Scientific Research Publishing

American Journal of Analytical Chemistry, 2026, 17(8), 303-326
https://www.scirp.org/journal/ajac
ISSN Online: 2156-8278
ISSN Print: 2156-8251

Validation of a Quantitative Electrochemical Method Using a Carbon Fiber Microelectrode for the Determination of Fenitrothion Residues in Soil

Boukaré Kaboré[1,2], Amidou Tall[1,2], Bibata Ouedraogo[1,3], Yibor Fabrice Roland Bako[1,4], Issa Tapsoba[1*]

[1]Laboratoire de Chimie Analytique, Environnementale et Bio-Organique (LCAEBiO), Université Joseph KI-ZERBO, Ouagadougou, Burkina Faso
[2]Laboratoire de Sciences et Technologies (LaST), Université Thomas SANKARA, Ouagadougou, Burkina Faso
[3]Laboratoire MRSI (LIRSA), Ecole Polytechnique de Ouagadougou (EPO), Ouagadougou, Burkina Faso
[4]Laboratoire Interdisciplinaire de Recherche en Sciences Appliquées (LIRSA), Ecole Normale Supérieure, Koudougou, Burkina Faso
Email: *issa.tapsoba@ujkz.bf

How to cite this paper: Kaboré, B., Tall, A., Ouedraogo, B., Bako, Y.F.R. and Tapsoba, I. (2026) Validation of a Quantitative Electrochemical Method Using a Carbon Fiber Microelectrode for the Determination of Fenitrothion Residues in Soil. *American Journal of Analytical Chemistry*, **17**, 303-326.
https://doi.org/10.4236/ajac.2026.178017

Received: June 27, 2026
Accepted: August 25, 2026
Published: August 28, 2026

Copyright © 2026 by author(s) and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).
http://creativecommons.org/licenses/by/4.0/

Open Access

Abstract

A square wave voltammetric method using a carbon fiber microelectrode (CFME) in 0.1 M phosphate-buffered saline (PBS) was developed and fully validated for the quantitative determination of fenitrothion (FNT) residues in soil, according to EURACHEM/CITAC guidelines and ISO/IEC 17025 requirements. FNT exhibited an irreversible diffusion-controlled cathodic peak at −1.02 V vs. saturated calomel electrode (SCE). Method validation supported by statistical analyses, including ANOVA, was employed. Key parameters such as pH, pulse amplitude, frequency, and step increments influencing the cathodic peak were optimized. Among the tested interferents, only 3-methyl-4-nitrophenol (MNP) significantly affected FNT detection, while no matrix effects were observed. The calibration curve was assessed using linear regression, which showed that the optimal line of best fit minimizes the sum of squared residuals. The calibration curve was linear in the range of 10 - 200 $\mu g \cdot L^{-1}$ with $R^2 = 0.9997$. Recovery rates varied from 89.12% to 94.76%, with relative standard deviations (RSDs) between 1.19% and 1.47%. The method precision was confirmed with within-day and between-day RSDs of 1.404% and 1.579%, respectively. Good reproducibility was observed through comparative analysis by gas chromatography with a Nitrogen Phosphorus Detector (GC-NPD). LOD and LOQ were estimated and were close to 6.56 $\mu g \cdot kg^{-1}$

and 19.87 μg·kg^{-1}, respectively. The FNT stock solution remained stable for at least three months at 7˚C. Measurement uncertainty was estimated as U = 0.04399 × C using the GUM approach. This validated electrochemical method offers a simple, accurate, and reliable approach suitable for environmental monitoring of FNT residues in soil.

Keywords

Fenitrothion, Carbon Fiber Microelectrode, Method Validation, Soil, ANOVA

1. Introduction

Organophosphorus pesticides (OPs) are among the most widely used pesticides in agriculture for insect control because of their high toxicity to insects and limited persistence in the environment [1]. Fenitrothion (FNT) (O, O-dimethyl O-4-nitro-m-tolyl phosphorothionate) (**Figure 1**) is a contact insecticide and selective acaricide belonging to the organophosphate family [2].

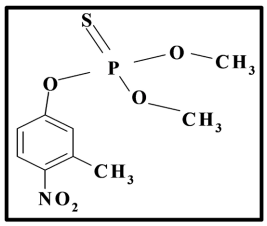

Figure 1. Structure of fenitrothion [1].

In soil, it can evolve through biotic and abiotic processes, producing metabolites, of which the most stable and toxic one is 3-methyl-4-nitro phenyl (MNP) [3]. As an organophosphate pesticide, the principal function of FNT is to inhibit the activity of acetylcholinesterase [4] [5]. Consequently, the presence of pesticide residues and metabolites in food, water, and soil currently represents a major issue in environmental chemistry [6].

Owing to its potential toxicity to non-target organisms and the persistence of its fate in the environment, monitoring FNT residues in soil is crucial for environmental and food safety [7].

Therefore, the rapid and sensitive detection of FNT residues is essential for ensuring environmental protection and public health.

Conventional methods for the analysis of FNT residues in environmental matrices include chromatographic methods combined with specific detectors and spectroscopic methods [8]-[11]. These methods have high sensitivity and are suitable for laboratory detection but require expensive equipment and time-consuming sample pretreatment [12].

Electrochemical detection technology has the advantages of high sensitivity, accuracy, portability, simple operation, fast analysis, and low cost; thus, it has gradually become a research hotspot in the field of pesticide detection [12] [13].

Although numerous electroanalytical methods for FNT in various matrices have been published [6] [12] [14], most report only linearity, accuracy, reproducibility, and selectivity/specificity, omitting ruggedness testing, formal uncertainty estimation, matrix effects, and the stability of stock solution evaluation required by ISO/IEC 17025. Furthermore, no statistical test was used to demonstrate the validity of the evaluated parameters. This incomplete validation limits their adoption for routine regulatory monitoring.

For example,

- Xinsheng Liu *et al*., 2023 [12] developed a non-enzymatic electrochemical sensor based on nitrogen-doped mesoporous carbon@hydroxyl functionalized ionic liquid composites modified electrode for the detection of fenitrothion in food. The performance of the method was validated using key parameters such as linearity, accuracy, reproducibility, stability of the sensor, selectivity/specificity, and limits of detection and quantification. However, critical parameters like matrix effects, ruggedness of the method, stability of stock solution over time, and measurement uncertainty, required by ISO/IEC 17025, were not evaluated. Moreover, no statistical test was used to demonstrate the validity of the studied parameters;
- Mir Reza Majidi *et al*., 2009 [14] validated a quantitative electrochemical method for the determination of Fenitrothion in river water and commercial formulations by adsorptive stripping voltammetry with a carbon ceramic electrode. Despite linearity, repeatability, selectivity, accuracy, and reproducibility in gas chromatography, limits of detection and quantification were evaluated to demonstrate the fit for purpose; key parameters such as ruggedness, stability of stock solution over time, and measurement uncertainty, required by ISO/IEC 17025, were not assessed. Moreover, no statistical test was used to confirm the validity of the evaluated parameters;
- Tefera M. *et al*., 2015 [6] validated an electrochemical method for the quantitative analysis of FNT residues in soil using a sensor based on a Multi-wall Carbon Nanotubes Modified Glassy Carbon Electrode. The fitness for purpose of the method was evaluated by means of key parameters such as linearity, repeatability, reproducibility, accuracy, selectivity, and limits of detection and quantification.

Despite these parameters demonstrating the fit for purpose of the method, critical parameters like ruggedness, measurement uncertainty, and stability of stock solution over time, required by ISO/IEC 17025, were not evaluated. Furthermore, statistical tests were not used to justify the validity of the evaluated parameters.

Carbon fiber microelectrodes (CFMEs), owing to their small size and resistance to fouling, have demonstrated superior sensitivity and reduced matrix effects for organophosphates in complex environmental samples [15]-[18].

