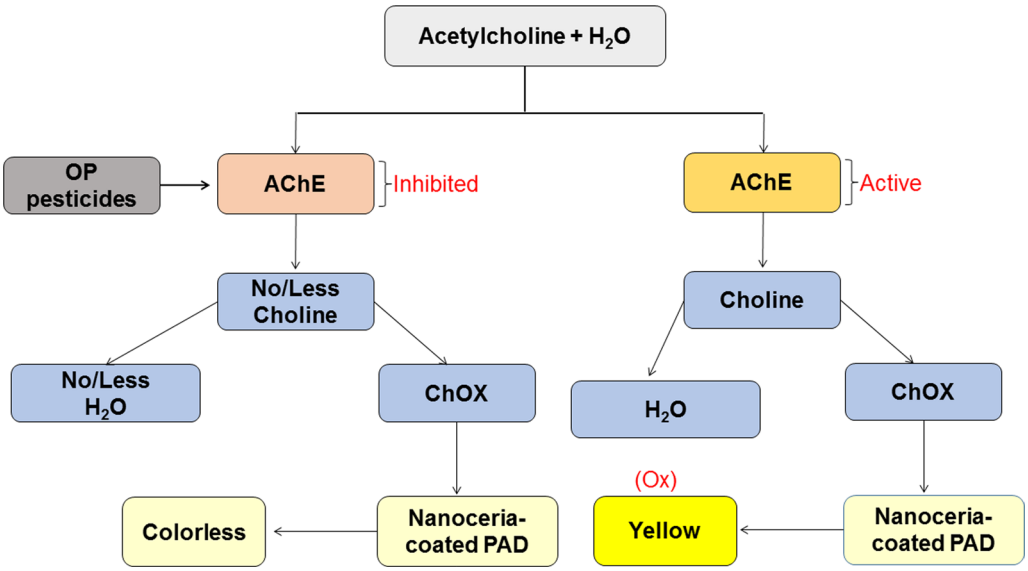

Fig. 4 The colour production process in nanoceria-coated μPAD colorimetric organophosphate pesticide detection

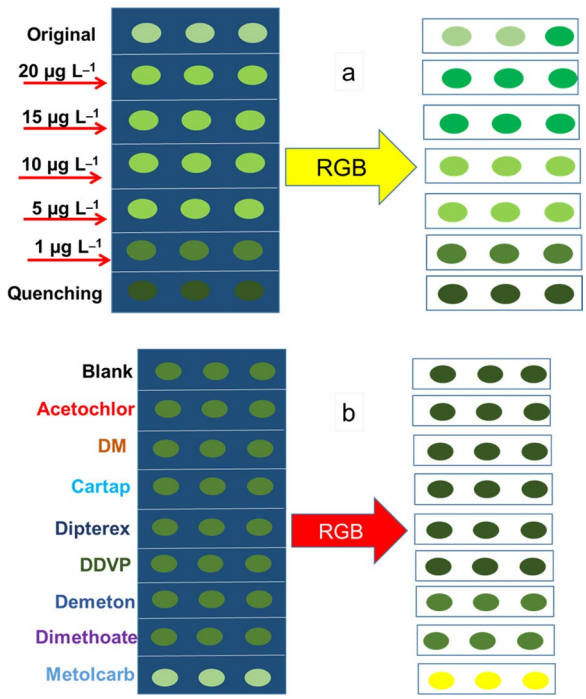

Fig. 5 Change in paper colour with rising of the metolcarb concentrations using a CdTe-nano-ZnTPyP-based paper sensor

6 Recent studies in rapid test paper technology

Pesticide enzymatic and immunoassay test kits have been produced. Enzyme-based test kits can indicate organophosphate (OP) and carbamate (CM) pesticides in water, ground, vegetables, fruits, and other ecological samples. Also, to evaluate enzyme activity before and after pesticide exposure, techniques such as fluorimetry, amperometry, spectrophotometry, potentiometry, and thermometry are used [96]. There are several recent studies in rapid test paper technology, as summarized in Table 3.

