

Development and Validation of GC-MS/MS Method For Multi-Pesticide Residue in Nutraceutical Products

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Abstract

Nutraceutical raw materials, being largely of plant origin, are vulnerable to contamination by pesticides applied during cultivation, storage and post-harvest handling. Because such residues can persist into finished products at trace levels, sensitive and validated multi-residue methods are required to protect consumer health and to meet regulatory limits. This study reports the development and validation of a gas chromatography–tandem mass spectrometry (GC-MS/MS) method for the simultaneous determination of ten pesticides (dichlorvos, chlorpropham, trifluralin, phorate, simazine, fluchloralin, chlorothalonil, tri-allate, parathion-methyl and ametryne) in nutraceutical matrices. Sample extraction and clean-up were carried out using the QuEChERS approach (acetonitrile extraction with anhydrous magnesium sulphate/sodium sulphate salt-out, followed by dispersive solid-phase extraction with PSA and MgSO₄), and detection was performed on a triple-quadrupole GC-MS/MS system operated in multiple reaction monitoring (MRM) mode. The method was validated as per SANTE 11312/2023 v2 guidelines for specificity, matrix effect, linearity, limit of quantification (LOQ), recovery, repeatability (RSDr), reproducibility (RSDwR), robustness, relative ion ratio and retention time. The method showed no interfering peaks at the analyte retention times, linear response over 5–100 ng mL⁻¹ with correlation coefficients ≥ 0.99 , and mean recoveries of 89–119% at LOQ, 2×LOQ and 10×LOQ levels, with %RSD generally below 20%. Matrix-matched calibration was found necessary to compensate for pronounced signal suppression observed for several analytes. The validated method is suitable for routine multi-residue pesticide screening of nutraceutical products and supports compliance with FSSAI, Codex Alimentarius and pharmacopoeial safety requirements.

Keywords: Multi-pesticide residue; Nutraceuticals; GC-MS/MS; Method validation; QuEChERS; SANTE 11312/2023 v2; Matrix effect.

1. Introduction

The term “nutraceutical”, coined by Dr. Stephen DeFelice in 1989 from “nutrition” and “pharmaceutical”, refers to food-derived products or components that confer health or medical benefits beyond basic nutrition. Nutraceuticals are marketed as powders, tablets, capsules, beverages and fortified foods, and are typically derived from plants, proteins, vitamins or other bioactive sources. Because the raw materials used in their manufacture are predominantly agricultural, nutraceutical products are inherently susceptible to contamination

by pesticide residues carried over from cultivation, storage and processing. Even trace-level residues can pose a health risk to consumers and place a product outside the limits set by regulatory bodies such as the Food Safety and Standards Authority of India (FSSAI), the Codex Alimentarius Commission, and pharmacopoeias including the Indian Pharmacopoeia, USP and European Pharmacopoeia.

Reliable quality control therefore depends on analytical methods that are properly developed and validated. Method development establishes a procedure capable of separating, identifying and quantifying target analytes in complex matrices with adequate sensitivity, selectivity and robustness, while method validation confirms—against internationally recognised criteria such as ICH Q2(R1)/Q2(R2) and SANTE/11312/2021 (updated as SANTE 11312/2023 v2)—that the method consistently delivers accurate, precise and reproducible results. Gas chromatography coupled with triple-quadrupole tandem mass spectrometry (GC-MS/MS or GC-QqQ) has become a technique of choice for multi-residue pesticide analysis because it combines chromatographic separation with the high selectivity of multiple reaction monitoring (MRM), enabling simultaneous quantification of large numbers of semi-volatile and volatile pesticides at microgram-per-kilogram concentrations even in the complex matrices typical of herbal and protein-based nutraceuticals.

