Exploration of Foods and Foodomics

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Determination of neonicotinoid pesticides nitenpyram and dinotefuran by electroanalytical methods

Dilek Kul*

Department of Analytical Chemistry, Faculty of Pharmacy, Karadeniz Technical University, Ortahisar 61080, Türkiye

***Correspondence:** Dilek Kul, Department of Analytical Chemistry, Faculty of Pharmacy, Karadeniz Technical University, Farabi Street, No:46, Ortahisar 61080, Türkiye. dilekk@ktu.edu.tr

Academic Editor: Cem Erkmen, Ankara University, Türkiye

Received: October 12, 2023 **Accepted:** November 15, 2023 **Published:** December 29, 2023

Cite this article: Kul D. Determination of neonicotinoid pesticides nitenpyram and dinotefuran by electroanalytical methods. Explor Foods Foodomics. 2023;1:258–71. https://doi.org/10.37349/eff.2023.00020

Abstract

Nitenpyram (NIT) and dinotefuran (DNF) are neonicotinoid pesticides commonly used in the production and storage of agricultural products, as well as in forests and gardens, for the purpose of protection from insect pests. Although they are safer for mammals, their toxic effects on pollinators, such as bees, and their long-term accumulation in water and soil, are important problems. Therefore, it is crucial to ensure that their usage remains within certain specific limits and that their residues are quickly, precisely, and reliably monitored in various samples. In this review, electrochemical methods, which are voltammetry, amperometry, and potentiometry, for the determination of NIT and DNF in pure solutions, agricultural, and environmental samples by using various modified electrodes were reviewed. The results obtained from studies published since 2011 were compared, and the effectiveness of the selected methods was demonstrated. It was observed that the electrochemical methods, particularly voltammetry, used in the studies conducted for NIT and DNF yielded selective and sensitive results at detection limits at nmol L^{-1} levels. These methods also exhibited high precision and accuracy without being affected by the matrix of the studied samples, such as soil, water, or agricultural products.

Keywords

Electrochemical determination, dinotefuran, insecticide, nitenpyram, neonicotinoid, pesticide

Introduction

Selective and sensitive determination of pollutants such as heavy metals, pharmaceuticals, pesticides, and fungicides, which are increasingly found in air, water, and soil with the development of industry and technology [1]. The fact that neonicotinoids are safer because their toxic effects on insects are much greater than on mammals, they are water-soluble, and therefore easy to apply, distinguish them from other pesticides and make them the most widely used pesticides [2]. Consumption of agricultural products in which these pesticides are used frequently and in high quantities can cause serious health problems over

time. Therefore, it is very important to monitor neonicotinoids in crops, natural resources, animals, and humans and take necessary precautions to protect both the ecological system and human health [3]. Many different methods have been developed and used to detect these pesticides. However, different methods continue to be studied in order to determine pesticide residues in the most accurate, fastest, most sensitive, and inexpensive way. Electrochemical methods are important because they allow for easy, economical, rapid, sensitive, and selective determination of electrochemically active substances. They also have advantages that most spectroscopic and chromatographic methods do not have, such as no pre-treatment, achieving the desired sensitivity with very small amounts of substance, low toxicity, allowing the analysis of colored or turbid solutions, and even the availability of portable devices.

In this review, the determination studies of the widely used neonicotinoid pesticides dinotefuran (DNF) and nitenpyram (NIT) using various electrodes and electrochemical sensors modified with different substances were reviewed from the literature, and the results were compared and interpreted. As a result of the comparison of these studies, the electrochemical sensors used and the electrochemical methods developed were evaluated in terms of accuracy, precision, speed, cost, applicability, and simplicity.

Neonicotinoids

Neonicotinoids are an important class of pesticides that have been widely used since the mid-1990s, after the first patenting and subsequent commercialization of imidacloprid in 1985 [4–6]. They are mainly used in seed growing and agricultural production to protect the product from harmful insects during storage, as well as in forestry, parks, and gardens. The use of neonicotinoids is increasing due to the fact that they offer a favorable safety profile and are limited by the harmful effects of other insecticides such as organophosphates, methylcarbamates, pyrethroids, and organochlorines [2]. Neonicotinoids are frequently used not only in crop protection but also in veterinary medicine to prevent parasites in domestic animals [7]. Ease and variety of applications (e.g., spraying, seed coating, stem injection, pollination) also play a role in the preference for these pesticides.