7 Conclusions

The usage of pesticides can lead to toxic residues in horticulture crops, which, if consumed, can lead to decreased immunity, splenomegaly, renal failure, hepatitis, respiratory disorders, and cancer in humans. As a result, safe and practical strategies for detecting these residues in horticultural crops and monitoring food security is essential. Each of the discussed methods can be used in a certain situation, and the variety of methods enable detection of different types of pesticides in the environment. For instance, conventional methods, such as ECDs, are effective for organochlorine pesticides detection, while NPD, LC, HPLC, and NIR are suitable for organophosphate and nitrogenous pesticides, single compounds, organophosphates/triazines, and prediction of soil composition/pesticide absorption, respectively. Recently, rapid detection technologies have proved a great success, such as TLC that has enhanced resolution and shorter development time. Paper chromatography has a significant advantage over TLC, because the paper can be processed along with the sample. Colorimetric analysis and SERS that combine nano-markers, tablets, or smartphones for measurements are more effective to detect pesticides

Table 3 Advantages and disadvantages of the techniques used for pesticide detection in horticulture crops

Techniques	Advantages	Disadvantages	References
High-performance liquid chromatography (HPLC)	Automated operation; flexible; appropriate for different types of analytes or samples; high separation power with sensitive detection; and highly accurate and duplicatable quantitative analysis.	High cost; coelution; complex for beginners or novices; it does not work for all samples; adsorbed compounds; less separation efficiency; and it is lacking of an ideal universal detector.	[50, 173]
Gas chromatography (GC)	High efficiency for the separation of the components from complex mixtures in an adequate interval of time; multiple detectors with high sensitivity; and exact quantitation.	It is limited to thermally stable and volatile compounds; most of the gas chromatography detectors are destructive.	[4, 151]
Mass spectrometry (MS)	Extremely sensitive; it easily detects sample's unknown components compared to the other techniques such HPLC and GC; it is a rapid and precise technique; it is capable to be combining with other techniques such a HPLC (LC-MS) and GC (GC-MS); and it operates with very small sample amounts.	High cost and requires expert technician.	[12, 167]
Flame ionization detector (FID)	It is inexpensive to acquire; simplicity; versatile; large linear range; low noise; good sensitivity and easy to operate.	The most common disadvantage of FID is its destructive nature; also, it is unable to couple directly to other GC detectors.	[75]
Liquid chromatography (LC)	Its capacity of separating complex samples; combination with MS; higher resolution and sensitivity.	Instrumental complexity; increased analysis time	[11, 98, 135, 144]
Electrochemical detector (ECD)	Low cost in real time; simplicity; miniaturization; and continuous analysis on diverse analytes	It takes a lot of time; sensitive (i.e. to the surrounding environment); requires redox elements to improve the power generation	[49, 95]
Nitrogen–phosphorous detector	Obtention of qualitative information; high sensitivity for compounds which contain N and P; ratios of response of the N-P detector; less extensive sample clean-up, and good linear range.	It is a destructive technique; and it is not applicable for many analytes.	[76, 145]
Flame photometric detector	Low cost; it is selective and sensitive; rapid technique; it is qualitative and quantitative in nature; and it can determine very low concentrations of compounds in the samples.	It works only with liquid samples; it cannot directly detect inert gases in the samples; it cannot measure the accurate concentration of the metal ion in the solution	[29]
Electron capture detector	It is adjustable; higher electron densities and energies; it is simple and robust; low maintenance; non-destructive and very sensible.	Low linear dynamic range; presence of radioactive material (precautions for use)	[30]
Colorimetric technique	It is easy to operate; quick response; long linear range of the quantitative assay; result accessible in less than 1 second; and it is sensitive.	It is expensive; it does not work in UV and IR regions; it cannot be used in colourless compound	[107, 108]
Paper chromatography	Less time-consuming; it is cheaper than other techniques; simple; it is quite easy to be configurated and handled	This technique is not suitable for quantitative analysis and the separation of volatile substances (such as hydrocarbons and volatile fatty acids); it cannot be coupled with testing large numbers of samples; and it is very difficult to separate complex mixtures by using this technique	[74]
Reversed-phase liquid chromatography	This technique provides greater solubility for polar analytes; sample recovery with little solvent evaporation in a short time; separation of complex samples; and it works with nontoxic solvents.	It is time-consuming	[59, 154]
Near-infrared transmission spectroscopy	Quick and automatic; easy to use; high penetration depth; reproducible	Low sensitivity; its high cost	[117]
Enzyme-linked immunosorbent assay	High specificity and sensitivity; simple procedure;high efficiency; and quantitative and qualitativeanalysis	Instability of this technique; insufficient level of sensitivity; laborious assay procedure	[82, 153]
Nano-biosensors	Selectivity, sensitivity, rapid detection, and response	Its development and implementation can be very costly; and tedious process	[119]