However, no fully validated CFME-based method for FNT in soil has been reported. Without such validation, laboratories cannot adopt CFME methods for regulatory compliance under ISO/IEC 17025, forcing reliance on more expensive and time-consuming chromatographic techniques.

According to the ISO 17025 (2017) requirements, "The laboratory shall validate non-standard methods, laboratory-developed methods, and standard methods used outside their intended scope or otherwise modified. The validation shall be as extensive as necessary to meet the needs of the given application or field of application" [19].

The objective of this study was to develop and validate an electrochemical method using a carbon fiber microelectrode for the quantitative analysis of FNT residues in soil using a single-laboratory approach in accordance with the requirements of ISO/IEC 17025 and EURACHEM/CITAC recommendations [20].

2. Experimental

2.1. Chemicals and Standards

Carbon fibers (diameter: 12 µm, length: 5 mm) were purchased from Cytec Engineered Materials (West Paterson, NJ, USA) and used for CFME elaboration. Standards of FNT (97%), MNP (98%), potassium ferrocyanide (99%), potassium mono- and dihydrogen phosphate (99%), sulfuric acid (98%), and sodium hydroxide (98%) were purchased from Sigma-Aldrich. Absolute ethanol (99.9%) and acetonitrile (99.9%) were purchased from AnalaR NORMAPUR. All solutions were prepared using deionized water (pH 6.5, conductivity < 0.1 µS/cm, and DOC < 0.1 mg/L).

2.2. Apparatus

A helical steel auger with 99% screw-on tools was employed for neutral soil sampling. A RETSCH brand analytical sieve with a 75 µm mesh, certified according to ISO 3310/1 standards, was utilized for sieving neutral soil samples. An OHAUS brand analytical balance with a precision of 10^{-4} g was employed to weigh the samples. For the separation of liquid and solid phases following extraction, a CU-5000 IEC brand centrifuge was used. Extracts were concentrated using a BüCHI brand R-200 and B-490 rotary evaporator.

A Rotating Tubular Divider TT-RSD200 brand was used for sampling replicates of blank soil and spiked soil samples.

An Agilent Technologies chromatograph equipped with an Agilent J&W HP-5 column (30 m × 0.32 mm × 0.25 µm) and a Nitrogen Phosphorus Detector was utilized for reproducibility assessment. GC-NPD conditions:

Injection volume 1 µL, splitless mode at 150˚C (held for 1 min), ramped at 10˚C/min to 260˚C; temperature of the detector 310˚C, carrier gas He at 1.5 mL/min. FNT retention time: 13.348 min.

A PalmSens Instrument PC233 Potentiostat (Netherlands), controlled using PalmSensVs1.60 software, was used to carry out voltammetric measurements.

PSLITE 1.7.3 software was used to control data management.

2.3. Analysis

Stock solution (1 g·L^{-1}) of FNT was prepared by dissolving the equivalent mass of FNT in absolute ethanol. Working solutions of FNT at 10 mg/L were then prepared by suitable dilution. 0.1 M PBS (pH 7.2) was used as the supporting electrolyte.

Electrochemical experiments were performed using square wave voltammetry (SWV), which offers higher sensitivity and faster scan rates than differential pulse voltammetry, making it suitable for trace-level FNT detection in complex matrices [15].

Measurements were performed using a PalmSens 3 type potentiostat (Netherlands) connected to a personal computer using Ivium PC and PSLite software. A three-electrode configuration was employed, consisting of a naked carbon fiber microelectrode as the working electrode (CFME) (diameter Φ = 12 µm), a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. The carbon electrode surface was renewed using a homemade electrochemical treatment. Indeed, the carbon fiber microelectrode was first pretreated electrochemically in a mixture of sulfuric acid H_2SO_4 (0.5 M)/ethanol (50/50 w/w) followed by a treatment in 0.1 M Phosphate Buffered Saline (PBS) pH = 7.2 using the following conditions: potential scanning rate: 100 mVs^{-1} in the potential range −1.8 to +1 V for 20 cycles. Quality control of the CFME cleanliness was performed using visual and electrochemical tests. Electrochemical experiments were conducted in a 50 mL glass voltammetric cell at room temperature.

The appropriate solutions were transferred into the electrochemical cell. The analytical procedure for SWV was then optimized by systematically studying the experimental parameters that affect the responses, such as the pulse potential frequency related to the total pulse duration, amplitude of the pulse, and height of the potential step.

Scanning was performed from −1.8 to +1 V vs. SCE, with a step potential of 10 mV, an amplitude of 60 mV, and a pulse potential frequency of 60 Hz.

Before each experiment, the solutions were deaerated by bubbling nitrogen, and the electrochemical cell was maintained under a nitrogen atmosphere throughout the experiments.

For example, to record the SWV voltammograms of FNT, 50 mL of the supporting electrolyte was introduced into the electrochemical cell. Next, the supporting electrolyte was bubbled with nitrogen and stirred simultaneously for ten (10) minutes. The SWV voltammogram of the blank, represented by PBS, was then recorded ten seconds after stopping the stirring and bubbling of the solution.

Analytical curves were obtained for the pure electrolyte using the standard addition method.

This was carried out in 0.1 M PBS at pH 7.2 and at varying concentrations of FNT.

LOD and LOQ were calculated using formula (1):

$$\text{LOD} = 3.3 \times S_0 \text{ and } \text{LOQ} = 10 \times S_0 \quad \text{(Figure 2)} \tag{1}$$

where S_0 is the standard deviation.

Recovery (%) was calculated using formula (2):

$$\text{Recovery rate}(\%) = \left(C_{\text{soil}}\left(\mu\text{g}\cdot\text{kg}^{-1}\right)\times 100\right) \Big/ \left(C_{\text{theor}}\left(\mu\text{g}\cdot\text{kg}^{-1}\right)\right) \tag{2}$$

FNT residue levels in spiked soil were assessed using formula (3) and (4):

$$C_{\text{soil}}\left(\mu\text{g}\cdot\text{kg}^{-1}\right) = C_{\text{cell}}\left(\mu\text{g}\cdot\text{L}^{-1}\right)\times\left(V_{\text{solvent}}\left(\text{L}\right)\right) \Big/ \left(m_{\text{soil}}\left(\text{kg}\right)\right) \tag{3}$$

- C_{soil}: concentration of FNT residues in soil;
- C_{cell} (μg·L^{-1}): concentration of residues in the cell, evaluated using the calibration curve;
- C_{theor}: theoretical value expected from spiked soil;
- m_{soil}: mass of soil used for analysis.

$$C_{\text{theor}}\left(\mu\text{g}\cdot\text{kg}^{-1}\right) = \left(C_{\text{stand}}\left(\mu\text{g}\cdot\text{L}^{-1}\right)\times V_{\text{stand}}\left(\text{L}\right)\right) \Big/ \left(m_{\text{soil}}\left(\text{kg}\right)\right) \tag{4}$$

V_{stand}: volume of FNT standard solution used to spike soil.

2.4. Extraction and Clean-Up of FNT Residues

A 20 g soil sample with a predetermined moisture content was placed in a 250 mL Erlenmeyer flask. Acetonitrile was selected based on its high extraction efficiency for organophosphates in soil [8]. The mixture was stirred for one hour (optimized in preliminary tests to maximize recovery) and centrifuged at 500 rpm for 15 minutes to separate the solid and liquid phases. At the end of centrifugation, two phases were separated: the solid phase consisting of the soil and a liquid phase or aliquot, represented by the extracts. The aliquot was collected, filtered, and evaporated to dryness using a rotary evaporator at a temperature of approximately 50˚C. The dried residues were then solubilized with a minimum amount of absolute ethanol and transferred to a 50 mL flask. The flask was then filled with phosphate buffer at pH 7.2. The solution thus obtained was then transferred into the electrochemical cell for analysis.