Neonicotinoids can be applied to seeds or directly to the soil before planting. Since they are water-soluble, they are found in every part of the plant, such as the roots, leaves, flowers, nectar, and pollen [8]. The widespread use of these pesticides for the protection of agricultural crops from pests and weeds is of concern given the huge problems posed by the decline of the most important pollinators, bees, and especially honeybees [9]. Neonicotinoids limit the ability of bees to learn and remember their food sources, lower their immunity, and make it difficult for them to breed. These changes in nutrition and breeding shorten the lifespan of bee colonies [9–11]. For these reasons, neonicotinoids are still the most widely used pesticides worldwide, although there are some restrictions on their use in some countries, such as the USA and Canada, and in the European Union [12, 13].

While neonicotinoids bind irreversibly to nicotinic acetylcholine receptors (nAChRs) in the Central Nervous System (CNS) in insects, their penetration of the mammalian blood-brain barrier is low, and therefore their toxic effects are much weaker in birds and mammals than in insects [14]. The reason why neonicotinoids affect mammals less is the abundance of nAChRs in insects and the stronger and more selective binding of these pesticides to insects than to mammals [15]. This selectivity makes neonicotinoids superior to other pesticide groups such as organophosphates, methylcarbamates, and organochlorines [16].

Since the widespread use of neonicotinoids pollutes soil, streams, rivers, and seas, all living things in nature are constantly exposed to neonicotinoids [17, 18]. However, the number of studies investigating the negative effects on human health is quite limited [19–21]. However, in 2018, the outdoor use of some neonicotinoids was banned by the European Union.

Neonicotinoids are broadly classified into four generations: first-generation imidacloprid, NIT, acetamiprid, and thiacloprid; second-generation thiamethoxam and clothianidin; third-generation DNF; and fourth-generation cycloxaprid, sulfoxaflor, and imidaclothiz [22–24].

NIT

NIT, (E)-N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methyl-2-nitrovinylidenediamine, is a first-generation neonicotinoid with the closed formula $C_{11}H_{15}ClN_4O_2$ (Figure 1). This substance, which has a molecular weight of 270.72 g mol^{-1} and is derived from nicotine, exists in the form of a water-soluble pale yellow solid.

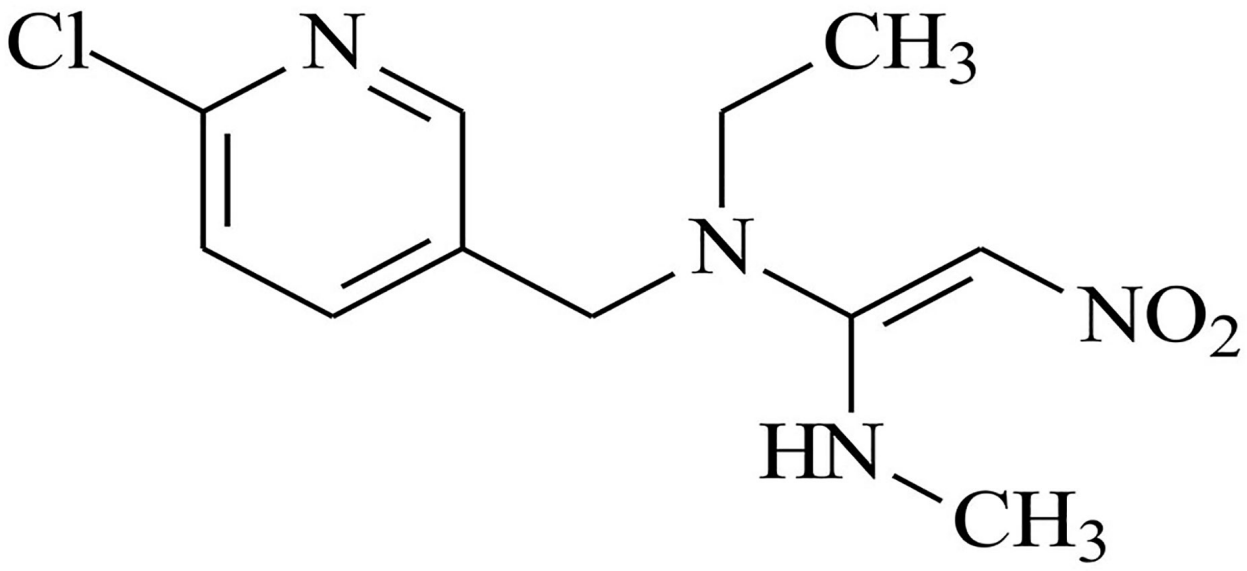

Figure 1. Chemical structure of NIT

NIT was first used commercially in 1995 and received the US Food and Drug Administration (FDA) approval for use as a flea treatment in animals in 2000 [25]. Like other neonicotinoids, it binds irreversibly to nAChRs in insects, blocking neural signaling, but shows a much lower affinity in mammals. This causes paralysis and subsequent death in insects. Due to its broad insecticidal spectrum, NIT is nowadays frequently used in agricultural fields to control all kinds of pests and weeds [26].