Table 4 Summary of recent studies in rapid test paper technology

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
1	Pesticide enzymatic and immunoassay test kits	The kits are qualitative colorimetric acetylcholinesterase (AChE) inhibition-based tests. Acetylcholinesterase hydrolyses acetylcholine (ATC) when an inhibitor, such as an organophosphate or carbamate, is absent. After that it interacts with 5,5′-dithiobis-(2-nitrobenzoic acid), resulting in a yellow colour which can be visualized with the naked eye or with a colorimeter at 405 nm wavelength. If OP or CM molecules are found in the sample, it will inhibit AChE, preventing or decreasing colour creation, depending on the quantity.	Water, vegetables, fruits, other ecological samples	Organophosphate (OP) and carbamate (CM) pesticides	Kumar et al. [96]
2	ELISA kits were used in the Mississippi River (immunoassays)	The first commercial immunoassay kit for pesticide analysis was made available in 1988. This kit was utilized to detect atrazine [10]. Immunoassays have been established for various analytes found in water, soil, and sediments. They are well suited for large-scale detection of metals, pesticides, and organic chemicals such as polychlorinated biphenyls, polyaromatic hydrocarbons, bacterial toxins, and TNT.	Water, soil, vegetables	Herbicides, pesticides such as Atrazine, and organic chemicals such as polychlorinated biphenyls, polyaromatic hydrocarbons, bacterial toxins, TNT	Thurman et al. [172], Plaza et al. [146]; Ercegovich [54]
3	Nanoparticle-based electrochemical, optical, and magnetic environmental sensors	Wang et al. [185] detected microcystin-LR in water from a Chinese lake with the use of antigen-coated filter paper and single-walled carbon nanotubes (SWNTs). The SWNT paper card serves as the electrode surface, the platinum wire serves as the counter electrode, and Hg2Cl2 serves as the reference electrode. As analytes spread through the SWNT layers, an interaction occurs between the antibodies in the paper and the analyte, forming an Ag-Ab complex that drives apart from the SWNT layers, reducing the current travelling through them. Thus, current decreases as the concentration of the analyte increases. This approach is simple, mobile, and highly sensitive, specialized, and inexpensive. This technique is equivalent to enzyme-linked immunosorbent assay (ELISA), but it is approximately 28 times quicker.	Apple fruit samples, water, air, dirt	Pesticides including phenoxy organophosphates, carbamates, pyrethroids, atrazine, neonicotinoids, organochlorines	Willner and Vikesland, [187], Motaharian et al. [129], Wang et al. [186], Wang et al. [185], Zhang et al. [193]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
4	Biosensors	Biosensors for pesticides depend on enzyme inhibition, such as how carbamate and organophosphorus pesticides inhibit cholinesterase (ChE) by blocking the enzyme's binding site. Pesticide toxicity is assessed by detecting the reduction in enzymatic activity following exposure to the sample. Calculating the percentage of inhibition of enzyme activity induced by pesticide exposure can be used to measure the concentration of the pesticide. The activity of the enzyme can be evaluated to identify substrata or enzyme reaction products by using amperometry, potentiometry, spectrometry, fluorimetry, or thermometry. Herbicides disrupt photosynthesis or phosphorylation, which is the basis for whole-cell biosensors and can be observed using an oxygen electrode, an amperometric sensor, or an optical sensor. Whole-cell sensors based on organophosphorus hydrolase were created using microalgae and bacteria (OPH).	Bananas, fruits, vegetables, food	Organophosphorus insecticides, for example, parathion, paraoxon, methyl-parathion	Mathivanan, [119], Zamora-Sequeira et al. [190], Liu et al. [110]