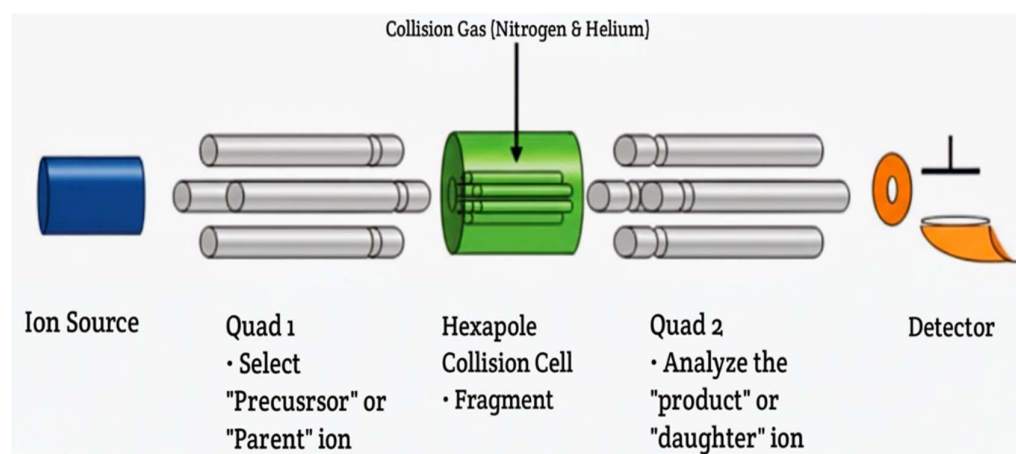
The present work describes the development and full validation of a GC-MS/MS method, using QuEChERS-based sample preparation, for the simultaneous determination of ten pesticides representing the organophosphate, carbamate, dinitroaniline, triazine, organochlorine and thiocarbamate classes: dichlorvos, chlorpropham, trifluralin, phorate, simazine, fluchloralin, chlorothalonil, tri-allate, parathion-methyl and ametryne. These compounds were selected as they represent a broad cross-section of insecticide, herbicide and fungicide chemistries with differing modes of toxicity (e.g., acetylcholinesterase inhibition for the organophosphates, microtubule/mitotic disruption for the dinitroanilines, and photosystem II inhibition for the triazines), making them representative markers for multi-class residue screening of nutraceutical raw materials and finished products.

2. Materials and Methods

2.1 Chemicals, Reagents and Gases

LC-MS grade acetonitrile and ethyl acetate, Millipore water, anhydrous magnesium sulphate, anhydrous sodium acetate, primary secondary amine (PSA), C18 and graphitised carbon black (GCB) sorbents were used. High-purity helium (99.999%) served as carrier gas and nitrogen (99.999%) as collision/evaporation gas. Analytical reference standards of the ten target pesticides were used for calibration and spiking.

2.2 Instrumentation



An analytical balance, a triple-quadrupole GC-MS/MS system (GC/TQ), micropipettes (20–200 μL and 100–1000 μL), a vortex mixer, a refrigerated centrifuge, a nitrogen concentrator, 0.22 μm and 0.45 μm syringe

filters, conical flasks (250 and 500 mL) and volumetric flasks (10 and 25 mL) were used throughout method development and validation.

2.3 Standard and Calibration Solution Preparation

Individual stock solutions (1.0 mg mL^{-1}) were prepared by dissolving approximately 10 mg of each reference standard in a 10 mL volumetric flask and diluting to volume with a suitable solvent; solutions were sonicated to clarity and stored at -10 to -20°C . A mixed working stock (100 mg L^{-1}) was prepared by diluting 0.1 mL of each 1000 mg L^{-1} stock to 10 mL, and a further intermediate stock (1 mg L^{-1}) was prepared by diluting 1 mL of the 100 mg L^{-1} solution to 10 mL. Matrix-matched calibration standards were then prepared at six concentration levels (5, 10, 25/20, 50, 75, 100/200 ng mL^{-1} , denoted CC-1 to CC-6) spanning 5–200 ppb, to establish the linear range for each pesticide.

2.4 Sample Preparation (QuEChERS)

A 10.0 g (± 0.1 g) test portion was weighed into a 50 mL centrifuge tube and extracted with 10 mL acetonitrile by vortexing for 5 min. Anhydrous sodium sulphate (10 g) and magnesium sulphate (6 g) were added and the mixture was vortexed for a further 5 min, then centrifuged at 10,000 rpm for 5 min. An aliquot of the supernatant was transferred to a 15 mL dispersive-SPE clean-up tube (12.5 mg PSA and 25 mg MgSO_4 per mL of extract), shaken for 1 min and centrifuged again (10,000 rpm, 5 min). One millilitre of the cleaned supernatant was evaporated to dryness under nitrogen at 30 – 45°C , reconstituted in 1 mL ethyl acetate, vortexed for 30 s and filtered through a $0.22 \mu\text{m}$ membrane prior to GC-MS/MS injection.

