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Optimization and Validation of a Modified QuEChERS-UPLC-MS/MS Method for Multi-Residue Pesticide Analysis in Tea and Rosemary Leaves with Experimental Uncertainty Assessment

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Abstract

This study developed and validated a modified QuEChERS extraction procedure for the determination of 32 pesticide residues in tea (*Camellia sinensis*) found in Moroccan market originating from China and rosemary (*Salvia rosmarinus*) leaves using UPLC-MS/MS. A total of 202 pesticide residues were initially screened using the NF EN 15662 method, and 32 compounds showed satisfactory recovery and precision in tea. The optimized method, based on freezing before extraction and using PSA + BCG as purification sorbents, achieved recoveries of 70–120% for 97% of analytes. Calibration linearity ranged from 0.001 to 0.2 mg/kg ($R^2 \geq 0.980$), with spiking levels at 0.01–0.1 mg/kg analyzed in duplicate per level and per matrix. Results of LOQ and LOD are compared to multiple MRL databases of Tea (EU, USA, Canada, Codex Alimentarius) despite the scarcity of tea MRLs in most databases, providing an accurate representation of the complexity of the analysis. Uncertainty was evaluated through both validation-based and Horwitz-based approaches, allowing a robust comparison of theoretical and experimental variability. The optimized method was also applied to rosemary, where 31 of the 32 pesticides validated in tea showed satisfactory performance. Similar recoveries, precision, and LOQs were obtained for both matrices, demonstrating the robustness of the method across chemically diverse herbal substrates. Only carbofuran exhibited reduced performance in rosemary, requiring an increased functional LOQ because of matrix-induced ion suppression. This dual-matrix approach provides a reliable and reproducible method for pesticide monitoring in herbal products. This dual-matrix approach provides a reliable and reproducible method for pesticide monitoring in herbal products.

Keywords: QuEChERS; tea; rosemary; pesticide residues; validation; uncertainty measurement; UPLC-MS/MS

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1. Introduction

Pesticide residues in tea and medicinal plants represent an important analytical and regulatory challenge due to chronic dietary exposure and the strict maximum residue limits

(MRLs) established for these commodities. Tea (*Camellia sinensis*) is among the most widely consumed beverages globally, while rosemary (*Salvia rosmarinus*) is extensively used as a medicinal and aromatic plant in Morocco. Both matrices are chemically complex, containing high levels of pigments, polyphenols, caffeine, and essential oils, which can interfere with multiresidue determination by liquid chromatography–tandem mass spectrometry (LC-MS/MS) [1–3]. The optimized method was also applied to rosemary, where 31 of the 32 pesticides validated in tea showed satisfactory performance. Recovery values in rosemary ranged from 72 to 99%, comparable to those obtained in tea, demonstrating that the method remained robust in both polyphenol-rich and essential-oil-rich matrices. Only carbofuran required an increased functional LOQ in rosemary because of matrix-induced ion suppression. This dual-matrix approach provides a reliable and reproducible method for pesticide monitoring in herbal products.

The study targets 32 commonly used pesticides spanning multiple chemical classes, including organophosphates, carbamates, pyrethroids, and strobilurins. These compounds are relevant to Moroccan agricultural practices and regulatory monitoring, and their chemical diversity ensures a comprehensive assessment of method applicability and robustness across different analyte types.

The QuEChERS approach is widely applied for pesticide residue analysis; however, matrix-specific optimization remains necessary for pigment-rich and essential-oil-rich herbal products. Previous studies have demonstrated that the composition of the cleanup sorbent must often be adapted to the characteristics of the matrix. For example, Khan et al. [4] optimized a QuEChERS-GC-MS method for tobacco, a matrix rich in pigments and alkaloids, and showed that modifications of the cleanup step were required to reduce matrix interferences and improve recoveries. Similarly, Li et al. [5] reported that the incorporation of graphitized carbon black (GCB) into the QuEChERS cleanup significantly improved the removal of chlorophyll and pigments in spinach, thereby enhancing analytical performance.

More recent investigations have further emphasized the need for tailored cleanup strategies and matrix-matched calibration in complex tea and herbal matrices. Dong et al. [6] developed a multi-plug filtration cleanup (m-PFC)-LC-MS/MS method for the simultaneous determination of 14 pesticide residues in tea and demonstrated that the combined use of multi-walled carbon nanotubes, PSA, and $MgSO_4$ effectively reduced matrix interferences, yielding recoveries between 74.2 and 106.3%. Likewise, Ly et al. [7] validated highly accurate LC-MS/MS and GC-MS/MS methods for the determination of 397 pesticide residues in commercial teas and reported pronounced matrix effects for numerous analytes, highlighting the importance of matrix-matched calibration to ensure reliable quantification. These findings confirm that matrix constituents such as polyphenols, caffeine, pigments, and essential oils can substantially influence extraction efficiency and ionization, thereby requiring matrix-specific optimization of sample preparation and calibration procedures.

These findings highlight the importance of matrix-specific cleanup optimization for complex plant matrices. Nevertheless, despite such efforts, the application of systematic experimental design approaches for optimizing QuEChERS procedures in herbal matrices remains relatively limited. Furthermore, while method validation parameters are commonly reported, comprehensive evaluation of measurement uncertainty, particularly in routine laboratory settings, remains insufficiently addressed.

The present study aims to optimize a modified QuEChERS protocol for tea using factorial experimental design (NemrodW® software 2017 version), validate the method in accordance with NF EN 15662 requirements, assess its applicability to rosemary as a chemically distinct matrix, and compare experimentally derived uncertainty with theoretical

estimates based on the Horwitz model. By integrating matrix-specific optimization with uncertainty evaluation, this work provides a structured framework for reliable multiresidue pesticide monitoring in complex herbal matrices.

2. Materials and Methods

2.1. Apparatus

Analyses were performed using a Waters Acquity UPLC system coupled to a Xevo TQD triple-quadrupole mass spectrometer (Waters Corporation, Milford, MA, USA) operating in positive electrospray ionization (ESI^+) mode. Data were processed with MassLynx 4.2 and TargetLynx software. A BEH C18 (2.1 × 100 mm, 1.7 µm) column was maintained at 40 °C. The injection volume was 5 µL. Detailed chromatographic gradients, mobile-phase composition, source parameters, and MRM conditions are described in Section 2.7.