3. Results and Discussion

3.1. Electrochemical Behavior of FNT

The electrochemical behavior of FNT was studied using square wave voltammetry, and the obtained signal is shown in Figure 3.

Figure 3 shows that no peak was observed in the SWV voltammogram of the PBS. However, in the presence of FNT (100 μg·L^{-1}), a well-resolved peak is observed at −1.02 V versus SCE. This peak is characteristic of the reduction of the nitro group (-NO_2) of FNT to a hydroxylamine group (-NHOH) according to the electrochemical equation below [13].

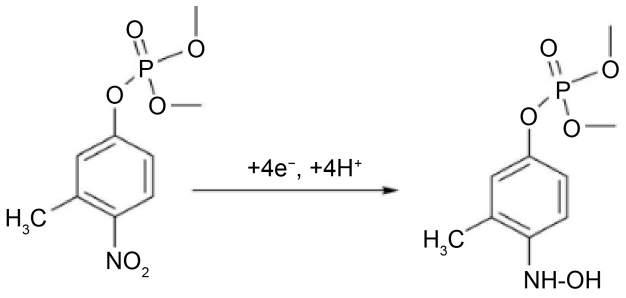

Figure 2. Electrochemical reduction of nitro group to hydroxylamine group [13].

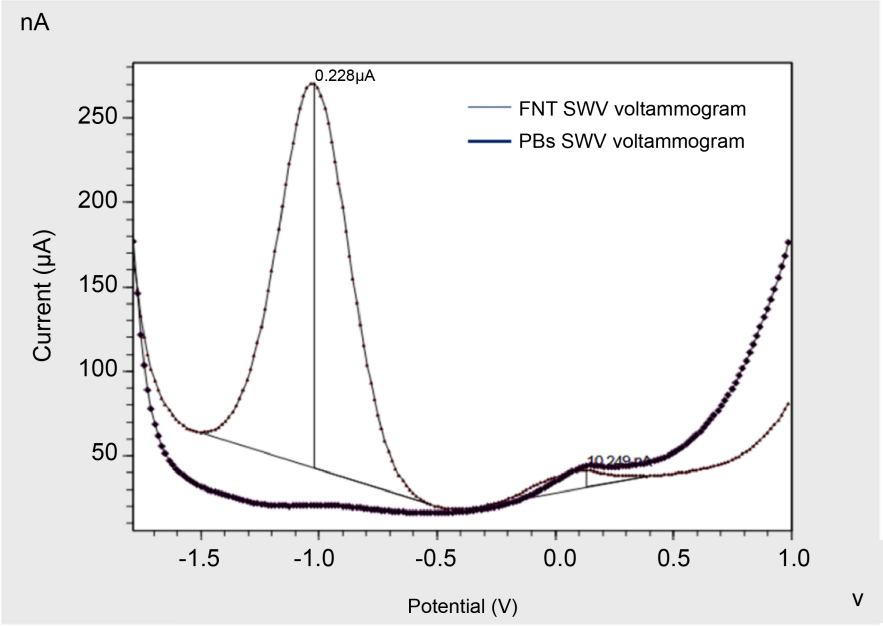

Figure 3. Electrochemical behavior of PBS and FNT 100 μg·L^{-1}; pH = 7.2; frequency = 10 Hz; amplitude = 100 mV; increments = 20 mV; reference electrode: ECS.

3.2. Method Validation

The validation of the reported electrochemical method for the determination of fenitrothion (FNT) in soil was conducted comprehensively in accordance with EURACHEM/CITAC guidelines [20] and ISO/IEC 17025 [19] requirements, ensuring its fitness for purpose for quantitative analysis. The method underwent rigorous evaluation for key performance parameters, including ruggedness, specificity/selectivity, matrix effects, linearity, accuracy, precision, limits of detection (LOD) and quantification (LOQ), and measurement uncertainty.

According to IUPAC recommendations relating to harmonized guidelines for single-laboratory validation of methods of analysis [21], the key parameters of a method must be validated according to relevant criteria. Thus, this method will be validated when the following are met for the method to be adequate for its intended use:

- The calibration function must describe an optimal line of best fit, minimizing the sum of squared residuals.

- Precision < 5% RSD, at a 95% confidence interval.
- No detectable bias at 95% confidence interval.
- Limit of detection < 10 µg·kg^{-1}, with RSD < 10% at the 95% confidence interval.
- Accuracy ranges from 80% to 120%, with RSD < 10% at the 95% confidence interval.
- No significant interference with the matrix.
- Any potential interferences identified and, if needed, compensated for.
- Critical reagents used for method validation must be stable during the period covering the tests.
- Measurement uncertainty < 10%, at a 95% confidence interval.

3.2.1. Ruggedness Test

Ruggedness evaluation was carried out using the Plackett-Burman experimental design (Table S1, Table 1, and Table 2). The standard deviation (*S*) of the results for spiked soil samples containing FNT at 60 µg·kg^{-1} was previously estimated under repeatability conditions as 1.07 µg·kg^{-1} based on eight determinations. The critical difference (Δ_{crit}) is calculated according to the following formula (5):

$$\Delta_{crit} = \frac{t_{crit} \times s}{\sqrt{2}} \tag{5}$$

$$\Delta_{crit} = \left(2.262 \times 1.07\right) \Big/ \sqrt{2} = 1.711$$

The results showed that factors such as pH, pulse potential frequency, pulse amplitude, and increment height significantly influenced the analytical response. These critical factors were subsequently optimized. The optimal values were: pH = 7.2; pulse potential frequency of 10 Hz; pulse amplitude of 100 mV; and an increment of 20 mV (Figure 4).

Table 1. Parameters evaluated in the ruggedness test.

Parameter		*Value*		
Mass of assay	*A*	20 g	*a*	40 g
pH of phosphate buffer	*B*	5	*b*	9
Time of shaking	*C*	1 hour	*c*	2 hours
Increment of analytical method	*D*	5 mV	*d*	50 mV
Amplitude of the analytical method	*E*	20 mV	*e*	120 mV
Frequency of the analytical method	*F*	5 Hz	*f*	20 Hz
Volume of extraction solvent	*G*	20 ml	*g*	40 ml

Table 2. Evaluation of results from a ruggedness study of the analytical process.

Parameter	*Mean of results at normal values*	*Mean of results at the alternative value*	*Difference*	*Significant effect at the 95% confidence interval*
A	$\frac{(s+t+u+v)}{4} = 53.193$	$\frac{(w+x+y+z)}{4} = 53.233$	$\Delta_A = 0.040$	–

Continued

B	$\frac{(s+t+w+x)}{4}=54.833$	$\frac{(u+v+y+z)}{4}=51.593$	$\Delta_B=3.240$	+
C	$\frac{(s+u+w+y)}{4}=53.160$	$\frac{(t+v+x+z)}{4}=53.265$	$\Delta_C=0.105$	–
D	$\frac{(s+t+y+z)}{4}=54.805$	$\frac{(u+v+w+x)}{4}=51.620$	$\Delta_D=3.185$	+
E	$\frac{(s+u+x+z)}{4}=52.143$	$\frac{(t+v+w+y)}{4}=55.350$	$\Delta_E=3.208$	+
F	$\frac{(s+v+w+z)}{4}=55.593$	$\frac{(t+u+x+y)}{4}=50.833$	$\Delta_F=4.760$	+
G	$\frac{(s+v+x+y)}{4}=52.440$	$\frac{(t+u+w+z)}{4}=53.985$	$\Delta_G=1.545$	–