NIT is an effective flea treatment drug with low toxicity used not only in agriculture but also in cats and dogs [27]. Orally administered NIT has a very short half-life and is rapidly absorbed and excreted from the body. The duration of action on fleas is approximately 24 hours. NIT is a frequently used pesticide due to its good solubility in water and ease of application and it remains stable in nature for a long time. For these reasons, although it has a lower affinity in mammals, it causes toxicity in humans and animals over time due to long-term exposure and also causes environmental problems [28]. Furthermore, the negative effects of NIT, especially on honey bees, are being investigated [29]. Therefore, rapid and accurate detection of NIT traces is important for environmental and human health. In the literature, various chromatographic [30, 31], spectroscopic [32, 33], and electrochemical methods have been used for the determination of NIT, including combined methods such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) [34, 35].

DNF

DNF, 2-methyl-1-nitro-3-[(tetrahydro-3-furanyl)methyl]guanidine, is a white powdery solid, well soluble in water, with the closed formula $C_7H_{14}N_4O_3$ and molecular weight 202.21 g mol^{-1} (Figure 2).

DNF, belonging to the third generation, like other neonicotinoids, binds irreversibly to nAChRs in insects as an agonist and causes insect extinction [36]. DNF is a contact poison, so even being touched by an insect is sufficient [37–39]. DNF, like NIT, is also used as a flea and tick preventative in cats and dogs [40–42].

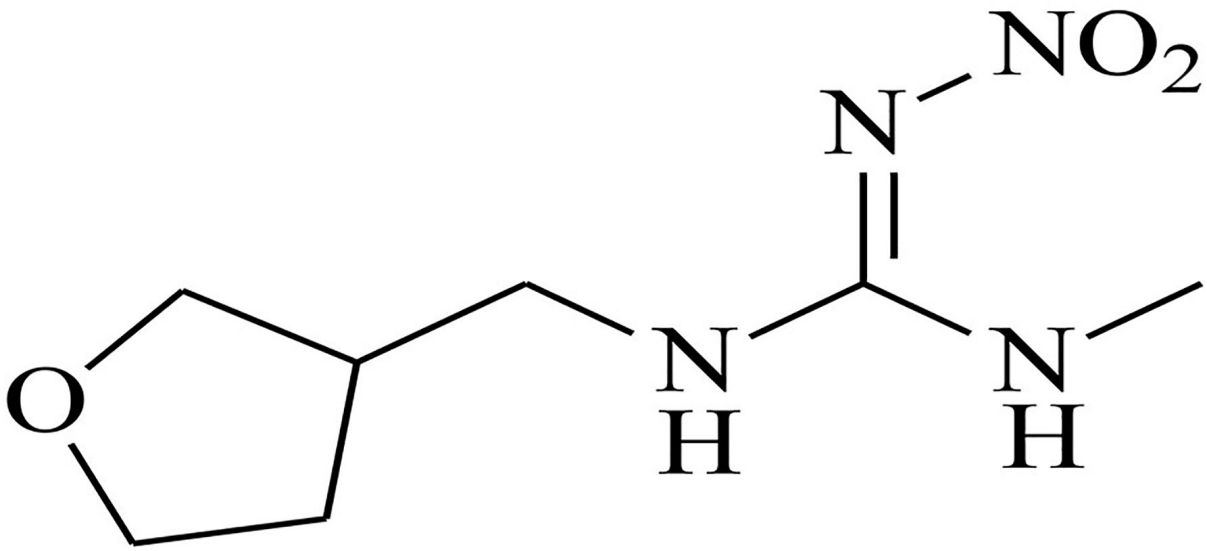

Figure 2. Chemical structure of DNF

DNF residues can be found in soil, water, and agricultural products for long periods of time and can pose serious risks to the health of humans and animals consuming these products [43]. Like all other neonicotinoids, the most controversial issue with DNF is that bees are adversely affected by the toxic effects of DNF. For this reason, many studies have been conducted on these effects in recent years [44–47].