2.2. Reagents and Standards

All solvents were LC-MS grade (Sigma-Aldrich, St. Louis, MO, USA). QuEChERS extraction and purification salts were supplied by Biocomma (Shenzhen, China) (4 g $MgSO_4$, 1 g NaCl, 1 g trisodium citrate × 2 H_2O, 0.5 g disodium hydrogen citrate × 1.5 H_2O per pouch). Purification sorbents included 900 mg $MgSO_4$ + 150 mg PSA ± 45 mg BCG. Standard pesticide mixtures (>97% purity) were obtained from CPA Chem (Bogomilovo, Bulgaria).

2.3. Samples

Commercial Chinese-origin tea samples purchased from Moroccan markets were used as blank matrices. Rosemary leaves were collected from Mansouria (Morocco). These matrices were selected because they are commonly consumed aromatic and medicinal plants and constitute chemically complex matrices that may interfere with pesticide residue determination.

2.4. Selection of Pesticides

A total of 202 pesticide residues were initially screened using the validated NF EN 15662 QuEChERS-LC-MS/MS method in the tea matrix. The selection of compounds for subsequent validation was based solely on their analytical performance during this preliminary screening. Pesticides exhibiting acceptable recovery (70–120%) and precision (RSD ≤ 20%) were retained for further validation. Based on these criteria, 32 pesticides were selected for validation in tea: Acephate, Azoxystrobin, Benalaxyl, Bifenazate, Buprofezin, Carbetamide, Carbofuran, Chlortoluron, Cyazofamid, Dicrotophos, Dimoxystrobin, Ethiofencarb, Fenamidone, Fenobucarb, Fenpyroximat, Flufenoxuron, Fluomethuron, Fluoxastrobin, Furathiocarb, Iprovalicarb, Mefenacet, Methamidophos, Myclobutanil, Pencycuron, Picoxystrobin, Pirimicarb, Prometon, Propoxur, Temephos, Thiophanate-methyl, Triadimefon, and Trifloxystrobin.

Of these compounds, 31 were subsequently validated in rosemary, while carbofuran did not meet the validation requirements in this matrix.

2.5. Preparation of Calibration and Spiking Solutions

Stock solutions (1 mg/mL) were diluted to working standards (0.001–0.2 mg/kg) in matrix-matched extracts. Calibration curves were constructed with seven levels (0.001, 0.005, 0.01, 0.025, 0.05, 0.1, and 0.2 mg/kg).

Method validation was performed at four fortification levels (0.01, 0.02, 0.03, and 0.1 mg/kg). For each pesticide and matrix, duplicate spiked samples (2 g ± 0.02) were analyzed on five different days, resulting in a total of 10 replicates per concentration level. This experimental design allowed the assessment of both repeatability (within-day

precision) and within-laboratory reproducibility (between-day precision) according to NF T90-210 requirements [8].

2.6. Extraction and Clean-Up

Extraction followed NF EN 15662 [9] with modifications generated by NemrodW® [10]. Four variables were tested: acidification (0.1% formic acid in ACN), freezing before extraction, freezing after purification, and purification sorbent type (standard PSA, PSA + BCG, or PSA + activated charcoal).

To optimize the QuEChERS procedure, a full factorial experimental design ($2^3 \times 3$) was generated using NemrodW® software. Four factors potentially affecting extraction efficiency and matrix cleanup were investigated (Table 1):

- Acidification: Consists of stabilizing the pesticide residues with 0.1% of FA in MS grade ACN for extraction (1 µL of formic acid in the final 1 mL injection vial). The purification mix used is (900 mg $MgSO_4$ + 150 mg PSA), with either an affirmative or a negative option.
- FRZbfrEXT: "Freeze before extraction", freezing the mixture of lyophilized matrix mixed in ACN for 15 min. Aims to counteract the heating effect caused by the addition of a commercial extraction mixture, with either an affirmative or a negative option.
- FRZaftPUR: "FREEZE after purification", freezing the purified solution for 1 h for a presupposed riddance of matrix effect, with either an affirmative or a negative option.
- TYPEofPUR: "Type of purification", includes "standardpur", which refers to the standard purification mixture (900 mg $MgSO_4$ + 150 mg PSA). "BGC" refers to the addition of 45 mg of black graphite carbon; "AC" refers to the addition of 50 mg activated charcoal.

Table 1. Input parameters for modified clean-up procedures by Nemrodw® software.

	Acidification	FRZbfrEXT	FRZaftEXT	TYPEofPUR
1	Yes	Yes	Yes	BCG
2	No	No	No	AC
3	-	-	-	standardofpur

The levels investigated for each factor were selected based on preliminary experiments, the standard NF EN 15662 procedure, and modifications previously reported in the literature for complex plant matrices.

Using NemrodW® Software, 24 experiments of 0.1 mg/kg spiking were generated to be tested for the best recovery of most pesticide residues (Table 2). Parameters at play were [FRZbfrEXT] freezing for 15 min the mixture of sample, water, ACN before adding the contents of the QuEChERS extraction pouches since it is an exothermic reaction that might lead to the degradation of some thermo-sensitive pesticides. [TYPEofPUR] parameters refer to the compounds in the purification pouches and their interaction with the pesticides (adsorption, affinity, etc.). [FRZaftPUR] parameter refers to freezing the extract after the d-SPE cleanup procedure in order to separate the pesticides from the heavy matrix load. [Acidification] parameter aims to stabilize the pesticide residues in the sample with 0.1% a FA in ACN (1 µL per 1 mL of final extract).

Experiments 1 to 8 used 45 mg black carbon graphite in addition to 900 mg of $MgSO_4$ and 150 mg PSA. Experiments 1 to 4 had filtrate that had been stabilized by acidification; experiments 2 to 8 were not stabilized before injection. Experiments 2, 4, 5 and 8 were frozen before extraction, whereas 1, 4, 5 and 7 were not; experiments 2, 4, 5 and 6 were chilled at −20 °C before d-SPE purification.