2.5 GC-MS/MS Conditions

Chromatographic separation used two 15 m HP-5MS Ultra Inert capillary columns ($250 \mu\text{m} \times 0.25 \mu\text{m}$) in a flush-back configuration; detection was performed in electron-impact MRM mode. Key instrument parameters are summarised in Table 1.

Table 1. GC-MS/MS instrument operating parameters.

Parameter	Value
Column oven initial temperature	60°C
Total run time	20.75 min
Injector type / temperature	Solvent vent / 70°C
Purge time / flow	1.5 min / 60 mL min^{-1}
Column	HP-5MS Ultra Inert $15 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$ ($\times 2$, flush-back configuration)
Column 1 / Column 2 flow	1.5 mL min^{-1} (constant) / 1.7 mL min^{-1} (constant)
Ion source temperature	300°C
Interface (AUX heater) temperature	280°C
Solvent delay	3.7 min
Carrier / collision gas	Helium 99.999% / Nitrogen–Helium
Ionisation mode	Electron impact, 70 eV
Acquisition mode	Multiple Reaction Monitoring (MRM)

2.6 Method Validation

The method was validated as per SANTE 11312/2023 v2 guidelines for the following parameters: specificity, matrix effect, linearity, limit of quantification (LOQ), recovery, repeatability (RSDr), reproducibility/intermediate precision (RSDwR), robustness, relative ion ratio and retention time. Acceptance criteria applied were: no interference exceeding 30% of the response limit (RL) at the analyte retention time for specificity; correlation coefficient (R) ≥ 0.99 with back-calculated concentrations within $\pm 20\%$ of the true value for linearity; a signal-to-noise ratio > 10 at the LOQ; mean recovery of 70–120% with $\% \text{RSD} \leq 20\%$ for

recovery, repeatability, reproducibility and robustness; relative ion ratio within $\pm 30\%$ of the calibration standard average; and retention time reproducibility within ± 0.1 min.

Recovery, repeatability and robustness experiments were performed by spiking blank matrix at three levels—LOQ, 2 $\times$ LOQ and 10 $\times$ LOQ (nominally 5, 10 and 50 ng mL⁻¹)—with six replicates per level. Reproducibility was assessed by repeating the recovery experiment on a different day. Robustness was evaluated by two analysts across a change in sample matrix, with recovery and %RSD calculated at each level.

3. Results and Discussion

3.1 Specificity

No response was observed for any of the ten target analytes in six independent blank matrix samples, while spiked samples at the LOQ level produced clear, well-resolved peaks at the expected retention times for all compounds. No interference from co-eluting matrix components or diluents was observed at the analyte retention times (NMT 30% RL), confirming that the method is specific for the target pesticides in the nutraceutical matrix studied.