Many analytical methods, such as high performance liquid chromatography [48], liquid chromatography-mass spectrometry [49, 50], mass spectrophotometry [51, 52], and voltammetry, have been used for the sensitive determination of DNF.

Electroanalytical methods

Electrochemical methods are frequently used for the qualitative and quantitative analysis of electroactive species. Potentiometry, amperometry, conductometry, voltammetry, and electrochemical impedance voltammetry are among the electrochemical methods frequently used today. In potentiometry, the potential is measured while the current is held constant, while in amperometry, the current is measured while the potential is held constant. In voltammetry, current is measured as a function of potential [53, 54].

Potentiometric measurements are often used to determine the amount of a particular analyte in a solution. For this purpose, two electrodes, one working (indicator) electrode and the other reference electrode, are placed in the solution containing the analyte, and the potential difference between the electrodes is measured. This method is simple and inexpensive compared to most spectroscopic and chromatographic methods, and it is possible to measure repeatedly in the same solution [55]. The ability to measure without being affected by the color or turbidity of the sample allows this method to be used in many clinical and environmental applications [56].

Amperometry is an electroanalytical technique that involves measuring the current obtained at a working electrode under a constant potential. Since the current measured in this method depends on the concentration of the oxidized and reduced substances, it can be used for a variety of analytical applications. In this method, a specific analyte in solution can be analyzed according to the electrode used and the applied potential [57]. Quantitative analysis of various substances can be done very precisely by amperometric titration [58, 59].

Voltammetric methods, which developed and became widespread after the discovery of polarography in 1922, are methods in which the oxidation and reduction of electroactive species on the microelectrode surface occur with great sensitivity in a short time over a wide temperature range [60]. The main advantage of these methods is that they can analyze different samples, such as biological samples, environmental samples such as water and soil, and pharmaceuticals, without the need for pretreatment, even if they are in

the form of turbid or colored solutions. Voltammetric methods include linear sweep voltammetry (LSV), cyclic voltammetry (CV), normal pulse voltammetry (NPV), differential pulse voltammetry (DPV), square wave voltammetry (SWV), and stripping voltammetry [61]. CV is a technique that provides information about the redox mechanism of electroactive substances, but it is not sensitive enough for quantitative analysis. The techniques used in quantitative analysis are usually differential pulse and SWV. Where quantitative determination with much higher sensitivity is required, stripping methods are used instead of DPV and SWV. These methods involve pre-concentration followed by analysis [62]. Voltammetry uses a three-electrode system consisting of a working (indicator) electrode, a reference electrode, and a counter (auxiliary) electrode. The redox reaction of the target analyte in the supporting electrolyte takes place on the surface of the working electrode [63].

Electroanalytical analysis of NIT

Electrochemical analysis studies of electrochemically active NIT published since 2011 are available in the literature. In these studies, quantitative determination of NIT from various agricultural products and environmental samples was also performed. Thus, methods have been developed for the sensitive, inexpensive, rapid, simple, and accurate determination of NIT from these samples. Some of the experimental conditions and calibration results for NIT in these studies are listed in Table 1, which is described in more detail below.

Table 1. Data obtained for the electrochemical determination of NIT

Method	Electrode type	Supporting electrolyte	Linear range (μmol L^{-1})	LOD (μmol L^{-1})	Application	Ref.
DPV	TPC-CPE	B-R buffer, pH 7.0	9.27–108.34	2.77	-	[64]
SWV	Hg(Ag)FE	B-R buffer, pH 7.0	2.14–22.01 (peak 1) 0.6–22.01 (peak 2)	0.66 (peak 1) 0.74 (peak 2)	River water	[65]
Amp.	Cu NPs/N-G/GCE	B-R buffer, pH 3.78	5–1,110	2.00	River water	[66]
DPV	Screen-printed sensors containing a sputtered bismuth thick-film	B-R buffer, pH 11.0	-	1.26–1.88	Distilled water Tap water Mineral water Surface water	[67]
LSV	β-CD-rGO/GCE	PB, pH 7.2	0.5–22	0.11	Three kinds of rice	[68]
DPV	HCNT/CNH/GCE	PB, pH 11.0	0.02–2.0	4×10^{-3}	Corn River water	[69]
LSV	CeO_2/MWCNTs/GCE	PB, pH 9.0	2–180	0.72	Corn River water	[70]
DPV	CQDs/AgNs/SDS/GCE	B-R buffer, pH 2.5	1×10^{-4}–0.02	1.5×10^{-3}	Tomatoes Paddy grains	[71]