Table 2. Modified QuEChERS experiments 1 to 24 with varying parameters.

Exp *n*°	Acidification	FRZ bfr EXT	TYPE of PUR	FRZ aft PUR
1	yes	no	bcg	no
2	yes	yes	bcg	yes
3	yes	yes	bcg	no
4	yes	no	bcg	yes
5	no	no	bcg	yes
6	no	yes	bcg	yes
7	no	no	bcg	no
8	no	yes	bcg	no
9	yes	no	Standard pur	no
10	yes	yes	Standard pur	yes
11	yes	yes	Standard pur	no
12	yes	no	Standard pur	yes
13	no	no	Standard pur	yes
14	no	yes	Standard pur	yes
15	no	no	Standard pur	no
16	no	yes	Standard pur	no
17	yes	no	ac	no
18	yes	yes	ac	yes
19	yes	yes	ac	no
20	yes	no	ac	yes
21	no	no	ac	yes
22	no	yes	ac	yes
23	no	no	ac	no
24	no	yes	ac	no

Experiments 9 to 16 only used the mixture of 900 mg of $MgSO_4$ and 150 mg PSA as purification compounds. Only experiments 9 to 12 were stabilized by acidification, experiments 10, 11, 14 and 16 were chilled before extraction, and only experiments 10, 12, 13 and 14 were chilled before d-SPE purification.

Experiments 17 to 24 used the acidification mixture in addition to the mixture of 900 mg of $MgSO_4$ and 150 mg PSA. Experiments 17, 18, 19 and 20 were stabilized by acidification, experiments 18, 19, 22 and 24 were chilled before extraction and experiments 18, 20, 21 and 22 were chilled before d-SPE purification.

For each experiment, samples were extracted with 10 mL ACN, vortexed, and centrifuged at 3000 *g* for 5 min at 5 °C. Six milliliters of supernatant were purified with the appropriate sorbent mixture, vortexed, centrifuged again under the same parameters, filtered (0.22 µm nylon), and injected.

2.7. Chromatographic and MS/MS Conditions

Mobile phase A: Ten mmol/L ammonium acetate in water (pH 5, adjusted with acetic acid); phase B: methanol. Flow rate: 0.45 mL/min; total run time: 17 min; gradient: 98%A → 2%A over 12.25 min, then re-equilibration.

Source settings: capillary 3500 V, cone 45 V, desolvation gas 100 L/h at 500 °C, cone gas 50 L/h, source temperature 150 °C, argon collision gas 4×10^{-3} mbar.

The MS/MS conditions were imported from the Waters database Quanpedia TM including the MRM data, RTs, MS transitions and collision energies (Table 3). Dwell times were updated automatically. RT window was optimized to ±0.5 min per analyte. A volume of 5 µL of sample extract was injected into the liquid chromatograph. The quantifying transitions were selected as the more abundant and intense peaks in order to ensure a better response on low concentration levels.

Table 3. RT, MS transitions and collision energies of analyzed pesticides.

PR	RT (min)	Transition-1	CE-1 (eV)	Transition-2	CE-2 (eV)
Acephate	2.63	184.1 > 143	8	184.1 > 125.1	18
Azoxystrobin	9.33	404 > 372	15	404 > 329	30
Benalaxyl	10.7	326.1 > 148	20	326.1 > 91	34
Bifenazate	9.94	301.1 > 198	10	301.1 > 170	20
Buprofezin	11.73	306.1 > 201	12	306.1 > 57.4	20
Carbetamide	6.88	237 > 192	9	237 > 118	14
Carbofuran	7.44	222.11 > 123	16	222.11 > 165.1	16
Carbofuran-3OH	5.49	238 > 181	10	238 > 163	16
Chlortoluron	8.13	213 > 72	18	213 > 46	16
Cyazofamid	10.2	325 > 107.9	20	325 > 261	10
Dicrotophos	4.88	238 > 112	10	238 > 193	10
Dimoxystrobin	10.48	327.1 > 116.1	21	327.1 > 205.2	10
Ethiofencarb	7.97	226.1 > 107	17	226.1 > 164	8
Fenamidone	9.47	312.1 > 92	25	312.1 > 236.1	14
Fenobucarb	9.18	208 > 94.9	14	208 > 152	8
Fenpyroximat	12.28	422.2 > 366.1	15	422.2 > 138.1	32
Flufenoxuron	12.21	489.12 > 158.02	22	489.12 > 141	46
Fluomethuron	8.01	233.2 > 72.2	18	233.2 > 46.4	18
Fluoxastrobin	10.06	459 > 427	18	459 > 188	36
Furathiocarb	11.58	383.2 > 194.9	18	383.2 > 252	12
Iprovalicarb	9.96	321.1 > 119.06	16	321.1 > 203.1	10
Mefenacet	9.84	299 > 148	15	299 > 120	25
Methamidophos	1.9	142 > 93.9	13	142 > 124.9	13
Myclobutanil	9.85	289.1 > 70.2	18	289.1 > 125.1	32
Pencycuron	11.08	329.1 > 125	25	329.1 > 218	15
Picoxystrobin	10.42	368 > 205.1	10	368 > 145.1	22
Pirimicarb	8.23	239.1 > 72	18	239.1 > 182.1	15
Prometon	9.07	226 > 86.3	28	226 > 184.3	18
Propoxur	7.33	210 > 111	16	210 > 168	10
Temephos	11.76	466.8 > 125	38	466.8 > 418.9	22
Thiophanate-methyl	7.36	343 > 151	22	343 > 93	46
Triadimefon	9.74	294.1 > 69.3	20	294.1 > 197.2	15
Trifloxystrobin	11.3	409 > 186	16	409 > 145	40

2.8. Validation Parameters

The method was validated for linearity, matrix effect, recovery, precision, LOD/LOQ, specificity, and measurement uncertainty according to NF EN 15662 and EU SANTE/11312/2021 [11] guidance.