5	Fluoroimmunoassay (TRFIA) with a fluorescent europium chelate label	This approach was selective and sensitive, and they were able to achieve a detection limit for 17-estradiol of 2.3 pg/ml, which is similar to that achieved by ELISA. With the TRFIA, The detection limit for estriol was 4.3 pg/ml, which is 1–2 levels higher than ELISA. This technique with TRFIA was utilized to quantify 17-estradiol at 32 pg/ml and estriol at 5.5 pg/ml in water. Bacigalupo [15] employed a fast TRFIA screening technique in which liposomes trap a terbium/citrate complex to detect atrazine in water [15]. This method-achieved a detection limit of 0.1 ng/ml, allowing multiple samples to be examinedsimultaneously. After a brief incubation period, atrazine covalently coupled to mastoparan, a polypeptide, facilitated the release of terbium citrate. Mastoparan is simple to make since it is made up of various amino acids. Mastoparan's lysine amino acids allow it to bind to a wide range of target analytes.	Major arable crops, grassland, fodder crops. horticultural crops include fruit, vegetables, protected crops, hops, mushrooms, bulbs, flowers and hardy nursery stock, Chinese cabbage, honey	Imidacloprid residue chlorpyrifos	Thomas and Hutton [171], Chen et al. [38], Majima et al. [114], Si et al. [165]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
6	Mass spectrometry (MS)	Researchers also designed a system using an ion trap mass-spectrometer whereby polydimethylsiloxane (PDMS) membranes were utilized to add analyte into the mass spectrometry system through membrane diffusion. After coarse filtering of the wastewater, the mass spectrometry system was installed into the treatment tank. At 12-minute intervals, the sampling apparatus injected 1 ml water samples into constant running water filtered by charcoal which was in contact with the membrane interface. The device measured chloroform, a product of clean water chlorination.	Fruits, vegetables	Carbaryl pesticides, imidacloprid, deltamethrin, cypermethrin, malathion, acetamiprid, monocrotophos, chlorpyrifos-methyl, diazinon	Kibelka [94]; Jallow et al. [86]
7	Azo-coupling reaction-based method	1-naphthol is produced when organic base pre-treated carbaryl insecticides react with a diazonium salt, resulting in a colour change from yellow to orange.	Fruits, vegetables	Carbaryl pesticides	Lee et al. [101], Zamora-Sequeira et al. [190]
8	Microfluidic arrays sensor	A method based on paraoxon as a typical Organophosphate. Different concentrations of paraoxon pre-inhibited AChE for 30 minutes before adding it to the detection system to be incubated. Colour change from red to blue.	Fruits, vegetables	Organophosphate pesticides	Fu et al. [60], Hu et al. [83]
9	Gold nanoparticle-based colorimetric aptasensor	A method based on AuNP colorimetric assay for rapid detection of organophosphorus pesticides. A method based on AuNP colorimetric assay. The AuNP solution turned blue.	Food, water	Organophosphorus, carbamate pesticides	Bai et al. [18], Liu et al. [109]
10	Acetylcholine and acetylcholinesterase inhibitors detection using gold nanoparticles coupled with dynamic light scattering	To identify organophosphorus pesticides quickly. The acetylcholinesterase hydrolysis reaction and the dissolution of AuNPs in Au3+ - CTAB solution. The colour changes from red to colourless or red to bright pink.	Food, water	Organophosphorus pesticides	Chawla et al. [37], El Alami et al. [52]
11	A method based on citrate-capped AuNPs	Citrate-capped AuNPs. The Colour change from wine-red to purple-blue.	Food, water samples	Dithiocarbamate pesticides	Chawla et al. [37], Li et al. [104]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
12	Immunoassay test card	The card is based on using alkaline phosphate (AP) to react with 5-BCIP/NBT to p-toluidine salt, 5-BCIP-4-chloro-3-Andolyphosphate nitro-blue tetrazolium chloride. In the sampled solution, there is competition between free atrazine and carbaryl for the antibodies of the card. The amount of free atrazine and carbaryl is indicated by the blue colour intensity. Atrazine band and carbaryl band do not conflict with each other. However, interference is observed when propazine is present at the same concentration or when ametryn, propazine, prometryn, simazine, and terbuthylazine are present in concentrations more than 10 ng/ml. However, this test card provides consistent measurement findings for GC-MS and HPLC-FD with concentrations 10 and 200 ng/ml visual atrazine and carbaryl in various fruits and vegetables.	Fruits, vegetables	Carbaryl, atrazine pesticides	Gabaldón et al. [62], Plaza et al. [146]