3.2 Matrix Effect

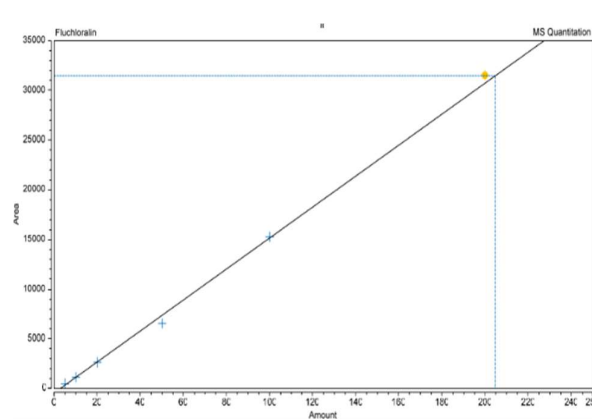
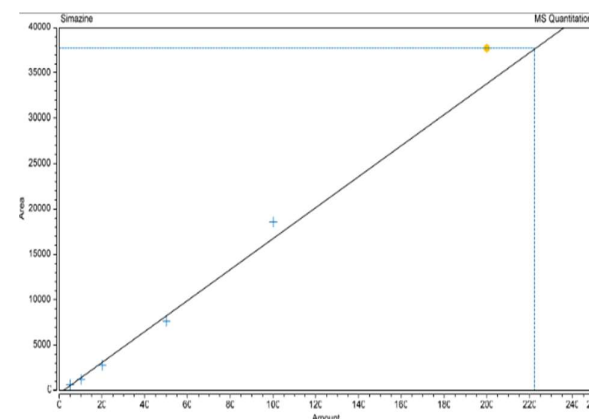
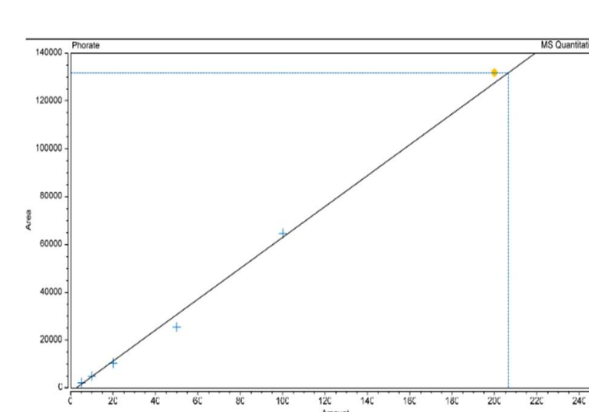
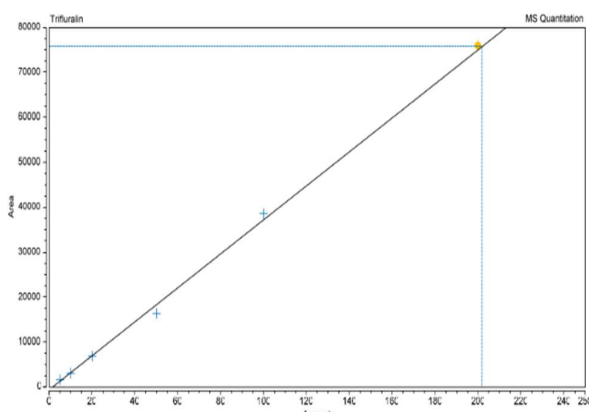
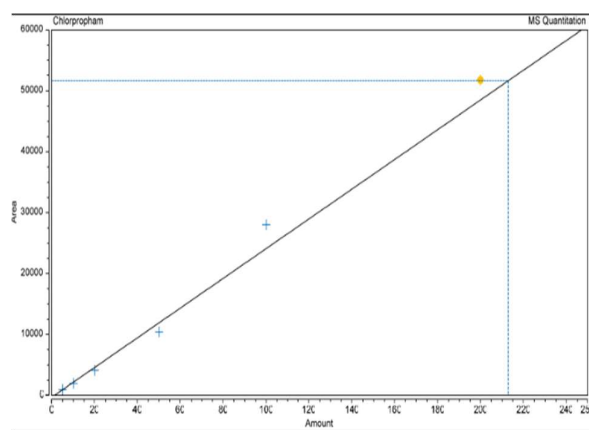
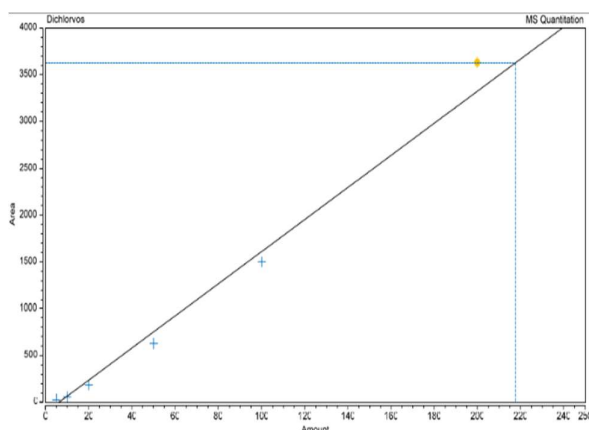
Comparison of analyte response in neat solvent standards versus matrix-matched standards revealed substantial signal suppression for most analytes, ranging from -11.2% (trifluralin) to -98.7% (parathion-methyl) (Table 2). Nine of the ten compounds exceeded the $\pm 20\%$ threshold defined in the SANTE guideline, indicating pronounced matrix-induced ion suppression consistent with the complex, co-extractive-rich composition of nutraceutical matrices (proteins, lipids, phytochemicals). In line with SANTE recommendations, matrix-matched calibration was therefore adopted for quantification throughout the study to compensate for this effect. The application of matrix-matched calibration effectively minimized the influence of matrix-induced ion suppression, thereby improving the accuracy and reliability of quantitative measurements. These findings emphasize the necessity of matrix effect evaluation during method validation and demonstrate the suitability of the proposed analytical method for reliable pesticide residue analysis in complex nutraceutical matrices.