An evaluation of the matrix effect is conducted to determine the deviation between the area of the pesticide in the solvent and the area of the same pesticide in the matrix using the formula below.

$$\text{Matrix Effect Deviation } (\%) = 100 \times \text{Abs}\left(\frac{\text{Area in solvent} - \text{Area in matrix}}{\text{Area in solvent}}\right)$$

The use of the absolute value was intended to estimate the magnitude of matrix effects irrespective of whether they resulted from signal suppression or enhancement. Therefore, the calculated values reflect the extent of matrix influence on the analytical response rather than its direction.

Table 4 showed that all pesticides were able to perform in a solvent-prepared calibration curve. Nevertheless, in order to get the best recoveries, we opted for the linearity in the blank tea matrix. The blank sample was analyzed following the experiment with the best yields. The same samples of tea leaves were spiked for method validation.

Table 4. Pesticide peak areas of 0.01 mg/kg in solvent and in matrix extract and the calculated deviation for day 1.

PR	Area in Solvent	Area in Matrix	Calculated Deviation (%)
Azoxystrobin	180,865.1	180,651.6	0.1
Benalaxyl	210,787.7	205,933.9	2.3
Bifenazate	94,750.6	97,181.3	2.6
Buprofezin	191,605.9	192,452.3	0.4
Carbetamide	66,964.3	57,647.7	13.9
Carbofuran	20,260.5	18,273.7	9.8
Chlortoluron	140,724.1	129,434.2	8.0
Cyazofamid	51,037.8	48,855.9	4.3
Dicrotophos	94,592.2	95,812.8	1.3
Dimoxystrobin	89,793.5	77,765.3	13.4
Ethiofencarb	70,047.8	66,862.8	4.5
Fenamidone	147,044.7	137,169.8	6.7
Fenobucarb	147,067.8	140,706.3	4.3
Fenpyroximat	72,347.5	70,150.8	3
Flufenoxuron	32,914.9	35,252.6	7.1
Fluomethuron	163,629.1	151,238.2	7.6
Fluoxastrobin	100,867	99,101	1.8
Furathiocarb	118,204.3	120,727.9	2.1
Iprovalicarb	146,157.2	141,050	3.5
Mefenacet	218,206.3	252,980.8	15.9
Methamidophos	17,166.7	17,491.6	1.9
Myclobutanil	57,784	62,180.9	7.6
Pencycuron	238,706.9	241,823.5	1.3
Picoxystrobin	116,001.3	114,959.1	0.9

Table 4. *Cont.*

PR	Area in Solvent	Area in Matrix	Calculated Deviation (%)
Pirimicarb	398,274.2	420,934.1	5.7
Prometon	133,067.1	117,167.5	11.9
Propoxur	81,381.9	73,195	10.1
Temephos	799.5	776.5	2.9
Thiophanate-methyl	109,850.2	102,869	6.4
Triadimefon	47,622.4	46,330.3	2.7
Trifloxystrobin	155,903.3	150,151.3	3.7

2.9. Measurement of Uncertainty

The uncertainty of the analytical method was evaluated using two complementary approaches to ensure both theoretical rigor and practical relevance.

Validation-based uncertainty:

The first approach used the method validation results obtained from tea spiked at four concentration levels (0.01, 0.02, 0.03 and 0.1 mg/kg). For each pesticide, duplicate spiked samples were analyzed over five different days, resulting in 10 recovery values per concentration level. The relative standard deviation (RSD) was calculated from these 10 replicate recoveries at each spiking level and subsequently used to estimate the expanded uncertainty, providing a direct measure of the variability observed under laboratory conditions. This approach captures compound-specific effects, such as differences in repeatability, extraction efficiency, and analyte stability, which are not accounted for by theoretical models.

$$\text{RSD } (\%) = \left(\frac{\text{SD of replicates}}{\text{Mean recovery}}\right) \times 100$$

$$\text{U} = 2 \times \text{RSD } (\%) \quad (1)$$

Horwitz-based uncertainty:

To complement the experimental estimates, the theoretical Horwitz equation was applied. According to Horwitz [12], the RSD of a measurement is inversely related to the analyte concentration, following a characteristic "trumpet-shaped" curve. The Horwitz-Ratio (HorRat) was calculated for each pesticide and spiking level to evaluate method performance (Table 5). This approach provides a standard reference for expected variability, particularly for low-concentration measurements, and allows comparison between compounds irrespective of the matrix or analytical technique.

$$\text{RSDR } (\%) = 2 \times \text{C}^{-0.15}$$

Table 5. Comparison of validation-based and Horwitz-based uncertainties for selected pesticides.

PR	U_val 0.01 mg/kg	U_val 0.02 mg/kg	U_val 0.03 mg/kg	U_val 0.1 mg/kg	U_Horwitz 0.01 mg/kg	U_Horwitz 0.02 mg/kg	U_Horwitz 0.03 mg/kg	U_Horwitz 0.1 mg/kg
Acephate	3.62	12.7	2.73	0.77	7.98	7.19	6.77	5.65
Azoxystrobin	-	9.09	16.36	15.45	7.98	7.19	6.77	5.65
Benalaxyl	-	-	24.55	0.77	7.98	7.19	6.77	5.65
Bifenazate	-	8.18	10.91	0	7.98	7.19	6.77	5.65
Buprofezin	-	4.77	7.27	1.09	7.98	7.19	6.77	5.65
Carbetamide	10	2	8	0	8.0	7.2	6.77	5.65