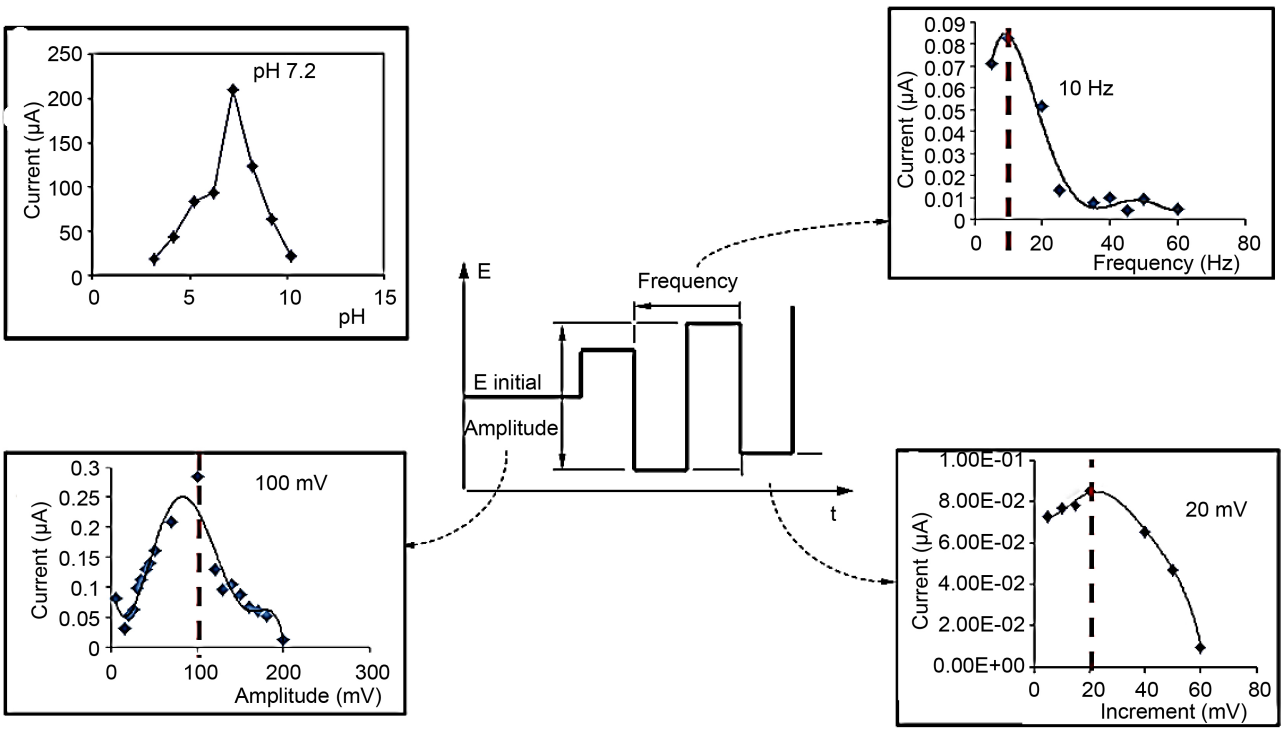

Figure 4. Optimal values of pH, amplitude, frequency, and increments.

3.2.2. Specificity/Selectivity Assessment

FNT is detected based on the reduction potential of its nitro group. To ensure the specificity of the method, the voltammogram of FNT 100 µg·L^{-1} was recorded in the presence of electroactive compounds that could potentially interfere, such as profenofos, p-nitrophenol, p-aminophenol, 3-methyl-4-nitrophenol (MNP), dimethoate, SO_4^{2-}, NO_3^-, Na^+, K^+ ions. The results in **Table 3** show that, apart from MNP, none of the studied interferents has a significant effect on the detection of FNT.

MNP, a major FNT metabolite in soil, strongly interferes with FNT detection, as both compounds exhibit similar reduction potentials. This limits the method's selectivity in aged or heavily contaminated soils where MNP may coexist with FNT. Future work should explore chromatographic pre-separation or chemometric deconvolution to resolve this interference.

The interference of these two molecules has already been reported in many previous works and could be explained by the fact that the reduction potential of MNP is very close to the reduction potential of FNT [22] [23].

Table 3. Effect of interferents on the detection of FNT.

Interfering substance	*Interferent concentration* ($\mu g \cdot L^{-1}$)	*Measured current response* (%)	*RSD* (*%*) (*n* = 3)
Na^+	50	99.5	1.73
K^+	50	99.7	1.02
NO_3^-	50	99.2	1.86
SO_4^{2-}	50	99.2	1.06
4-nitrophenol	50	95.8	0.97
4-aminophenol	50	94.8	1.13
Profenofos	50	98.4	1.35
Dimethoate	50	99.8	1.26
3-methyl-4-nitrophenol	50	89.6	0.93

3.2.3. Matrix Effects

The matrix effect was evaluated based on the contribution of the residual current from the matrix to the faradaic current. Matrix effect affects the intercept and the slope of a calibration function and then sample quantification by increasing or decreasing the signal attributed to the measurand. To overcome matrix effect, standard addition has been used for calibration, and the value of the intercept has been evaluated to be equal to zero (**Table 5**).

However, a formal matrix-matched calibration study (comparing slopes in solvent vs. soil extract) was not performed; future work should confirm the absence of signal suppression or enhancement.

3.2.4. Assessment of the Calibration Function

Linear regression was used to assess the expected relationship between the analytical response and the concentration of FNT. The assays were carried out by the standard addition method, adding increasing volumes of the standard stock solution of FNT. A fresh stock solution of FNT was prepared each day, and all assays were performed under controlled light conditions to prevent photodegradation.

To confirm the reliability of the linear regression model, three sets of independent quality control samples at 15 $\mu g \cdot L^{-1}$, 30 $\mu g \cdot L^{-1}$, 50 $\mu g \cdot L^{-1}$, 90 $\mu g \cdot L^{-1}$, and 150

$\mu g \cdot L^{-1}$ were prepared by spiking from the standard stock solution of FNT. Control was carried out over a three-day period to improve precision and provide additional checks on the calibration solution.

In the absence of an independent standard solution, the same FNT standard solution was used to prepare the quality control solutions.

The plot of peak current versus the respective concentration of FNT was found to be linear in the working range (10 - 200 $\mu g \cdot L^{-1}$) and was represented by the linear equation: $I_p = 0.0022 \times C\left(\mu g \cdot L^{-1}\right) + 0.0065$ with $R^2 = 0.9997$ (Figure 5). The statistical analysis of the data, based on the assumption that there is no relationship between variables at a 95% confidence interval, showed that the slope coefficient is significantly different from zero (Tables S2-S4, Table 4 and Table 5).

Furthermore, data analysis showed that the optimal line of best fit minimizes the sum of squared residuals, indicating that at least one predictor variable has a non-zero coefficient. That assumes linear regression is a useful model.

Moreover, the statistical analysis of quality control data showed that there is no significant difference between variances of QC data collected over three-day periods (Table S5 and Table 6).

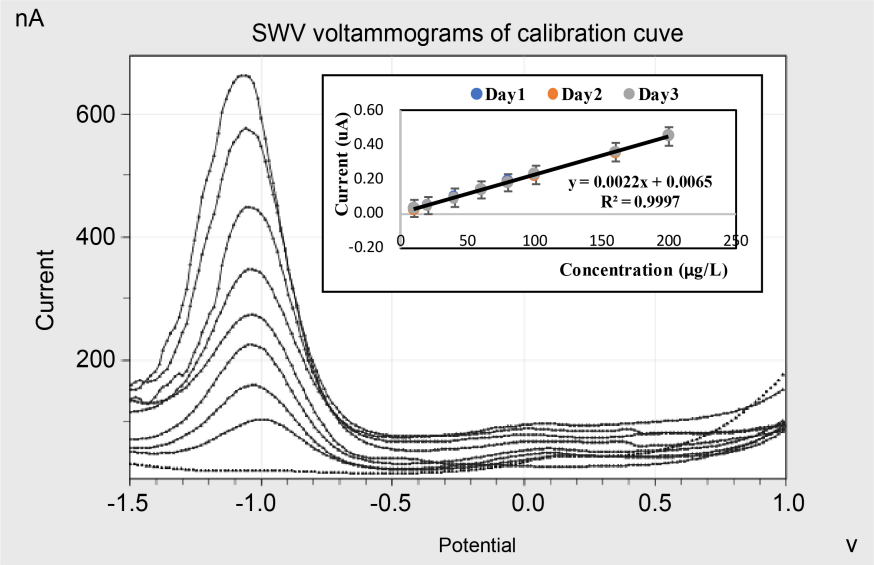

Figure 5. Square wave voltammetry of different concentrations of FNT in PBS 0.01 M, pH = 7.2, frequency = 10 Hz, amplitude = 100 mV, increments = 20 mV, FNT concentration range: 10 - 200 $\mu g \cdot L^{-1}$.