LOD: limit of detection; Ref.: reference; TPC-CPE: tricresyl phosphate-based carbon paste electrode; B-R: Britton-Robinson; Hg(Ag)FE: silver-amalgam film electrode; Amp.: amperometry; Cu NPs/N-G/GCE: copper nanoparticles functionalized nitrogen-doped graphene nanocomposites modified glassy carbon electrode; β-CD-rGO/GCE: β-cyclodextrin-reduced graphene oxide nanosheets modified glassy carbon electrode; PB: phosphate buffer; HCNT/CNH/GCE: the binary nanohybrid of hydroxylated multiwall carbon nanotubes/single-wall carbon nanohorn modified glassy carbon electrode; CeO2/MWCNTs/GCE: nano-structured cerium oxide and multiwall carbon nanotube composite modified glassy carbon electrode; CQDs/AgNs/SDS/GCE: carbon quantum dots, silver nanoparticles, and sodium dodecyl sulfate modified glassy carbon electrodes; -: none

A voltammetric investigation of NIT was carried out by Papp et al. [64] using a TPC-CPE. In the study, cyclic voltammograms of NIT showed a reversible and well-defined reduction peak. The determination of NIT was performed by DPV in solution with oxygen removed to avoid interference. The sensitivity value calculated from the calibration graph obtained in B-R buffer solution at pH 7.0 was 0.0714 μA mL μg^{-1}. The reproducibility value of the peak current of NIT was calculated as the relative standard deviation (RSD; %)

for DPV, which was 0.83%. In this study, photodegradation of NIT was performed, and the concentration of NIT during degradation could be monitored by the developed DPV method.

NIT was studied in the cathodic direction by SWV in B-R buffer solution at pH 7.0 using a renewable Hg(Ag)FE by Brycht et al. [65]. NIT showed two reduction peaks, one around –1.40 V (peak 1) and the other around –1.55 V (peak 2) at the selected pH 7.0. The sensitivity values obtained as a result of the determination study for both peaks were 0.46 μA mL μg^{-1} for peak 1 and 0.31 μA mL μg^{-1} for peak 2. Other calibration data are given in Table 1. Accordingly, peak 1 showed a wider linearity range and a lower LOD than peak 2. The precision of the SWV method was expressed by RSD, which was 0.51% for peak 1 and 0.55% for peak 2. The proposed method was applied to determine NIT in spiked river samples with a recovery of 118.3% and an RSD of 4.1%.

Amperometric determination of NIT was carried out by oxidation of NIT with the Cu NPs/N-G/GCE [66]. A scan rate study was performed by CV in B-R buffer solution at pH 3.78, and it was concluded that the oxidation of NIT was diffusion-controlled at Cu NPs/N-G/GCE. The amperometric determination of NIT was conducted at an applied potential of +1.0 V with a sensitivity of 71.4 μA $(mmol/L)^{-1}$. The RSD value for the amperometric determination of NIT was 3.7%. Three different concentrations of NIT were spiked into the river water samples, and recoveries between 98.7% and 101.5% were obtained, and the RSD value was below 2.57%.

Lezi et al. [67] performed voltammetric determination of NIT using screen-printed sensors containing a sputtered bismuth thick film. Voltammetric experiments were carried out in a deoxygenated buffer solution. Cyclic voltammograms showed an irreversible reduction peak in B-R buffer at pH 11.0. The determination of NIP was performed by DPV in distilled water, tap water, mineral water, and surface water samples, both by direct measurement and after solid-phase extraction. Sensitivity values for all samples ranged from 0.166 μA mg^{-1} L to 0.260 μA mg^{-1} L. After solid phase extraction of surface water samples, 95% recovery and reproducibility with 6.5% RSD were achieved.

In a study [68], the β-CD-rGO/GCE was used to determine NIT by LSV in 0.1 mol L^{-1} PB solution at pH 7.2. Cyclic voltammograms showed an irreversible reduction peak for NIT at –1.1 V. The scan rate study indicated a diffusion-controlled process at β-CD-rGO/GCE. The sensitivity obtained from the calibration slope was 1.64 μA $(\mu mol/L)^{-1}$. The RSD was calculated to be 3.0%, showing good reproducibility of β-CD-rGO/GCE. Three kinds of rice samples were used in the application of the developed method for NIT determination, and the recovery ranged from 74.56% to 107.15%.