Table 5. *Cont.*

PR	U_val 0.01 mg/kg	U_val 0.02 mg/kg	U_val 0.03 mg/kg	U_val 0.1 mg/kg	U_Horwitz 0.01 mg/kg	U_Horwitz 0.02 mg/kg	U_Horwitz 0.03 mg/kg	U_Horwitz 0.1 mg/kg
Carbofuran	-	-	6	1	8.0	7.2	6.77	5.65
Chlortoluron	-	-	25	24	8.0	7.2	6.77	5.65
Cyazofamid	20	7	4	15	8.0	7.2	6.77	5.65
Dicrotophos	25	5	10	16	8.0	7.2	6.77	5.65
Dimoxystrobin	22	11	8	15	8.0	7.2	6.77	5.65
Ethiofencarb	3	20	12	20	8.0	7.2	6.77	5.65
Fenamidone	-	-	22	23	8.0	7.2	6.77	5.65
Fenobucarb	-	-	22	19	8.0	7.2	6.77	5.65
Fenpyroximat	-	-	20	17	8.0	7.2	6.77	5.65
Flufenoxuron	-	9	15	2	8.0	7.2	6.77	5.65
Fluomethuron	-	10	13	7	8.0	7.2	6.77	5.65
Fluoxastrobin	-	-	13.5	15	8.0	7.2	6.77	5.65
Furathiocarb	-	-	23	14	8.0	7.2	6.77	5.65
Iprovalicarb	-	-	22	13	8.0	7.2	6.77	5.65
Mefenacet	-	-	26	20	8.0	7.2	6.77	5.65
Methamidophos	3	3	22	23	8.0	7.2	6.77	5.65
Myclobutanil	-	23	11	14	8.0	7.2	6.77	5.65
Pencycuron	-	-	23	18	8.0	7.2	6.77	5.65
Picoxystrobin	-	-	17	4	8.0	7.2	6.77	5.65
Pirimicarb	-	-	23	12	8.0	7.2	6.77	5.65
Prometon	-	7	4	15	8.0	7.2	6.77	5.65
Propoxur	12	11	9	4	8.0	7.2	6.77	5.65
Temephos	-	-	23	19	8.0	7.2	6.77	5.65
Thiophanate-methyl	0	13	9	12	8.0	7.2	6.77	5.65
Triadimefon	2	8	2	5	8.0	7.2	6.77	5.65
Trifloxystrobin	-	23	18	20	8.0	7.2	6.77	5.65

Notes: "-" = unsatisfactory recovery at that spiking level. Validation-based uncertainty (U_val) was calculated as 2 × RSD of replicate recoveries (coverage factor k = 2). Horwitz uncertainty (U_Horwitz) calculated from concentration, showing the expected "trumpet" trend.

Comparison of approaches:

Both approaches were compared across all pesticides and spiking levels. While the Horwitz-based uncertainty offers a concentration-dependent, method-independent benchmark, the validation-based uncertainty provides a more realistic estimate reflecting laboratory performance and compound-specific variability. This dual approach ensures a robust and transparent characterization of uncertainty for all pesticides analyzed in tea.

3. Results and Discussion

3.1. Optimization of Clean-Up Procedure

The 24 designed experiments demonstrated that freezing prior to extraction and acidification (0.1% FA in ACN) reduced losses of thermolabile analytes and limited matrix effects; inclusion of BCG in the d-SPE mix effectively reduced pigment interference. The optimal extraction conditions were selected based on the proportion of pesticides exhibiting

recoveries within the acceptable range of 70–120%. Experiment 3 (acidification + freezing before extraction + PSA + BCG) provided the best overall results, yielding recoveries in the 70–120% range for 97% of the targeted pesticides. Use of activated charcoal caused significant adsorption for certain analytes and frequently reduced recoveries below acceptable levels -often <60 (Table 6).

Table 6. Mean recoveries of PR in the 24 modified QuEChERS extraction procedures.

Exp	Criteria 2: Maximum Yield of Pesticide Residues	Exp	Criteria 2: Maximum Yield of Pesticide Residues
Exp 1	65% of PR with recovery between 70% and 120%	Exp 13	49% of PR with recovery between 70% and 120%
Exp 2	91% of PR with recovery between 70% and 120%	Exp 14	55% of PR with recovery between 70% and 120%
Exp 3	97% of PR with recovery between 70% and 120%	Exp 15	55% of PR with recovery between 70% and 120%
Exp 4	72% of PR with recovery between 70% and 120%	Exp 16	61% of PR with recovery between 70% and 120%
Exp 5	55% of PR with recovery between 70% and 120%	Exp 17	61% of PR with recovery between 70% and 120%
Exp 6	61% of PR with recovery between 70% and 120%	Exp 18	72% of PR with recovery between 70% and 120%
Exp 7	55% of PR with recovery between 70% and 120%	Exp 19	81% of PR with recovery between 70% and 120%
Exp 8	65% of PR with recovery between 70% and 120%	Exp 20	72% of PR with recovery between 70% and 120%
Exp 9	55% of PR with recovery between 70% and 120%	Exp 21	55% of PR with recovery between 70% and 120%
Exp 10	72% of PR with recovery between 70% and 120%	Exp 22	61% of PR with recovery between 70% and 120%
Exp 11	72% of PR with recovery between 70% and 120%	Exp 23	55% of PR with recovery between 70% and 120%
Exp 12	65% of PR with recovery between 70% and 120%	Exp 24	49% of PR with recovery between 70% and 120%

3.2. Recoveries and Precision

Mean recoveries (n = 10 per fortification level, obtained from duplicate analyses performed over five days) for the 32 pesticides validated in tea ranged from approximately 73 to 117%, with RSDs generally $\leq$20% at concentrations $\geq$0.03 mg/kg. At the lowest spiking level (0.01 mg/kg) the following compounds showed unsatisfactory recoveries (<70%): Benalaxyl, Chlortoluron, Fenamidone, Fenobucarb, Fenpyroximat, Fluoxastrobin, Iprovalicarb, Mefenacet, Picoxystrobin, and Temephos. Most of these compounds achieved acceptable recoveries at $\geq$0.03 mg/kg. These results informed the practical LOQs assigned for each analyte and are consistent with matrix complexity reported in the literature.

3.3. Matrix Effect

Matrix vs. solvent area deviations at 0.01 mg/kg were <20% for the validated pesticides, supporting the use of matrix-matched calibration curves to mitigate residual matrix effects and ensure quantitative accuracy. Matrix-matched calibration proved important for the analysis of tealeaves with relatively high matrix-effect results, as reported by Cladière et al. [13]. Other references suggest that the regular 3% of caffeine in dry tealeaves may lead to low recoveries, despite numerous trials to reduce it [14].