Table 4. ANOVA calculations for least-squares linear regression.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F_{calc}	F_{crit}
Regression	0.161190	1	0.1611897	18676.364	5.987
Residual	0.000052	6	0.0000086		
Total	0.161241	7			

Table 5. Statistical analysis of linear regression data.

Parameters	10 - 200 µg·L^{-1} (N = 24)	*Critical values*	*Null hypothesis*	*Acceptance criteria*
Correlation coefficient	0.9997			
Intercept	0.002841	Standard deviation S_a = 0.001730	There is no significant difference from zero at the 95% confidence interval.	The intercept equals zero at the 95% confidence interval.
Slope	0.0023	Standard deviation S_b = 0.0000165	The slope coefficient is significantly different from zero at the 95% confidence interval.	Slope should be different from zero at the 95% confidence interval.
Confidence interval for the population slope	[0.002225; 0.002293]	2.074 (α = 0.05; ν = 22)	The population slope does not contain zero at the 95% confidence interval.	The confidence interval should not contain zero.
Cochran's test	t_{calc} = 0.498	0.516 C(0.05; 8; 3)	The treatments are equally effective at a 95% confidence interval.	$C_{calc} < C_{crit}$ at the 95% confidence interval.
Comparative test of the homogeneity of variances *LEVENE's test*	F_{calc} = 1.80	2.657 F(0.05; 7; 16)	The variance is equal across groups at the 95% confidence interval.	$F_{calc} < F_{crit}$ at the 95% confidence interval.
Significant slope *Fisher test*	F_{calc} = 35686.50	2.657 F(0.05; 7; 16)	The slope coefficient equals zero at the 95% confidence interval.	Slope should be different from zero at the 95% confidence interval. $F_{calc} > F_{crit}$
Validity of regression *Student test*	t_{calc} = 136.662	2.074 (α = 0.05; ν = 22)	The changes in predictor variables do not significantly influence the outcome variable at a 95% confidence interval.	$t_{calc} > t_{crit}$ at the 95% confidence interval.
Comparative test of intercept with 0 *Student test*	t_{calc} = 1.65	2.074 (α = 0.05; ν = 22)	The population intercept equals zero at the 95% confidence interval.	The intercept equals zero at the 95% confidence interval. $t_{calc} < t_{crit}$

Table 6. ANOVA table for Levene's test for QC data.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F_{calc}	F_{crit}
Between-concentrations	2.00E−05	4	5.01E−06	2.66E−01	3.478
Residual	1.88E−04	10	1.88E−05		
Total	2.08E−04	14			

3.2.5. Assessment of Method Accuracy

The bias of the method was evaluated using independently spiked blank soil samples and expressed as the relative recovery rate of the spiking. Specifically, five concentration levels—30 µg·kg^{-1}, 60 µg·kg^{-1}, 90 µg·kg^{-1}, 120 µg·kg^{-1}, and 150 µg·kg^{-1}—were prepared from 500 g of blank soil.

To do this, an appropriate volume of the FNT standard solution was added to 100 g of blank soil to obtain the concentration corresponding to each level. Subsequently, each of the 100 g of fortified soil corresponding to each level was used

to prepare three replicates using a Rotating Tubular Divider TT-RSD200.

All 15 independent spiked samples were subjected to the extraction procedure in the presence of five soil blank samples, as described in subsection 2.4 on "Extraction and Clean-up of FNT Residues".

The aliquots were analyzed, and C_{soil} (μg·kg^{-1})—corresponding to the difference between the mean concentration of the spiked sample and the unspiked sample—was then calculated. Recovery (%) was finally calculated against matrix-matched standards using formula (2) above.

Experimental data and results of statistical analysis of the data are shown in Table S6, Table S7, and Table 7.

The results showed that there is no bias inherent in the method.

Recovery rates of 89.12% - 94.76% (Table 7) suggest that the extraction and dilution procedure minimizes matrix effects for the tested soil. However, validation was performed on a single neutral soil type; applicability to acidic, alkaline, or high-organic-matter soils requires further investigation.

Table 7. Statistical assessment of method accuracy.

Parameters	*Calculated values*	*Critical values*	*Null hypothesis*	*Acceptance criteria*
Cochran's test	C_{calc} = 0.405	0.684 C(0.05; 5; 3)	The treatments are equally effective at a 95% confidence interval.	$C_{calc} < C_{crit}$ at 95% confidence interval.
Comparative test of the homogeneity of variances *Levene's test*	F_{calc} = 0.412	3.478 F(0.05; 4; 10)	The variance is equal across groups at a 95% confidence interval.	$F_{calc} < F_{crit}$ at the 95% confidence interval.
Validity of the average recovery rate			Average recovery rate range of 80% - 120% at 95% confidence interval.	80% - 120% (RSD < 10%)
Confidence limits (%)	89.12 - 94.76 (RSD ranges from 1.19% to 1.47%).			

3.2.6. Assessment of Method Precision

The precision of the method was evaluated by means of a nested design. Four batches of spiked blank soil samples were used to prepare four groups of eight independent samples. Samples were prepared from soil samples spiked to 60 μg·kg^{-1} by adding an appropriate volume of FNT standard solution. Each group of samples was analyzed under repeatability conditions.

Three series of eight samples were analyzed over three different days using three different carbon fiber microelectrodes.

The fourth series of eight samples was used for reproducibility assessment, carried out by GC-NPD analysis using an Agilent J&W HP-5 column (30 m × 0.32 mm × 0.25 μm). The FNT peak was found at 13.348 min.

The results of the paired t-test showed that there is no significant difference between both analytical methods (Table S9), indicating that the method offers good reproducibility.

Statistical analyses of data (Table S8) are given in Table 8, Table S10, and Table S11.

Table 8. Statistical analysis of precision data.

Parameters	Calculated values	Critical values	Null hypothesis	Acceptance criteria
Cochran's test	C_{calc} = 0.398	0.617 C (0.05; 3; 10)	The treatments are equally effective at a 95% confidence interval.	$C_{calc} < C_{crit}$ at 95% confidence interval
Within-group standard deviation (S_r)	0.0021 (N = 24)	-	S_r is less than the Repeatability Limits (95% confidence interval).	$S_r < 0.007$
between-group standard deviation (S_b)	0	-		-
Intermediate precision standard deviation (S_I)	0.0021 (N = 24)	-	There is no significant difference in the analytical results obtained under different conditions.	$S_r \approx S_b$
Reproducibility standard deviation (S_R)	1.043 (n = 8)	-	S_R is less than the Reproducibility Limits (95% confidence interval).	$S_R < 3.488$
Repeatability Limits (95% confidence interval)	0.007 (n = 8)	2.365 (α = 0.05; ν = 7)	-	-
Reproducibility Limits (95% confidence interval)	3.488 (n = 8)	2.365 (α = 0.05; ν = 7)	-	-
Validity of reproducibility Paired t-test	t_{calc} =0.2	2.365 (α = 0.05; ν = 7)	There is no significant difference between the GC-NPD and SWV results (95% confidence interval).	$t_{calc} < t_{crit}$ at 95% confidence interval.
Validity of intermediate precision Fisher test	F_{calc} = 0.621	2.657 F (0.05; 7; 16)	There is no significant difference between the groups.	$F_{calc} < F_{crit}$ at 95% confidence
Comparative test of homogeneity of variances Levene's test	F_{calc} = 0.472	2.657 F (0.05; 7; 16)	The variance is equal across groups at the 95% confidence interval.	$F_{calc} < F_{crit}$ at 95% confidence interval.
Within-day precision	1.404%	-	The precision is equal across groups at 95%. No significant difference exists between within-day precision and between-day precision.	
Between-day precision	1.579%	-		
Method precision	2.113%	5%	Method precision is less than the precision limit.	Method precision < 5%

3.2.7. Assessment of Limit of Detection (LOD) and Limit of Quantification (LOQ)

Due to the lack of a measurable signal obtained from soil blank samples, test samples with concentrations of analyte were prepared by spiking soil blank samples with a small volume of the FNT stock solution.