Table 2. Matrix effect (%) for the ten target pesticides.

Compound	Matrix Effect (%)
Dichlorvos	-84.16
Chlorpropham	-68.45
Trifluralin	-11.22
Phorate	-12.24
Simazine	--87.90
Fluchloralin	-29.74
Tri-allate	-24.33
Chlorothalonil	-87.90
Parathion-methyl	-98.66
Ametryne	-51.44

3.3 Linearity and Range

Six-point matrix-matched calibration curves (5–100 ng mL⁻¹) were constructed for each pesticide. All compounds showed a coefficient of determination (R^2) ≥ 0.99 , and the deviation of back-calculated concentrations from the true concentration remained within the $\pm 20\%$ acceptance limit at every calibration level (Table 3), confirming acceptable linearity across the validated range. The excellent linear correlation demonstrates that the analytical method provides a proportional response over the studied concentration range. These results confirm the suitability of the calibration model for accurate and reliable quantitative determination of the target pesticides in nutraceutical matrices.



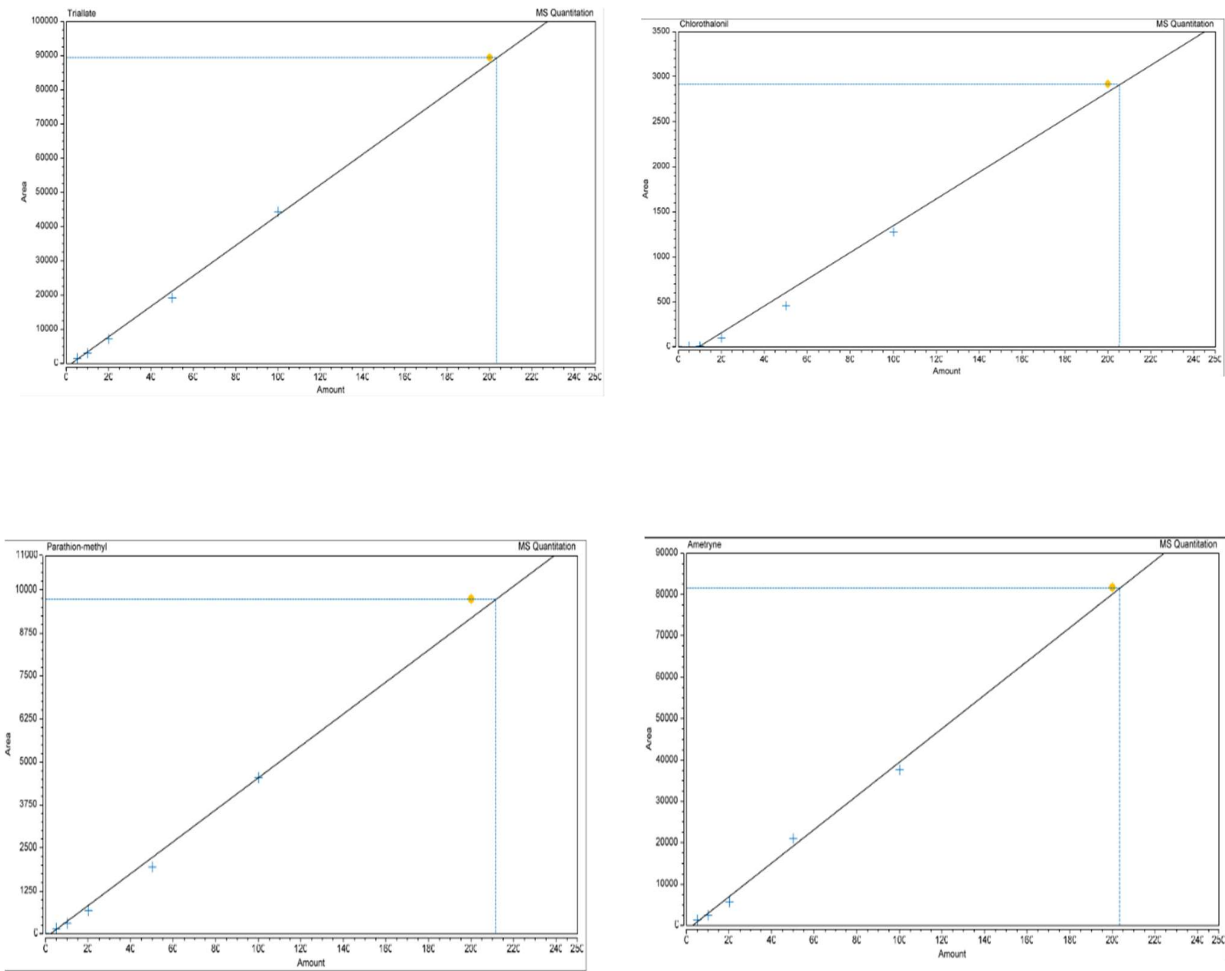


Table 3. Linearity summary: coefficient of determination and range of back-calculated deviation.

Compound	R ²	Deviation range (%)
Dichlorvos	0.9911	-11.46 to +11.57