13	Bioactive paper-based sensors	Acetylcholinesterase is a type of enzyme that breaks down acetylcho (AChE). The test card is made of paper and is based on Ellman's colorimetric test (1 to 10 cm), in which a biopolymer chitosan gel immobilized by glutaraldehyde with AChE and 5,5′-dithiobis (2-nitrobenzoic) acid (DTNB) is cross-linked and acetylthiocholine iodide is utilized as an external reagent (ATChI). The test protocol includes introducing a pesticide-containing solution in the sensing zone. The paper is put in ATChI solution for the induction of enzymes catalysed hydrolyses after an incubation time. The card is placed in the ATChI solution after incubation to trigger enzyme-catalysed hydrolysis of the substratum, which causes the change of yellow colour. A lack of yellow colour or a decrease in yellow colour indicates AChE inhibitor levels. The Biosensor has a high sensitivity to organophosphate and carbamate pesticides (methomyl = 6.16 10(-4) mM and profenophos = 0.27 mM) and may respond quickly (5 minutes). The results pointed to a paper-based biosensor that is quick, sensitive, cost-effective, portable, disposable, and simple to use.	Fruits, vegetables	Organophosphate, carbamate pesticides	Badawy and El-Aswad [16]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
14	A novel biosensor test card	Fernández-Ramos et al. [56] created a new organophosphate and carbamate pesticide biosensor. The test card is made of support paper (1 ~17.6 mm), which contains a small hole in place between the acetylcholine chloride (AChCl) and acetylcholine esterase (AChE), which ensures that they touch the reaction zone only when transported to the BCP (Bromocresol Violet-containing Reaction Zone) through a sample solution lateral flow. The sensor works at ambient temperature, and the inhibited reaction rate is used as an analytical message, determined by the suitable colour coordination with the camera. Forcarbaryl and chlorpyrifos, calibration courts of 0.24 to 20 g L-1 and 2.00 to 45 g L-1 were obtained, respectively. The limits for detection were 0.24 and 2.00 µg L-1, and replicability was between 4.2 and5.5 per cent correspondingly. The procedure was used to determine pesticides without sample pre-treatment in diverse water samples.	Fruits, vegetables	Organophosphate, carbamate pesticides	Fernández-Ramos et al. [56], Jain et al. [85]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
15	Multi-detection techniques based on enzyme inhibitions	Organophosphate and carbamate pesticides, according to Jia et al. [90], can inhibit cholinesterases, acetylcholinesterase (AChE), and butyrylcholinesterase. This technique allows multi-residue inhibition detection based on enzymes to be employed in the monitoring of multi-analytes. The level of inhibition is associated with pesticide content, which can be quantitatively detected. The nucleophile serine hydroxyl group present in the active site of AChE can form covalent bonds with the phosphorus atoms of the organophosphates. AChE is the most frequently utilized enzyme for the creation of multi-detection techniques based on enzyme inhibitions. In the presence of OP or CM insecticides, AChE may hydrolyze some colour-based substrates, whereas colour development can be reduced. Consequently, different colorimetric screening methods based on this idea have been developed. An optimized and validated AChE assay was utilized for carbofuran, carbofuran-3-hydroxy, and dichlorvos extracts. AChE test was performed. Indoxyl acetate was employed to build a substratum that can be degraded quickly by AChE.	Fruits, vegetables	Organophosphate, carbamate pesticides	Jia et al. [90], Akkad and Schwack [5]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