A voltammetric study of NIT was carried out by Wang et al. [69] using HCNT/CNH/GCE with CV and DPV. The variation of the reduction peak of NIT with scan rate by CV indicated a diffusion-controlled process. The calibration study was performed by DPV in PB solution at pH 11.0 and gave a sensitivity of 0.0158 μA $(nmol/L)^{-1}$. Precision was achieved by repeatability experiments with an RSD of 5.19%. The proposed method was used for the determination of NIT in corn and river water samples. The recovery ranged from 93.41% to 112.68%, and the RSD was below 7.8%.

In the study by Al et al. [70], NIT was determined by LSV in PB solution at pH 9.0 using the CeO_2/MWCNTs/GCE. Cyclic voltammograms showed that the oxidation peak of NIT increased linearly with the increasing scan rate, indicating an adsorption-controlled process. The sensitivity of NIT determination was obtained from the calibration graph as 1.028 A $(\mu mol/L)^{-1}$. The repeatability result was calculated as RSD and found to be 3.1%. According to the recovery studies of the spiked corn and river water samples, the recovery values of all samples ranged from 90.06% to 114.4%, and the RSD was less than 3.94%.

NIT was electrochemically analyzed in the cathodic direction by Ammasai [71] using CQDs/AgNs/SDS/GCE. Deoxygenated B-R buffer solution at pH 2.5 was used as a supporting electrolyte for NIT analysis. The relationship between the peak current of NIT and scan rate indicated a diffusion-controlled reduction process on the modified electrode. Reproducibility was given as RSD with 2.7%. NIT was determined in commercial tomato and paddy grain samples by the standard addition method at different NIT concentrations by DPV using CQDs/AgNs/SDS/GCE. As a result, recovery values ranging from 95.33% to 118.0% were obtained for all samples.

As a result of the NIT values [64–71] given in Table 1, the amperometry method using copper nanoparticles functionalized nitrogen-doped graphene nanocomposites modified GCE (Cu NPs/N-G/GCE) developed by Dong et al. [66] presented the widest linear range. However, the lowest LOD among all NIT studies with a linearity range close to that of Dong et al. [66] was obtained by Ammasai [71] using DPV with carbon quantum dots, silver nanoparticles, and sodium dodecyl sulfate modified GCE. In the studies, it was seen that the redox reaction of NIT was generally irreversible, and it was studied in the direction of reduction. The only study in which NIT was studied in the oxidation direction was the amperometric determination of NIT [66]. In addition, NIT had a diffusion-controlled process in all studies except the study by Al et al. [70]. In the studies, it was seen that DPV and SWV methods were more dominant in NIT determination. According to the reproducibility data obtained with the developed methods, the RSDs of all methods were between 0.51% and 5.19%. In order to use the methods for the sensitive and rapid determination of NIT, recovery studies were carried out on samples where pesticides can be found intensively, such as water, rice, corn, tomato, and paddy grain samples, and all methods gave satisfactory recovery results with RSDs below 7.8% and were found to be suitable for the determination of NIT from real samples.

Electroanalytical analysis of DNF

A literature search revealed that the published electrochemical analysis studies of DNF were conducted between 2012 and 2022. As in NIT, the methods developed in DNF studies were applied to various agricultural products and environmental samples, thus demonstrating that these methods are suitable for sensitive, precise, accurate, and simple DNF determination. The data from these studies, detailed below, are given in Table 2.

Table 2. Data obtained for the electrochemical determination of DNF

Method	Electrode type	Supporting electrolyte	Linear range (μmol L^{-1})	LOD (μmol L^{-1})	Application	Ref.
SWV	Hg(Ag)FE	B-R buffer, pH 6.5	1.0–30.0	0.201	Carrot juice	[72]
DPV	Screen-printed sensors containing a sputtered bismuth thick-film	B-R buffer, pH 11.0	-	1.93–3.12	Distilled water	[67]
					Tap water	
					Mineral water	
					Surface water	
LSV	β-CD-rGO/GCE	PB, pH 7.2	0.5–22.0	0.10	Millet	[73]
Pot.	Sensor 1	0.01 mol L^{-1} HCl	0.1–10,000	1.73×10^{-3}	Soil	[74]
	Sensor 3				Cucumber	
	Sensor 2		0.1–1,000	4.98×10^{-2}		
	Sensor 4			3.41×10^{-2}		
	Sensor 5			2.12×10^{-2}		
CV	N/Cu-HPC/GCE	PB, pH 7.0	0.5–60	0.01	Rice	[75]
					Corn	
					Oats	
CV	N/NiCu@C/GCE	PB, pH 7.0	0.5–60.0	0.001	Apples	[76]
					Tomatoes	
					Potatoes	