So, ten (10) independent measurements of the test samples were prepared and

analyzed under repeatability conditions according to the whole measurement procedure, including any sample preparation steps. The standard deviation (S_0) was then calculated. No baseline correction was carried out on the test results.

The statistical analysis of the results is summarized in Table 9.

The LOQ was then validated by analyzing three spiked samples at the quantification limit, yielding recoveries of 91.43 to 93.87 µg·kg^{-1}.

Table 9. Experimental data for LOD and LOQ assessments.

N° Sample	*Current* (10^{-6}A)	*Concentration* (µg·kg^{-1})	*LOD* (µg·kg^{-1})	*RSD* (%)	*LOQ* (µg·kg^{-1})
1	0.0114	18.98			
2	0.0137	21.52			
3	0.0115	19.14			
4	0.0134	21.19			
5	0.0097	17/11	**6.56 (*n* = 10)**	**9.87**	**19.87 (*n* = 10)**
6	0.0100	17.41			
7	0.0105	18.05			
8	0.0141	22.02			
9	0.0146	22.61			
10	0.0152	23.22			

3.2.8. Assessment of the Stability of the FNT Stock Standard Solution

The stability of the standard stock solution of FNT (10 mg·L^{-1}) was evaluated by measuring the current of a fresh 100 µg·L^{-1} quality control sample prepared from the standard stock solution of 100 mg/L FNT using the standard addition method. The stock solution was conserved at 7˚C for three months. Measurements were carried out once a week over a period of three months.

The stability of FNT in ethanolic stock solution was confirmed over three months at 7˚C (Table 10). However, FNT stability in spiked soil samples during storage was not assessed. To ensure accurate results, soil samples should be analyzed promptly after collection, or a stability study should be conducted to establish acceptable storage conditions.

Statistical analysis of the data in Table 10, Tables S12-S14 confirms the homogeneity of the variances of the data collected over three-month periods.

Table 10. Statistical analysis of data for stock solution stability assessment.

Parameters	Calculated values	Critical values	Null hypothesis	Acceptance criteria
Cochran's test	C_{calc} = 0.496	0.798 C (0.05; 3; 4)	The treatments are equally effective at the 95% confidence interval.	$C_{calc} < C_{crit}$ at 95% confidence interval.
Comparative test of homogeneity of variances Levene's test	F_{calc} = 1.454	4.256 F (0.05; 2; 9)	The variance is equal across groups at the 95% confidence interval.	$F_{calc} < F_{crit}$ at the 95% confidence interval.

Continued

Comparative test of variances				
Fisher test	$F_{calc} = 0.369$	4.256 F (0.05; 2; 9)	There is no significant difference between the groups.	$F_{calc} < F_{crit}$ at the 95% confidence interval.

3.2.9. Measurement Uncertainty

Measurement uncertainty was estimated using the GUM approach [24].

Measurement uncertainty was estimated by integrating contributions from weighing, volumetric measurements, calibration, and reagent purity, resulting in an expanded uncertainty of $U = 0.04399 \times C_{soil}$ (**Table S15**).

The uncertainties associated with each component were combined accordingly:

$$\frac{u(x)}{C_{soil}\left(\frac{\mu g}{kg}\right)} = \sqrt{\begin{aligned}&0.00185^2 + 0.00087^2 + 0.00023^2 + 0.00003^2 + 0.00069^2 + 0.00001^2\\&+ 0.00012^2 + 0.00058^2 + 0.00255^2 + 0.00019^2 + 0.01732^2\\&+ 0.01155^2 + 0.00577^2 + 0.00058^2 + 0.00058^2 + 0.00219^2\end{aligned}}$$

$$\frac{u(x)}{C_{soil}\left(\frac{\mu g}{kg}\right)} = \sqrt{0.00048} = 0.02199$$

$$u(x) = 0.02199 \times C_{soil}\left(\frac{\mu g}{kg}\right)$$

The expanded uncertainty $U(x)$ is obtained by applying a coverage factor of 2, based on a 95% confidence interval.

$$U(x) = 0.02199 \times 2 \times C_{soil}\left(\mu g/kg\right)$$

$$U(x) = 0.04399 \times C_{soil}\left(\mu g/kg\right)$$

The results of the uncertainty assessment, which include both random and systematic errors, show that $\frac{U(x) \times 100}{C_{soil}\left(\frac{\mu g}{kg}\right)} = 4.399\%$. This value, being less than 10%, suggests that the true value lies within a smaller range. This suggests that the validated method is accurate and precise.

4. Conclusions

The electrochemical reduction of FNT on carbon fiber microelectrodes was studied, and the optimal conditions were used for the rapid quantitative analysis of FNT in soil samples.

The procedure for the extraction and cleanup of FNT residues from soil samples has the main advantages of being simple and quick. Carbon fiber microelectrodes are stable, reliable tools that are easy to design.

The proposed CFME method achieves within-day and between-day RSDs of 1.404% and 1.579%, respectively, and offers good reproducibility with GC-NPD.

Statistical tests were used to successfully demonstrate that the method can be validated according to ISO/IEC requirements and EURACHEM/CITAC guide-

lines.

Acknowledgements

The authors gratefully acknowledge Laboratoire National de Santé Publique for carrying out GC-NPD analysis.

Author Contributions

Boukaré KABORÉ: Writing—original draft, Software, Investigation, Formal analysis.

Amidou TALL: Writing—review & editing, Methodology, Formal analysis.

Bibata OUEDRAOGO: Writing—review & editing, Formal analysis.

Yibor Fabrice Roland BAKO: Writing—review & editing, Methodology, Formal analysis.

Issa TAPSOBA: Writing—review & editing, Supervision, Methodology, Formal analysis.

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Geremedhin, W., Amare, M. and Admassie, S. (2013) Electrochemically Pretreated Glassy Carbon Electrode for Electrochemical Detection of Fenitrothion in Tap Water and Human Urine. *Electrochimica Acta*, **87**, 749-755. https://doi.org/10.1016/j.electacta.2012.09.046

[2] Richard, P.P. (2014) Sittig's Handbook of Pesticides and Agricultural Chemicals. 2nd Edition, William Andrew.

[3] International Programme on Chemical Safety (1992) Environmental Health Criteria 133—Fenitrothion. https://iris.who.int/bitstreams/e6f51b6f-8522-44f9-b03b-309a8ba0e1fc/download

[4] Australian Pesticides and Veterinary Medicines Authority (2024) Fenitrothion Review Technical Report. https://www.apvma.gov.au/sites/default/files/2024-04/Fenitrothion%20-%20Review%20Technical%20Report.pdf

[5] Wijeyesakere, S.J. and Richardson, R.J. (2010) Neuropathy Target Esterase. In: Krieger, R., Ed., *Hayes' Handbook of Pesticide Toxicology*, 3rd Edition, Elsevier, 1435-1455. https://doi.org/10.1016/b978-0-12-374367-1.00067-7

[6] Tefera, M., Tessemaa, M., Admassiea, S. and Mehretiea, S. (2015) Electrochemical Sensor for Determination of Fenitrothion at Multi-Wall Carbon Nanotubes Modified Glassy Carbon Electrode. *Analytical and Bioanalytical Chemistry Research*, **2**, 139-150.