Trifluralin	0.9937	-14.18 to +15.55
Chlorpropham	0.9949	-9.37 to +14.58
Phorate	0.9937	-14.28 to +15.37
Simazine	0.9927	-11.51 to +14.42
Fluchloralin	0.9968	-14.14 to +16.81
Tri-allate	0.9914	-13.96 to +12.80
Chlorothalonil	0.9960	-7.20 to +13.69
Parathion-methyl	0.9926	-13.11 to +8.40
Ametryne	0.9902	-14.10 to +8.91

3.4 Limit of Quantification (LOQ)

The LOQ, defined as the lowest fortification level giving a signal-to-noise ratio greater than 10, was established at 5 ng mL⁻¹ for all ten analytes, with %RSD of replicate LOQ-level responses ranging from 3.5% (trifluralin) to 20.1% (chlorothalonil). The established LOQ was below the relevant regulatory maximum residue limit for each pesticide, satisfying the acceptance criterion (LOQ < MRL).

3.5 Recovery

Recovery was assessed at LOQ, 2×LOQ and 10×LOQ fortification levels (six replicates each). Mean recoveries ranged from 89.9% to 119.0% across the three levels for all analytes (Table 4), within the 70–120% acceptance range specified by SANTE 11312/2023 v2, with associated %RSD values generally below 20%. Recovery was

closer to 100% at the higher fortification levels for most compounds, consistent with proportionally greater relative uncertainty near the LOQ.