Ref.: reference; Pot.: potentiometry; N/Cu-HPC/GCE: three-dimensional nitrogen-doped macro-meso-microporous carbon composites derived from polyvinylpyrrolidone doped Cu-metal organic framework modified glassy carbon electrode; N/NiCu@C/GCE: NiCu nanoalloy embedded in *N*-doped porous carbon composite modified glassy carbon electrode

DNF was electrochemically analyzed in the direction of reduction in B-R buffer solution at pH 6.5 using a silver amalgam film electrode [Hg(Ag)FE] by Smarzewska et al. [72]. Scan rate study showed that DNF had an irreversible and diffusion-controlled process on Hg(Ag)F. Quantitative determination of DNF was carried

out by a calibration study by SWV with a sensitivity of 0.23 A $(mol/L)^{-1}$. Precision was tested using different concentrations of DNF solutions, and the RSD values were below 8.4%. DNF was determined in spiked carrot juice with SWV, and the recovery was in the range 96.8–105% with an RSD below 4.4%.

Voltammetric determination of DNF was carried out using screen-printed sensors containing a sputtered bismuth thick film in the reduction direction [67]. Cyclic voltammograms showed two irreversible reduction peaks of DNF in deoxygenated B-R buffer at pH 11.0. Distilled water, tap water, mineral water, and surface water samples were used for the determination of DNF by DPV, both by direct measurement and after solid phase extraction. Sensitivities obtained from the calibration graphs for all water samples ranged from 0.104 μA mg^{-1} L to 0.188 μA mg^{-1} L. Recovery and reproducibility (RSD) values of the surface water samples after solid phase extraction were 96% and 7.0%, respectively.

In a study by Zhang et al. [73], voltammetric determination was performed with a β-cyclodextrin-graphene composite modified glassy carbon electrode (β-CD-rGO/GCE) in 0.1 mol L^{-1} PB solution at pH 7.2. The irreversible reduction peak of DNF showed a diffusion-controlled process as a result of the scan rate study. The determination study was carried out using LSV, and sensitivity was 1.86 μA $(\mu mol/L)^{-1}$. The recovery results obtained by adding different concentrations of DNF to millet samples ranged from 75.25% to 90.43%.

Potentiometric determination of DNF was studied by Abdel-Ghany et al. [74] using a new potentiometric membrane sensor based on molecularly imprinted polymers in 0.01 mol L^{-1} HCl. For this purpose, five different molecularly imprinted polymers were prepared: sensor 1 (acrylamide washed), sensor 2 (acrylamide non-washed), sensor 3 (metacrylic acid washed), sensor 4 (metacrylic acid non-washed), and sensor 5 (carboxylated-polyviniyl chloride). Sensitivities of the proposed sensors were obtained from the calibration graphs as 66.3, 39.1, 50.8, 27.2, and 33.0 mV $decade^{-1}$ for sensors 1, 2, 3, 4, and 5, respectively. The recoveries were in the range of 87.93–106.43% with an RSD below 13.73% for cucumber samples and 97.46–108.71% with an RSD below 10.66% for soil samples.

A glassy carbon electrode modified with N/Cu-HPC/GCE was developed by Wang et al. [75] and used for DNF determination in 0.1 mol L^{-1} PB solution at pH 7.0. According to the scan rate study, DNF reduction was a diffusion-controlled process on the surface of N/Cu-HPC/GCE. The calibration study of DNF gave two linear plots with a slope of 3.388 μA $(\mu mol/L)^{-1}$ in the range 0.5–10 μmol L^{-1} and 0.872 μA $(\mu mol/L)^{-1}$ in the range 10–60 μmol L^{-1}. The reproducibility of N/Cu-HPC/GCE was given as RSD less than 5%. The developed method was applied to determine DNF in oat, corn, and rice samples, and the recovery values were between 92.8% and 99.6% with an RSD less than 4.7%.