3.4. Limits of Detection and Recoveries

Functional LOQs (based on acceptable recovery and precision) ranged between 0.01 and 0.03 mg/kg depending on the analyte. Experimental LODs (signal-to-noise > 3 for both transitions) ranged from 0.001 to 0.01 mg/kg across analytes.

Ten molecules (Acephate, Carbetamid, Cyazofamid, Dicrotophos, Dimoxystrobin, Ethiofencarb, Methamidophos, Propoxur, Thiophate-methyl and Triadimefon) had an Avg. Rec. at 0.01 mg/kg; 8 molecules (Azoxystrobin, Bifenazate, Buprofezin, Flufenoxuron, Myclobutanil, Prometon and Trifloxystrobin) had appropriate responses at 0.02 mg/kg and 14 molecules had the appropriate yield at 0.03 mg/kg (Benalaxyl, Carbofuran, Chlorotolu-

ran, Fenamidone, Fenobucarb, Fenpyroximat, Fluoxastrobin, Furathiocarb, Iprovalicarb, Mefenacet, Pencycuron, Picoxystrobin, Pirimicarb and Temephos) (Table 7).

Table 7. Average recoveries of spiked tea leaves at 4 spiking levels.

PR	Avg. Rec. (%) 0.01 mg/kg	Avg. Rec. (%) 0.02 mg/kg	Avg. Rec. (%) 0.03 mg/kg	Avg. Rec. (%) 0.1 mg/kg	PR	Avg. Rec. (%) 0.01 mg/kg	Avg. Rec. (%) 0.02 mg/kg	Avg. Rec. (%) 0.03 mg/kg	Avg. Rec. (%) 0.1 mg/kg
Acephate	96	86	97	83	Fluomethuron	-	91	90	87
Azoxystrobin	-	90	82	117	Fluoxastrobin	-	-	73	85
Benalaxyl	-	-	73	83	Furathiocarb (with carbofuran)	-	-	77	86
Bifenazate	-	88	84	100	Iprovalicarb	-	-	78	87
Buprofezin	-	93	89	80	Mefenacet	-	-	74	80
Carbetamide	90	98	84	100	Methamidophos	103	97	78	77
Carbofuran	-	-	94	90	Myclobutanil	-	77	111	86
Chlortoluron	-	-	75	76	Pencycuron	-	-	73	82
Cyazofamid	80	93	103	85	Picoxystrobin	-	-	83	96
Dicrotophos	75	95	79	84	Pirimicarb	-	-	77	88
Dimoxystrobin	78	89	108	85	Prometon	-	93	104	85
Ethiofencarb	97	80	112	80	Propoxur	88	89	90	96
Fenamidone	-	-	78	77	Temephos	-	-	77	81
Fenobucarb	-	-	78	81	Thiophanate-methyl	100	87	91	88
Fenpyroximat	-	-	80	83	Triadimefon	102	92	98	93
Flufenoxuron	-	91	85	102	Trifloxystrobin	-	77	82	80

"-": Molecule presented unsatisfactory results at the selected spiking level.

Results were calculated from 10 measurements obtained using the optimized extraction procedure (Experiment 3), from duplicate analyses performed at each fortification level over five consecutive days, in accordance with NF T90-210. This experimental design enabled the evaluation of both repeatability and within-laboratory reproducibility.

The limit of detection was theoretically set at LOQ/3. LODexp was set as the concentration at which the pesticide peaks had a signal-to-noise ratio greater than 3 in both transitions by simple addition of the standard in the matrix blank. Tests at 0.001 mg/kg, 0.003 mg/kg, 0.005 mg/kg and 0.01 mg/kg were done. Acephate, Carbetamide, Cyazofamid, Dicrotophos, Dimoxystrobin, Etiofencarb, Methamidophos, Propoxur, Thiophanate-methyl and Triadimefon showed appropriate peaks at 0.001 mg/kg (defined as chromatographic signals with correct retention time, symmetrical peak shape without significant tailing, absence of interfering background at the analyte retention time, and a signal-to-noise ratio $S/N \geq 3$ at the lowest detectable concentration). Azoxystrobin, Bifenazate, Buprofezin, Flufenoxuron, Fluomethuron, Myclobutanil, Prometon and Trifloxystrobin had appropriate peaks starting at 0.003 mg/kg. Carbofuran, Fenpyroximat and Picoxystrobin only had appropriate peaks at 0.005 mg/kg whereas Benalaxyl, Chlorotoluron, Fenamidone, fenobucarb, Fluoxastrobin, Furathiocarb, Iprovalicarb, Mefenacet, Pencycuron, Pirimicarb and Temephos only responded to the LOD conditions at the 0.01 mg/kg level (Table 8) with further comparison to MRLs in the European Union database (EU), Codex Alimentarius database, Canadian database and USA database. The comparison highlights the low results compared to the high MRL values in most cases, except for a few EU MRL set at 0.01 mg/kg.

Table 8. Results of LOQ and LODexp, compared to EU, Codex, Canadian and American MRLs in mg/kg.