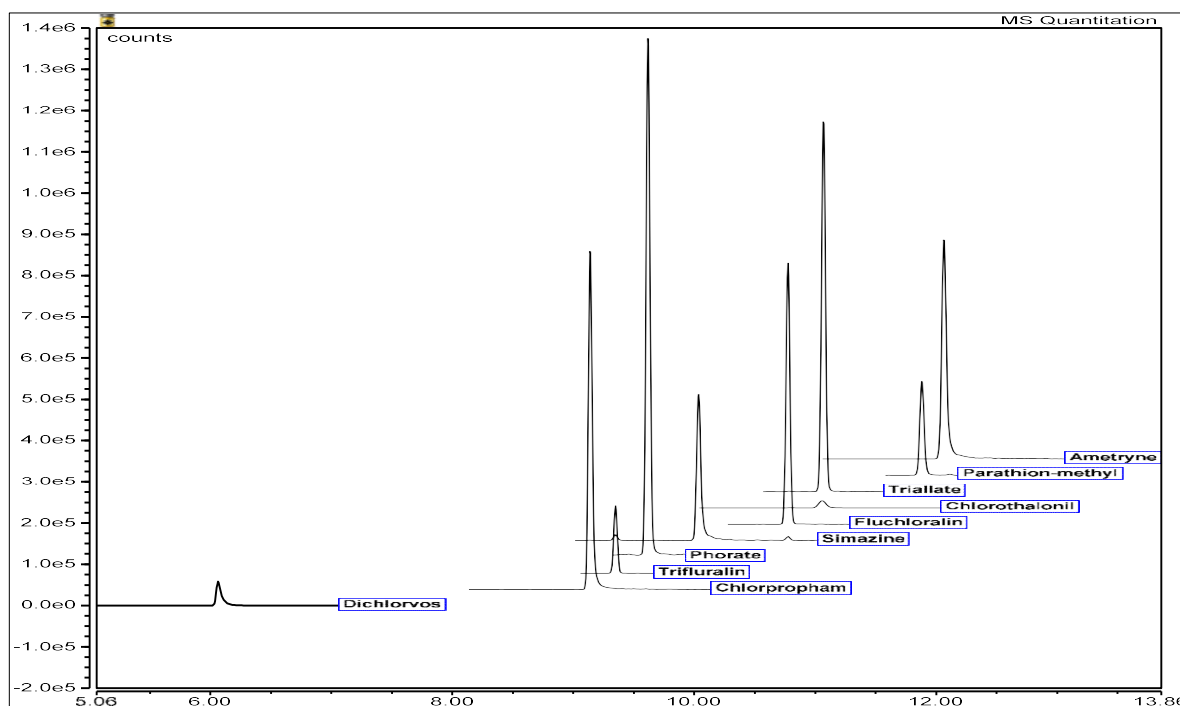


Table 4. Mean % recovery at LOQ, 2×LOQ and 10×LOQ.

Compound	LOQ (%)	2×LOQ (%)	10×LOQ (%)
Dichlorvos	116.53	103.61	100.69
Trifluralin	118.27	114.69	99.51
Chlorpropham	116.88	101.83	94.07
Phorate	97.35	89.93	108.41
Simazine	118.21	104.82	105.75
Fluchloralin	108.54	109.33	91.31
Tri-allate	113.17	108.94	109.04
Parathion-methyl	113.04	114.90	103.13
Chlorothalonil	119.04	98.82	93.33
Ametryne	114.50	103.10	107.87

3.6 Precision: Repeatability (RSDr) and Reproducibility (RSDwR)

Repeatability, evaluated as intra-day %RSD of recovery at the three fortification levels, ranged from 3.1% to 20.6% (Table 5); only fluchloralin at the 10×LOQ level marginally exceeded the 20% acceptance limit. Reproducibility (inter-day precision), obtained by repeating the recovery study on a separate day, ranged from 3.0% to 15.9% across all analytes and levels (Table 6), meeting the ≤20% acceptance criterion throughout and confirming that the method delivers consistent results across different analytical occasions.

Table 5. Repeatability (RSD_r, %) at LOQ, 2×LOQ and 10×LOQ.

Compound	LOQ	2×LOQ	10×LOQ
Dichlorvos	3.35	7.02	7.92
Trifluralin	7.32	5.37	6.90
Chlorpropham	4.65	6.21	4.32
Phorate	5.15	8.40	5.93
Simazine	3.75	7.00	11.73
Fluchloralin	19.90	4.83	12.59
Tri-allate	4.25	4.98	5.89
Parathion-methyl	6.56	11.84	7.28
Chlorothalonil	7.83	5.65	9.80
Ametryne	3.53	5.71	3.05

Table 6. Reproducibility (RSD_{wR}, %) at LOQ, 2×LOQ and 10×LOQ.