[7] Zelayaran, L.M. and Machado, S.A.S. (2005) Determination of Fenitrothion in Commercial Formulations by Square Wave Voltammetry and UV-Vis Spectroscopy. *Journal of the Brazilian Chemical Society*, **16**, 743-748. https://doi.org/10.1590/s0103-50532005000500011

[8] Sánchez, M.E., Méndez, R., Gómez, X. and Martín-Villacorta, J. (2003) Determina-

tion of Diazinon and Fenitrothion in Environmental Water and Soil Samples by HPLC. *Journal of Liquid Chromatography & Related Technologies*, **26**, 483-497. https://doi.org/10.1081/jlc-120017184

[9] Malhat, F., Boulangé, J., Abdelraheem, E., Abd Allah, O., Abd El-Hamid, R. and Abd El-Salam, S. (2017) Validation of QuEChERS Based Method for Determination of Fenitrothion Residues in Tomatoes by Gas Chromatography-Flame Photometric Detector: Decline Pattern and Risk Assessment. *Food Chemistry*, **229**, 814-819. https://doi.org/10.1016/j.foodchem.2017.03.017

[10] Baroja, O., Unceta, N., Sampedro, M.C., Goicolea, M.A. and Barrio, R.J. (2004) Optimization and Validation of a Method of Analysis for Fenitrothion and Its Main Metabolites in Forestry Air Samples Using Sorbent Tubes with Thermal Desorption Cold Trap Injection and Gas Chromatography-Mass Spectrometry. *Journal of Chromatography A*, **1059**, 165-170. https://doi.org/10.1016/j.chroma.2004.10.038

[11] Aly, M.I., Fouad, R.M., Abou-Elnasr, S.H. and El-Aswad, F.A. (2021) Comparison of Dissipation Kinetics and Residual Behaviour for Fenitrothion Insecticide and Thiobencarb Herbicide in Clay Soil. *Alexandria Journal of Agricultural Sciences*, **66**, 1-11.

[12] Liu, X.S., Li, Y.T., Qiao, W.L., Chang, M.J. and Li, Y. (2023) A Non-Enzymatic Electrochemical Sensor Based on Nitrogen-Doped Mesoporous Carbon@hydroxyl-Functionalized Ionic Liquid Composites Modified Electrode for the Detection of Fenitrothion. *RSC Advances*, **13**, 13030-13039.

[13] Wang, R., Wang, S., Qin, C., Nie, Q., Luo, Y., Qin, Q., *et al*. (2022) An Electrochemical Sensor Based on Electropolymerization of *β*-Cyclodextrin on Glassy Carbon Electrode for the Determination of Fenitrothion. *Sensors*, **23**, Article No. 435. https://doi.org/10.3390/s23010435

[14] Majidi, M.R., Asadpour-Zeynali, K. and Nazarpur, M. (2009) Determination of Fenitrothion in River Water and Commercial Formulations by Adsorptive Stripping Voltammetry with a Carbon Ceramic Electrode. *Journal of AOAC International*, **92**, 548-554. https://doi.org/10.1093/jaoac/92.2.548

[15] Allen, J.B. and Larry, R.F. (2001) Electrochemical Methods: Fundamentals and Applications. 2nd Edition, John Wiley & Sons, Inc. https://electrochem.xmu.edu.cn/UserFiles/File/Electrochemical%20methods.%20Fundamentals%20and%20applications.pdf

[16] Tapsoba, I., Bourhis, S., Feng, T. and Pontié, M. (2009) Sensitive and Selective Electrochemical Analysis of Methyl-Parathion (MPT) and 4-Nitrophenol (PNP) by a New Type p-NiTSPc/p-PPD Coated Carbon Fiber Microelectrode (CFME). *Electroanalysis*, **21**, 1167-1176. https://doi.org/10.1002/elan.200804529

[17] Tapsoba, I., Paré, S., Toé, A., Kaboré, B., Koulibaly, B. and Bonzi-Coulibaly, Y. (2013) SWV Determination of Glyphosate in Burkina Faso Soils Using Carbon Fiber Microelectrode. *International Journal of Biological and Chemical Sciences*, **6**, 2211-2220. https://doi.org/10.4314/ijbcs.v6i5.27

[18] Bako, Y.F.R., Mbokou, S.F., Kaboré, B., Tapsoba, I. and Pontié, M. (2024) Indirect Electroanalysis of 3-Methyl-4-Nitrophenol in Water Using Carbon Fiber Microelectrode Modified with Nickel Tetrasulfonated Phthalocyanine Complex. *Materials Sciences and Applications*, **15**, 25-35. https://doi.org/10.4236/msa.2024.152003

[19] International Standard ISO/IEC 17025 (2017) General Requirements for the Competence of Testing and Calibration Laboratories. 3rd Edition. https://www.iso.org/standard/66912.html

[20] Cantwell, H. (2025) Eurachem Guide: The Fitness for Purpose of Analytical Methods—A Laboratory Guide to Method Validation and Related Topics. 3rd Edition.

https://www.eurachem.org/index.php/3-publications/guides/144-gdmv2014

[21] Thompson, M., Ellison, S.L.R. and Wood, R. (2002) Harmonized Guidelines for Single-Laboratory Validation of Methods of Analysis (IUPAC Technical Report). *Pure and Applied Chemistry*, **74**, 835-855. https://doi.org/10.1351/pac200274050835

[22] Bako, Y.F.R., Kaboré, B., Tall, A., Sawadogo, W.F. and Tapsoba, I. (2026) Direct Electrochemical Analysis of 3-Methyl-4-nitrophenol in Water Using Carbon Fiber Microelectrode Modified with Nickel Tetrasulfonated Phthalocyanine Complex. *Materials Sciences and Applications*, **17**, 1-14. https://doi.org/10.4236/msa.2026.171001

[23] Galeano-Díaz, T., Guiberteau-Cabanillas, A., Espinosa-Mansilla, A. and López-Soto, M.D. (2008) Adsorptive Stripping Square Wave Voltammetry (Ad-SSWV) Accomplished with Second-Order Multivariate Calibration: Determination of Fenitrothion and Its Metabolites in River Water Samples. *Analytica Chimica Acta*, **618**, 131-139. https://doi.org/10.1016/j.aca.2008.04.058

[24] Ellison, S.L.R. and Williams, A. (Eds.) (2012) Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement. 3rd Edition. https://www.eurachem.org/index.php/publications/guides/quam

Appendix

Table S1. Results from a ruggedness study of the analytical process.

Experimental parameter	*Experiment number*							
	1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Observed result (μg·kg^{-1})	56.89	55.92	47.25	52.71	57.43	49.09	51.07	55.34
Results idenfier	s	t	u	v	w	x	y	z

Table S2. Calibration curve data.

		Concentration Levels							
Periods	Concentrations (μg/L)	10	20	40	60	80	100	160	200
Day 1		0.02834	0.0492	0.0932	0.1365	0.1809	0.2283	0.3608	0.459
Day 2	Current (μA)	0.027	0.0484	0.096	0.141	0.1834	0.2289	0.361	0.462
Day 3		0.0242	0.0476	0.0942	0.1371	0.1818	0.2311	0.3603	0.4573

Table S3. ANOVA table for Levene's test for linear regression.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F	F_{crit}
Between-group	0.0686002	7	0.0098	3.57E+04 F(0.05; 7; 16)	2.657 F(0.05; 7; 16)
Within-group	4.39E−06	16	2.75E−07		
Total	6.86E−02	23			

Table S4. ANOVA calculation of data for calibration curve.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F_{calc}	F_{crit}
Between-concentrations	2.34E−05	7	3.35E−06	1.80E+00	2.657
Residual	2.98E−05	16	1.86E−06		
Total	5.32E−05	23			

Table S5. Quality control data.