16	Paper partition chromatography	Using paper partition chromatography could remove many of the issues connected to the use of stationary phases in reverse-phase chromatography. Chemically altered papers could be used in many areas of pesticide detection, e.g. ion exchange papers that separate polar pesticides such as some herbicides, fungicides, and organophosphates. In some cases, fibreglass and acetylated papers have been used, and the results rationalize a further examination of their applicability in the chromatography of pesticides. Low temperatures limit the use of paper chromatographic separation for pesticides. Decreased temperatures reduce the chromatogram development rate and vastly improve the resolution by reducing the size of dots on the chromatogram. Low temperatures may allow volatile solvents to be used for both stationary phases and as developing solvents.	Fruits, vegetables	Water-soluble organophosphate pesticides, herbicides, fungicides	Islam et al. [84], Coffin [43]
17	Colorimetric technique	After pre-treating carbaryl with an organic base, 1-naphthol will be produced and quickly undergoes an azo-coupling reaction with Formylbenzene diazonium hexafluorophosphate (FBDP). Decomposing less reactive carbaryl into 1-naphthol and N-methyl carbamates into phenols can be done quickly in 1 minute. Both quantitative and qualitative analyses of carbaryl could be done based on colour differences with the FBDP solution. This colorimetric method can detect 50 µM of carbaryl from a sample of fruit without further processing. Cao et al. [32] covered the techniques and applications of many enzyme inhibition-based methods in their review. These included rapid detection of organophosphates and carbamates using electrochemical biosensors, optical colorimetric assays, assays based on fluorescence, test cards, and a microfluidic device.	Fruits, vegetables	Carbamate pesticides, carbaryl residue	Lee et al. [101], Agrawal and Gupta [3]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
18	Microarray method	Antibodies and antigens of sixteen pesticide pairs were tested for cross-reactivity and reactivity. A microarray chip with 7 antigens immobilized on a nitrocellulose membrane was made. To acquire a sensitive colorimetric immunoassay, gold nanoparticles were utilized for labelling and signal amplification. Primary and secondary antibodies such as gold compounds were used as tracers to compare the detection formats (directly and indirectly). Based on the indirect approach, a sevenplex immunochip test was designed and optimized. In the case of pesticides, the detection limit was 0.02–6.45 ng mL^{-1}. The visual assessment showed detection limits to be between 1 and 100 ng mL^{-1}. The immunoassay chip has the potential for pesticide multi-analysis in fruits and vegetables, according to this study. The proposed microarray method is versatile and applicable to multiplex immunoassays for small molecular complexes.	Fruit	Phenoxybenzoic acid, atrazine mercapturate	Lan et al. [97], Zhang et al. [192]
19	Nano-biosensors	Nano-biosensors have advantages like selectivity, sensitivity, rapid detection, and response. Nanosensors react and convert a target into a signal for rapid recognition with the help of biological parts. As per the previously mentioned methods, it is clear that the described techniques play an important role in pesticide determination. Pesticides have been detected using a variety of bio-elements, although enzyme-based biosensors are the most extensively used in comparison with other bio-elements for contaminant detection. This is due to the complex structure, which has a high selectivity for pesticide compounds and helps in recognizing them in multicomponent mediums. Nanobiosensors have shown exceptional results in pesticide detection. The progressions in nano-biosensors show encouraging and consistent data with no undesirable impacts while also offering new developments in pesticide identification.	Food, fruits, vegetables	Organophosphorus (OP), carbamates (C)	Christopher et al. [40]; Mathivanan, [119]