In the study by Zhangsun et al. [76], DNF was determined in 0.1 mol L^{-1} PB solution at pH 7.0 with N/NiCu@C/GCE. The irreversible reduction peak was used for the scan rate study, and DNF was found to have a diffusion-controlled reduction process. The calibration plot gave two linear segments: one with a slope of 4.023 μA $(\mu mol/L)^{-1}$ between 0.5 μmol L^{-1} and 5.0 μmol L^{-1} and the other with a slope of 1.842 μA $(\mu mol/L)^{-1}$ between 5.0 μmol L^{-1} and 60.0 μmol L^{-1}. Reproducibility was obtained as 3.13% RSD. Recovery was in the range 92.1–103.4% with an RSD below 4.7% for apple, tomato, and potato samples.

The DNF studies listed in Table 2 [67, 72–76] were evaluated. In the study by Abdel-Ghany et al. [74], molecularly imprinted polymer sensors prepared with different molecules were used in potentiometric DNF analysis and gave the widest linearity range among all studies. Two of the five sensors prepared had a wider linearity range and a relatively lower LOD. The second-widest linearity range and the lowest LOD among all studies were obtained by the CV method with N/Cu-HPC/GCE in the study by Zhangsun et al. [76]. Studies have shown that DNF generally has an irreversible and diffusion-controlled process, similar to NIT. All studies have worked towards the reduction of DNF. Voltammetric methods were used for the determination of DNF in all studies except the study by Abdel-Ghany et al. [74]. The reproducibility values in the studies were given as RSD% and were found between 3.13% and 8.4%. The methods developed in the studies were used for the determination of DNF from agricultural and environmental samples such as carrot, millet, cucumber, rice, corn, oats, apples, tomatoes, potatoes, water, and soil. The recovery

experiments showed that sensitive DNF determination from these samples with RSDs below 13.73% could be achieved with the proposed methods.

Conclusions

Neonicotinoid pesticides have been widely used since the mid-1990s to protect agricultural crops and green areas such as parks and gardens from pests. In order to determine the toxic effects of neonicotinoids, it is important to be able to determine them quickly and efficiently from real samples. In this review, electrochemical determination studies of the widely used NIT and DNF were reviewed. Accordingly, voltammetric methods (CV, DPV, LSV, and SWV) with various modified electrodes were mainly used in the studies. Apart from voltammetric methods, there are very few potentiometric and amperometric determination studies. In the studies, NIT and DNF were generally studied in the reduction direction. Detection limits were in the range of 1.5×10^{-3}–2.77 μmol L^{-1} for NIT and 1.73×10^{-3}–3.12 μmol L^{-1} for DNF. The electrodes used and the methods developed showed high selectivity and sensitivity for both NIT and DNF. Reproducibility studies showed RSDs below 5.19% for NIT and below 8.4% for DNF. The methods developed in literature studies were used for the determination of NIT and DNF in various agricultural products and environmental samples such as soil and water. The spiked samples showed satisfactory recoveries with RSDs of 2.57–7.8% for NIT and 3.13–13.73% for DNF without interference from other species in the samples. In summary, it was concluded that electrochemical methods, especially voltammetric methods, are suitable for the sensitive, selective, and rapid determination of electroactive neonicotinoids such as NIT and DNF.

Abbreviations

B-R: Britton-Robinson

CQDs/AgNs/SDS/GCE: carbon quantum dots, silver nanoparticles, and sodium dodecyl sulfate modified glassy carbon electrodes

Cu NPs/N-G/GCE: copper nanoparticles functionalized nitrogen-doped graphene nanocomposites modified glassy carbon electrode

CV: cyclic voltammetry

DNF: dinotefuran

DPV: differential pulse voltammetry

Hg(Ag)FE: silver-amalgam film electrode

LOD: limit of detection

LSV: linear sweep voltammetry

N/Cu-HPC/GCE: three-dimensional nitrogen-doped macro-meso-microporous carbon composites derived from polyvinylpyrrolidone doped Cu-metal organic framework modified glassy carbon electrode

nAChRs: nicotinic acetylcholine receptors

NIT: nitenpyram

PB: phosphate buffer

RSD: relative standard deviation

SWV: square wave voltammetry

β-CD-rGO/GCE: β-cyclodextrin-reduced graphene oxide nanosheets modified glassy carbon electrode

Declarations

Author contributions

DK: Conceptualization, Investigation, Visualization, Writing—original draft, Writing—review & editing.

Conflicts of interest

The author declares that he has no conflicts of interest.

Ethical approval

Not applicable.

Consent to participate

Not applicable.

Consent to publication

Not applicable.

Availability of data and materials

Not applicable.

Funding

Not applicable.

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