RP	LOQ	LODexp	EU MRL [15]	Codex MRL [16]	Canadian MRL [17]	USA MRL [18]
Acephate	0.01	0.001	0.02	NF	NF	NF
Azoxystrobin	0.02	0.003	70	300: Dried herbs Except hops (dry)	20	20
Benalaxyl	0.03	0.01	0.02: Sum of isomers	NF	NF	NF
Bifenazate	0.02	0.003	0.05: Sum of metabolites	NF	NF	NF
Buprofezin	0.02	0.003	0.02	NF	NF	NF
Carbetamide	0.01	0.001	0.02: Sum of isomers	NF	NF	NF
Carbofuran	0.03	0.005	0.02: Sum of metabolites	NF	NF	NF
Chlortoluron	0.03	0.01	0.02	NF	NF	NF
Cyazofamid	0.01	0.001	0.02	NF	NF	NF
Dicrotophos	0.01	0.001	Default MRL	NF	NF	NF
Dimoxystrobin	0.01	0.001	0.02	NF	NF	NF
Ethiofencarb	0.01	0.001	Default MRL	NF	NF	NF
Fenamidone	0.03	0.01	0.02	NF	NF	
Fenobucarb	0.03	0.01	Default MRL	NF	NF	NF
Fenpyroximat	0.03	0.005	0.02	8:Tea, green, black (black, fermented and dried)	NF	20
Flufenoxuron	0.02	0.003	0.02	20:Tea, green, black (black, fermented and dried)	NF	NF
Fluomethuron	0.02	0.003	0.02	NF	NF	NF
Fluoxastrobin	0.03	0.01	0.02: Sum of isomers	NF	NF	NF
Furathiocarb	0.03	0.01	0.02: Sum of metabolites	NF	NF	NF
Iprovalicarb	0.03	0.01	0.02	NF	NF	NF
Mefenacet	0.03	0.01	Default MRL	NF	NF	NF
Methamidophos	0.01	0.001	0.02	NF	NF	NF
Myclobutanil	0.02	0.003	0.05:Sum of isomers	NF	NF	NF
Pencycuron	0.03	0.01	0.04: Sum of metabolites	NF	NF	NF
Picoxystrobin	0.03	0.005	0.02	15: Tea, green, black (black, fermented and dried)	NF	NF
Pirimicarb	0.03	0.01	0.8	NF	NF	NF
Prometon	0.02	0.003	Default MRL	NF	NF	NF
Propoxur	0.01	0.001	0.01	NF	NF	NF
Temephos	0.03	0.01	Default MRL	NF	NF	NF
Thiophanate-methyl	0.01	0.001	0.1	NF	NF	NF
Triadimefon	0.01	0.001	0.02	NF	NF	NF
Trifloxystrobin	0.02	0.003	15	NF	NF	5

3.5. Specificity in Rosemary

When applied to rosemary, 31 of the 32 pesticides previously validated in tea met ion-ratio and retention-time criteria at the assigned LOQs (Table 9). Recovery values obtained in rosemary ranged from 72 to 99%, which was comparable to the recoveries observed in tea (70–120%), indicating that the modified QuEChERS procedure was equally effective for both matrices despite their different chemical compositions. These results demonstrate that the method is robust for both polyphenol- and caffeine-rich matrices such as tea and essential-oil-rich matrices such as rosemary. The main difference concerned carbofuran, which required an elevated functional LOQ in rosemary because of strong suppression of the qualifier ion, likely caused by co-extracted essential-oil components. Acceptable quantification was achieved at 1.5× LOQ. The median matrix effect across rosemary spikings was 12% (IQR 6–19%), confirming that matrix effects remained moderate and manageable through matrix-matched calibration.

Table 9. Specificity results in essays on rosemary leaves.

PR	Avg. Rec. (%) 0.01 mg/kg	Avg. Rec. (%) 0.02 mg/kg	Avg. Rec. (%) 0.03 mg/kg	Avg. Rec. (%) 0.1 mg/kg
Azoxystrobin	-	85	81	93
Benalaxyl	-	-	75	92
Bifenazate	-	-	88	97
Buprofezin	-	86	90	95
Carbetamide	88	92	95	98
Carbofuran	-	-	-	88
Chlortoluron	-	-	73	90
Cyazofamid	79	84	88	92
Dicrotophos	76	82	86	91
Dimoxystrobin	83	89	92	96
Ethiofencarb	74	81	85	89
Fenamidone	-	-	77	94
Fenobucarb	-	-	80	96
Fenpyroximat	-	-	84	90
Flufenoxuron	85	91	94	99
Fluomethuron	-	88	92	97
Fluoxastrobin	75	72	80	93
Furathiocarb	-	78	84	89
Iprovalicarb	79	85	90	95
Mefenacet	74	81	86	92
Methamidophos	83	89	93	97
Myclobutanil	-	86	90	94
Pencycuron	76	83	88	93
Picoxystrobin	-	-	89	95
Pirimicarb	-	83	87	92
Prometon	81	87	92	96
Propoxur	84	90	94	98
Temephos	-	78	86	91
Thiophanate-methyl	82	88	93	97
Triadimefon	85	91	95	99
Trifloxystrobin	-	86	91	96

3.6. Comparative Uncertainty Assessment

Measurement uncertainty was evaluated using two complementary approaches: validation-based and Horwitz-based estimation. The validation-based uncertainty (U_val) was derived from the variability of recoveries obtained during method validation at four concentration levels (0.01, 0.02, 0.03, and 0.1 mg/kg). Since measurement uncertainty in residue analysis is generally proportional to analyte concentration, the relative standard deviation (RSD) obtained from validation experiments was used as an estimate of the relative standard uncertainty, in accordance with EURACHEM recommendations. Expanded uncertainty was subsequently estimated by applying a coverage factor of k = 2, corresponding to an approximate confidence level of 95% [19,20]. In contrast, the Horwitz-based uncertainty (U_Horwitz) was estimated theoretically from the Horwitz equation ($RSD = 2 \times C^{-0.15}$) [20], offering a concentration-dependent benchmark for expected analytical performance. Comparison of both approaches (Figure 1) revealed that U_val values were generally higher at the lowest concentration (0.01 mg/kg), reflecting the increased variability typically associated with trace-level analysis. As concentration increased, U_val progressively approached the Horwitz-based estimates, indicating improved precision and stable analytical performance [21]. Overall, the agreement between experimental and theoretical uncertainty estimates supports the suitability of the method for quantitative

determination of pesticide residues in tea, while providing a transparent characterization of its measurement uncertainty.