Table 4 (continued)

No.	Techniques	Mechanisms	Samples	Type of pesticides	References
20	Drop-wipe-test	In the research article by Wang et al. [184], they clarified that to achieve quick detection of pesticides in fruit, a "drop-wipe-test" method is established which is based on wiper-type filter paper coupled with SERS. Silver nanoparticles were used to coat the paper which was used as a wiper-type SERS substrate. The "drop" and "wipe" steps were combined to make the sampling and extraction operations easier. The last step, "test", was done to acquire the data using a Raman spectrometer. The ideal wipe time was approximately 15 seconds which ensured a complete extraction of the analyte. SERS substratum was used to rapidly detect thiram in three different fruits by this technique. Pesticide concentrations increased, resulting in a linear association between average SERS spectra intensity and R-square values of 0.9991 for apple, 0.9872 for pear, and 0.9841 for grape. The limit of detection for thiram was 4.6261 in apple, 5.1799 in pear, and 5.7061 ng/cm2, in the grape peel. The detection limits are lower than the upper limits set for pesticides in food by China's National Food Safety Standard. Thus, the SERS technique together with an absorbent SERS substrate is rapid, practical, reliable, and sensitive to detect pesticides.	Fruit	Organophosphate pesticide	Wang et al. [184], Tsagkaris et al.[174]

This table represents the most relevant case studies in terms of rapid test paper technology

on horticulture crops on-site. Interestingly, the highly sensitive immunoassay, which offers the advantages of being low cost, specific, and sensitive, allows it to be integrated into many detection fields to accurately detect pesticides (Table 4).

Abbreviations

AChE: Acetylcholinesterase; AgNP/GO: Silver nanoparticles–graphene oxide; CM: Carbamate; DAD: Diode array detectors; DDT: Dichlorodiphenyltrichloroethane; DON-Chip: De-oxy-nivalenol; ECD: Electron capture detectors; ELISA: Enzyme-linked immunoassay; FIA: Fluorescence immunoassay; FID: Flame ionization detection; FITC: Fluorescein isothiocyanate; FPD: Flame photometric detection; GC: Gas chromatography; HPLC: High-performance liquid chromatography; HRMS: High-resolution MS; LC: Liquid chromatography; MRLs: Maximum residue limits; MS: Mass spectrometry; MSD: Mass selective detection; NPD: Nitrogen–phosphorous detection; OC: Organic carbon; OP: Organophosphate; OP: Organophosphorus; PCR: Polymerase chain reaction; PDMS: Polydimethylsiloxane; PLS: Partial least squares; PLS-DA: Partial least squares discriminant analysis; Q: Quadrupole; QqQ: Triple quadrupole; QTrap: Hybrid quadrupole ion trap; RPLC: Reversed-phase liquid chromatography; SERS: Surface-enhanced Raman spectroscopy; TLC: Thin-layer chromatography; TN: Total nitrogen; TOF: Time of flight.

Acknowledgements

The authors are grateful and thankful to the University of the Free State, South Africa, Tanta University, Egypt, Universidad Autónoma de Nuevo León, Mexico, and Alexandria University, Egypt, for the completion of this project.

Author contributions

SG contributed to conceptualization, data curation, investigation, methodology, writing—original draft, writing—review and editing, supervision, and validation. SSA helped in data curation, writing—original draft, writing—review and editing, and validation. CB and WA performed visualization and writing—review and editing. AMH was involved in writing—original draft and writing—review and editing. AEB, MHA, MBK, and EAM contributed to writing—review and editing. HB performed conceptualization, writing—original draft, and writing—review and editing.

Funding

The authors declare that there is no funding involved in this project.

Availability of data and materials

Not applicable.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that there are no competing interests involved in this project.

Author details

[1]Department of Genetics, Faculty of Natural and Agricultural Sciences, University of the Free State, Bloemfontein 9301, South Africa. [2]Chemistry Department, Division of Biochemistry, Faculty of Science, Tanta University, Tanta, Egypt. [3]Department of Agricultural and Food Engineering, Faculty of Agronomy, Universidad Autónoma de Nuevo León, Francisco Villa S/N Nuevo León, Ex-Hacienda El Canadá, 66050 General Escobedo, Mexico. [4]Biotechnology Department, Institute of Graduate Studies and Research, Alexandria University, Alexandria, Egypt. [5]Botany Department, Faculty of Science, Tanta University, Tanta, Egypt.

Received: 6 January 2022 Accepted: 3 May 2022
Published online: 26 May 2022

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