	QC concentration levels									
	15 µg/L		30 µg/L		50 µg/L		90 µg/L		150 µg/L	
Periods	Current (µA)	Concentration (µg/L)	Current (µA)	Concentration (µg/L)	Current (µA)	Concentration (µg/L)	Current (µA)	Concentration (µg/L)	Current (µA)	Concentration (µg/L)
Day 1	0.0339	13.7381	0.0679	28.8002	0.1081	46.5793	0.2025	88.3904	0.3355	147.2390
Day 2	0.0355	14.4353	0.0647	27.3925	0.1052	45.2900	0.1973	86.0696	0.3243	142.2810
Day3	0.0324	13.0962	0.0624	26.3655	0.1108	47.7690	0.1947	84.9120	0.3392	148.8935
RSD (%)	3.0139	3.2895	2.9672	3.1028	1.7517	1.7991	1.4692	1.4905	1.7444	1.7595

Table S6. Experimental data of accuracy assessment.

	Experiment data			
Theorical value	Current (µA)	Concentration (µg/kg)	RSD (%)	Recovery rate (%)
30	0.0273	27.43	1.19	91.43
	0.0280	27.85	(n = 3)	92.83
	0.0283	28.16		93.87
60	0.0519	54.32	1.25	90.53
	0.0512	53.47	(n = 3)	89.12
	0.0528	55.24		92.07
90	0.0764	84.42	1.47	93.8
	0.0789	83.21	(n = 3)	92.46
	0.0785	83.69		92.99
120	0.1030	112.87	1.41	94.06
	0.1069	113.18	(n = 3)	94.32
	0.1047	113.71		94.76
150	0.1249	138.07	1.25	92.05
	0.1292	136.86	(n = 3)	91.24
	0.1269	137.36		91.57

Table S7. ANOVA table for Levene's test for accuracy.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F_{calc}	F_{crit}
Between-groups	3.10E−06	4	7.74E−07	4.12E−01	3.478
Residual	1.88E−05	10	1.88E−06		
Total	2.19E−05	14			

Table S8. Intermediate precision data.

	N° Sample	1	2	3	4	5	6	7	8
Day 1	Current (µA)	0.1300	0.1247	0.1258	0.1276	0.1262	0.1240	0.1270	0.1295
	Concentration (µg/kg)	56.29	53.93	54.42	55.25	54.63	53.62	54.98	56.05
Day 2	Current (µA)	0.1301	0.1304	0.1254	0.1248	0.1277	0.1336	0.1298	0.1297
	Concentration (µg/kg)	56.32	56.47	54.24	53.97	55.26	57.88	56.18	56.15
Day 3	Current (µA)	0.1249	0.1261	0.1243	0.1281	0.1251	0.1262	0.1246	0.1279
	Concentration (µg/kg)	54.03	54.55	53.78	55.46	54.11	54.63	53.92	55.36

Table S9. Statistical analysis of GC-NPD and SWV data.

	GC-NPD results	SWV results				
N° sample	Concentration (µg/kg)	Concentration (µg/kg)	Difference (d)	Difference mean	t_{calc} value	t_{crit}
1	52.94	55.13	2.19	0.14	0.20	2.365
2	55.32	53.55	−1.77			
3	53.18	54.21	1.03			
4	56.39	53.46	−2.93			
5	53.41	55.11	1.70			
6	53.66	56.00	2.34			
7	55.45	54.92	−0.53			
8	54.28	53.36	−0.92			

Table S10. ANOVA table for precision assessment with 3 groups of data each containing 8 replicates.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F	F_{crit}
Between-group	3.05196E−05	7	4.35994E−06	6.21E−01	2.657
Within-group	1.12E−04	16	7.02E−06		F(0.05; 7; 16)
Total	0.0001				

Table S11. Levene's test for precision assessment with 3 groups of data each containing 8 replicates.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F	F_{crit}
Between-group	2.3191E−05	7	3.313E−06	4.72E−01	2.657
Within-group	1.12E−04	16	7.02E−06		F(0.05; 7; 16)
Total	0.0001	23			

Table S12. data of stock solution stability assessment.

Periods	Month 1		Month 2		Month 3	
	Current (µA)	Concentration (µg/L)	Current (µA)	Concentration (µg/L)	Current (µA)	Concentration (µg/L)
Week 1	0.2271	99.27	0.2335	102.11	0.2255	98.56
Week 2	0.2342	102.42	0.2274	99.4	0.2316	101.27
Week 3	0.2448	107.13	0.2323	101.58	0.2247	98.21
Week 4	0.2300	100.56	0.2259	98.74	0.2436	106.6

Table S13. ANOVA table for FNT stock solution stability assessment.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F	F_{crit}
Between-group	3.715E−05	2	1.858E−05	3.695E−01	4.256
Within-group	4.525E−04	9	5.028E−05		
Total	4.896E−04	11			

Table S14. Levene's test for stock solution stability assessment.

Source of variation	Sum of squares	Degrees of freedom ν	Mean square	F	F_{crit}
Between-group	1.462E−04	2	7.309E−05	1.454E+00	4.256
Within-group	4.525E−04	9	5.028E−05		F(0.05; 2; 9)
Total	5.987E−04	11			

Table S15. Sources of uncertainties and standard uncertainty estimate.

Parameters	Sources of uncertainty	Uncertainty components	Estimate (X)	Uncertainty	Uncertainty contribution u(x)	Relative Standard uncertainty u(x)/x
Weighing (m_{soil})	Balance routine use Balance daily drift	Standard deviation of balance calibration	20 g	0.064 g		0.00185
$V_{solvent}$	Pipette of 20 mL	Pipette calibration uncertainty	20 mL	0.03 mL		0.00087
	coefficient of volume expansion of acetonitrile	Volume of acetonitrile expansion	20 mL	$20 \times 4^{\circ}C \times 1 \times 10^{-3}$ $^{\circ}C^{-1}$		0.00023
C_{cell}	Micropipette of 50 µL	Micropipette calibration uncertainty	100 µL	0.50%		0.00003
	volumetric flask of 50 mL	volumetric flask calibration uncertainty	50 mL	0.06 mL		0.00069
	coefficient of volume expansion of the water in analysis conditions (24˚C)	Volume of water expansion	50 mL	$50 \times 4^{\circ}C \times 2.1 \times 10^{-3}$ $^{\circ}C^{-1}$		0.00001
	Agitation and centrifugation Volume of the aliquot Concentration of residues Recuperation with absolute ethanol	Mean recovery + Run to run variation in recovery	100	1.218	0.01218	0.00012
	Filling to 50 mL	volumetric flask calibration uncertainty	50 mL	0.05 mL		0.00058
	Calibration curve	Relative standard deviation of slope and intercept	100		0.2550	0.00255
	pH Increment Amplitude	Repeatability and reproducibility relative standards deviation	100		0.01940	0.00019

Continued

	Frequency					
	Microelectrode area					
	Temperature					
	viscosity of supporting electrolyte					
	Diameter of the microelectrode					
	Diffusion coefficient of species					
Purity and stability of reagents	FNT (97%)	Purity of reagent	100	3%		0.01732
	KH_2PO_4 (98%)		100	2%		0.01155
	K_2HPO_4 (99%)		100	1%		0.00577
	Acetonitrile (99.9%)		100	0.1%		0.00058
	Absolute ethanol (99.9%)		100	0.1%		0.00058
	Stability of stock solution	Stability of reagent relative standard deviation	100	$SI \times 100/S_{total}$	0.2187	0.00219