Compound	LOQ	2×LOQ	10×LOQ
Dichlorvos	9.66	13.56	15.87
Chlorpropham	5.57	8.40	11.80
Trifluralin	3.03	15.92	15.90
Phorate	14.75	13.60	12.70
Simazine	9.98	11.90	5.90
Fluchloralin	8.54	7.29	9.56
Tri-allate	4.42	3.97	9.01
Parathion-methyl	6.29	10.17	14.60
Chlorothalonil	5.80	12.30	10.39
Ametryne	5.66	11.24	7.79

3.7 Robustness

Robustness was verified by two analysts across a change in sample matrix, with mean recovery pooled across LOQ, 2×LOQ and 10×LOQ levels ranging from 94.4% to 107.2% (Table 7), and %RSD not exceeding 17.4%. These results indicate that minor, deliberate variation in analyst and matrix source did not materially affect method performance, confirming adequate robustness. The recovery values remained within the predefined acceptance criteria across all concentration levels, demonstrating the consistency and reproducibility of the analytical procedure under varied experimental conditions. The observed precision further confirms that the method is resistant to small, intentional changes introduced during routine analysis. Overall, these findings establish that the validated method is reliable, stable, and suitable for its intended application in the quantitative determination of the analyte in complex sample matrices. Furthermore, the consistent recovery and precision values obtained under the tested conditions demonstrate the reliability of the method during routine laboratory analysis. These findings confirm that the developed method is sufficiently robust for its intended analytical application.

Table 7. Robustness – pooled mean % recovery by analyst.

Compound	Analyst 1 (%)	Analyst 2 (%)
Dichlorvos	107.20	99.75
Chlorpropham	96.23	100.74
Trifluralin	105.94	98.80
Phorate	102.20	97.83
Simazine	98.51	105.41
Fluchloralin	100.46	105.99
Tri-allate	94.54	95.85
Parathion-methyl	100.56	98.54
Chlorothalonil	94.41	98.32
Ametryne	98.40	94.54

3.8 Relative Ion Ratio and Retention Time

The relative ion ratio of spiked LOQ-level samples, compared with the average ion ratio of calibration standards from the same sequence, remained within the $\pm 30\%$ acceptance window for all ten compounds (range: -12.9% to $+4.6\%$). Retention times were highly reproducible across five injection days, with mean deviations between standard and spiked-sample retention times not exceeding 0.04 min for any analyte—well within the ± 0.1 min acceptance criterion (Table 8).

Table 8. Mean retention time (standard vs. spiked sample) and relative ion ratio.

Compound	RT – Standard (min)	RT – Spiked (min)	Relative Ion Ratio (%)
Dichlorvos	4.62	4.62	-5.12
Trifluralin	6.10	6.09	0.24
Chlorpropham	6.09	6.09	-7.57
Phorate	6.29	6.28	-6.55
Simazine	6.40	6.39	-8.54
Fluchloralin	6.84	6.84	-12.90
Tri-allate	7.00	6.98	-1.44
Parathion-methyl	7.50	7.49	-1.29
Chlorothalonil	7.56	7.55	4.63
Ametryne	8.12	8.11	3.14

3.9 Overall Assessment

Across all nine SANTE 11312/2023 v2 validation parameters investigated, the GC-MS/MS method met the specified acceptance criteria for all ten target pesticides, with the exception of an isolated marginal exceedance for fluchloralin repeatability at the highest fortification level. The pronounced matrix effects observed underscore the necessity of matrix-matched calibration for accurate quantification in nutraceutical matrices, a finding consistent with prior reports on QuEChERS-GC-MS/MS multi-residue methods applied to complex plant-derived and herbal matrices.

4. Conclusion

A QuEChERS-based GC-MS/MS method was successfully developed and validated for the simultaneous determination of ten multi-class pesticide residues (dichlorvos, chlorpropham, trifluralin, phorate, simazine, fluchloralin, chlorothalonil, tri-allate, parathion-methyl and ametryne) in nutraceutical products, in accordance with SANTE 11312/2023 v2 guidelines. The method demonstrated adequate specificity, linearity ($R^2 \geq 0.99$), sensitivity (LOQ below regulatory MRLs), recovery (70–120%), precision (%RSD generally $\leq 20\%$), robustness, and acceptable relative ion ratio and retention time reproducibility, while matrix-matched calibration was essential to offset significant matrix-induced signal suppression. The validated method is fit for purpose for routine multi-residue pesticide monitoring of nutraceutical raw materials and finished products, supporting compliance with FSSAI, Codex Alimentarius and pharmacopoeial quality standards and contributing to consumer safety assurance in the nutraceutical industry.

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