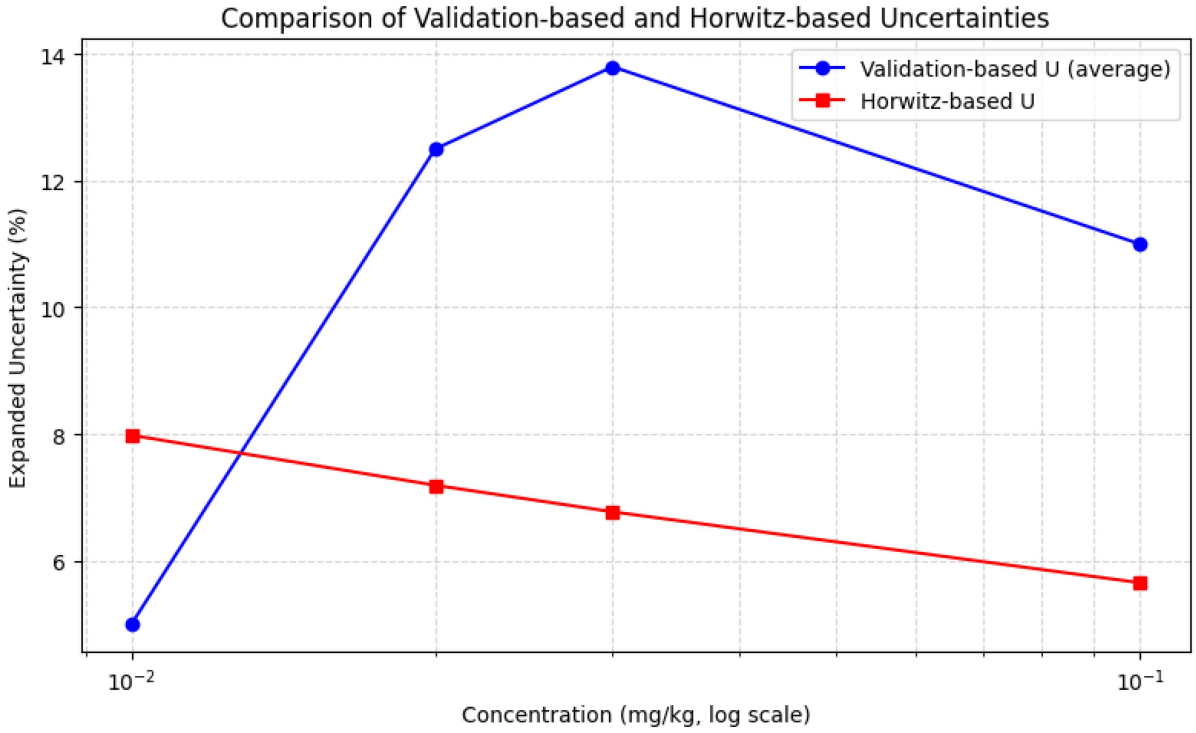

Figure 1. Validation-based (U_val) and Horwitz-based (U_Horwitz) expanded uncertainties for the analyzed pesticides at the four studied concentration levels.

Validation-based uncertainties reflect actual laboratory variability, while Horwitz uncertainties provide a theoretical benchmark.

Figure 1 compares the validation-based expanded uncertainties (U_val) with the theoretical Horwitz-based uncertainties (U_Horwitz) for the pesticides analyzed in tea at four spiking concentrations (0.01, 0.02, 0.03, and 0.1 mg/kg). The red line represents the Horwitz uncertainties, which decrease with increasing concentration following the characteristic "trumpet-shaped" trend, providing a theoretical benchmark for expected variability in analytical measurements. The blue line shows the validation-based uncertainties, calculated from replicate recoveries, reflecting the actual variability observed under laboratory conditions. Notably, at lower concentrations, U_val often exceeds the Horwitz values, highlighting higher experimental variability when analyte levels are low. At intermediate and higher concentrations, U_val aligns more closely with or slightly exceeds the theoretical predictions, illustrating both the influence of compound-specific factors (e.g., extraction efficiency, analyte stability) and the robustness of the method across different pesticides. This comparison demonstrates that combining validation-based and Horwitz-based approaches provides a comprehensive assessment of measurement uncertainty, capturing both method performance and theoretical expectations.

4. Conclusions

The modified QuEChERS method enabled the extraction and quantification of 32 pesticide residues in tea and rosemary matrices with satisfactory validation performance. Most analytes achieved recoveries within 70–120% and limits of quantification suitable for regulatory monitoring. Matrix-matched calibration improved analytical reliability in the complex tea matrix.

Measurement uncertainty was evaluated using both validation-based and Horwitz-based approaches, providing complementary insight into method precision across the studied concentration range. Uncertainty decreased with increasing concentration, consistent with theoretical expectations.

Tea and rosemary were selected as representative herbal matrices exhibiting markedly different chemical compositions, with tea being rich in polyphenols, pigments, and caffeine, and rosemary containing high levels of essential oils and other lipophilic compounds. These constituents are known to influence extraction efficiency and ionization during LC-MS/MS analysis, making both matrices analytically challenging. Despite these differences, comparable analytical performances were achieved in both matrices, demonstrating the robustness of the modified QuEChERS procedure across chemically diverse herbal products. The successful application of the method to both the polyphenol-rich tea matrix and the essential-oil-rich rosemary matrix indicates that the proposed procedure is not matrix-specific and may be extended to a wider range of aromatic and medicinal plants. Although rosemary presented slightly greater analytical challenges due to matrix-induced ion suppression, only carbofuran required an increased functional LOQ, while all other analytes fulfilled the validation criteria. Overall, the validated method provides a reliable and reproducible tool for routine pesticide residue monitoring in tea, rosemary, and related herbal matrices, thereby strengthening analytical quality control and supporting food safety surveillance programs. Nevertheless, the present study was limited to the validation of 32 pesticide residues in two representative herbal matrices. Although tea and rosemary were intentionally selected to cover chemically contrasting matrices, further studies involving a broader range of pesticides and aromatic or medicinal plants are warranted to confirm the wider applicability of the proposed method. Future work could also investigate additional matrix-induced effects in highly complex herbal products and evaluate the method under routine interlaboratory conditions.

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Abbreviations

AA	Acetic Acid
ACN	Acetonitrile
Avg. Rec.	Average Recovery
BCG	Black Carbon Graphite
d-SPE	dispersive Solid Phase Extraction
FA	Formic Acid
LODexp	experimental value of LOD
MRL	Maximum Residual Limit
NF	Not Found
PR	Pesticide Residues
PSA	Primary and Secondary Amines

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