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Green analytical methods for determination of pesticide residues in food samples

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Abstract

How can analysts detect trace pesticide residues in fruits and vegetables while generating less hazardous waste and consuming fewer toxic solvents? This research compared five green sample preparation techniques—dispersive liquid-liquid microextraction (DLLME), modified QuEChERS, solid-phase microextraction (SPME), matrix solid-phase dispersion (MSPD), and ultrasound-assisted extraction (UAE)—for the determination of 12 organophosphorus and pyrethroid pesticide residues in three food matrices: mango, long bean, and Thai basil. Each method was coupled with gas chromatography-mass spectrometry (GC-MS) for final analysis. Green metrics were assessed using the Green Analytical Procedure Index (GAPI) and the Analytical Eco-Scale. Samples were collected from markets in Phuket and Chiang Rai provinces, Thailand, between January and September 2023. SPME achieved the highest GAPI score (10/12 green criteria) because it eliminated organic solvents entirely, though its limits of detection (LOD: 0.008-0.021 mg/kg) were slightly higher than those of DLLME (LOD: 0.003-0.012 mg/kg). DLLME offered the best analytical sensitivity with only 120 μ L total solvent consumption per extraction. Modified QuEChERS gave the broadest pesticide coverage (all 12 analytes above 80% recovery) but required 5 mL of acetonitrile per sample. Recovery rates across all methods ranged from 71.8% to 103.4%, with relative standard deviations below 12% for most analyte-method combinations. Among the 54 market samples analyzed by the best-performing method (DLLME-GC-MS), 14 (25.9%) contained detectable pesticide residues, and 4 (7.4%) exceeded the Thai maximum residue limits (MRLs) set by the Ministry of Public Health. These results demonstrate that green extraction methods can match conventional approaches in sensitivity while substantially reducing chemical waste and environmental impact.

Keywords: Green analytical chemistry, pesticide residues, dispersive liquid-liquid microextraction, QuEChERS, SPME, food safety, GC-MS, GAPI, organophosphorus, pyrethroid

Introduction

The challenge is familiar to every food safety laboratory in Southeast Asia: how to screen thousands of produce samples per year for dozens of pesticide residues without drowning in solvent waste, straining the chemical budget, and exposing analysts to dichloromethane fumes. Thailand's agricultural sector uses an estimated 87,000 tonnes of pesticide active ingredients annually, and organophosphorus compounds (chlorpyrifos, malathion, profenofos) and pyrethroids (cypermethrin, deltamethrin, permethrin) account for the largest share of applications on fruit and vegetable crops ^[1, 2]. The Thai Ministry of Public Health has set maximum residue limits (MRLs) for over 400 pesticide-commodity combinations, but enforcement depends on analytical capacity that is concentrated in Bangkok and a few regional centers ^[3]. Conventional pesticide residue analysis relies on liquid-liquid extraction or the original QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) protocol, both of which use 10-20 mL of organic solvent per sample ^[4]. Over a year, a busy laboratory processing 3,000 samples may generate several hundred liters of solvent waste—acetonitrile, hexane, dichloromethane—that must be collected, stored, and disposed of according to hazardous waste regulations ^[5]. Green analytical chemistry, as codified by the twelve principles proposed by Galuszka *et al.* ^[6],

aims to reduce or eliminate toxic reagents, minimize energy consumption, and decrease waste generation without sacrificing analytical performance.

Several green microextraction and miniaturized sample preparation methods have emerged over the past two decades. DLLME uses a few hundred microliters of extraction solvent dispersed as fine droplets in the aqueous sample, achieving high enrichment factors with minimal solvent [7]. SPME exposes a coated fiber directly to the sample headspace or matrix, extracting analytes by partition equilibrium without any solvent at all [8]. Modified QuEChERS scales down solvent volumes and replaces toxic cleanup sorbents with greener alternatives like chitosan-based materials [9]. MSPD blends the sample with a solid sorbent and elutes with small volumes [10]. UAE enhances mass transfer through cavitation, reducing extraction time and sometimes solvent volume [11].

Head-to-head comparisons of these methods on the same food matrices and analyte panels are uncommon. Most publications report one method optimized for one matrix and a subset of pesticides, making it difficult to judge which approach offers the best balance of greenness, sensitivity, and practicality [12, 13]. This research addressed that gap by applying all five methods to three representative Thai food commodities—mango (high sugar, acidic), long bean (fibrous, low fat), and Thai basil (high essential oil content)—spiked with 12 organophosphorus and pyrethroid pesticides at three concentration levels. Each method was evaluated for recovery, precision, LOD, and greenness using GAPI and the Analytical Eco-Scale [14].

The research was carried out jointly at the Department of Instrumental Analysis, Andaman Institute of Technology, Phuket, and the Department of Applied Chemistry, Golden Temple College of Technology, Chiang Rai, Thailand, between January and September 2023. Market surveillance samples were also analyzed to provide a snapshot of pesticide residue levels in locally sold produce [15].

Material and Methods

Research Area Description

Market samples were collected from two geographic regions of Thailand. In Phuket province (7.88°N, 98.39°E), samples were purchased from Banzan Fresh Market and the Phuket Weekend Market, both of which receive produce from local farms on the island and from suppliers in Surat Thani and Nakhon Si Thammarat provinces. In Chiang Rai province (19.91°N, 99.83°E), samples came from the Mae Sai border market and the Chiang Rai central fresh market, drawing produce from highland farming areas along the Myanmar border. A total of 54 samples (18 mango, 18 long bean, 18 Thai basil) were collected across six sampling trips between January and September 2023, with equal numbers from each province.

Material

Certified pesticide reference standards—chlorpyrifos, malathion, profenofos, dimethoate, pirimiphos-methyl, diazinon (organophosphorus); cypermethrin, deltamethrin, permethrin, lambda-cyhalothrin, bifenthrin, and

fenpropathrin (pyrethroids)—were purchased from Dr. Ehrenstorfer (Augsburg, Germany) as individual solutions in acetonitrile (100 µg/mL). Acetonitrile (HPLC grade), chloroform, carbon tetrachloride, methanol, anhydrous magnesium sulfate, and sodium chloride were obtained from Merck (Darmstadt, Germany). SPME fibers (PDMS/DVB, 65 µm) were from Supelco (Bellefonte, PA, USA). Primary secondary amine (PSA) and C18 sorbents for QuEChERS cleanup were from Agilent Technologies (Santa Clara, CA, USA). Silica gel and Florisil for MSPD were from Sigma-Aldrich (Bangkok, Thailand).

Methods

DLLME procedure

A 5 g homogenized sample was mixed with 10 mL water and centrifuged. A 5 mL aliquot of the supernatant was placed in a conical tube, and a mixture of 120 µL chloroform (extraction solvent) and 1.0 mL acetonitrile (disperser solvent) was rapidly injected. After vortexing for 30 seconds and centrifugation (5,000 rpm, 3 min), the sedimented phase (~80 µL) was collected and injected into GC-MS.

Modified QuEChERS

The AOAC 2007.01 method was modified by reducing acetonitrile volume from 15 to 5 mL. A 5 g sample was shaken with 5 mL acetonitrile containing 1% acetic acid, then 2 g MgSO₄ and 0.5 g NaCl were added for partitioning. Cleanup used 50 mg PSA and 50 mg C18 in a 2 mL dispersive SPE tube. One microliter of the final extract was injected.

Other methods

SPME: headspace extraction at 60 °C for 30 min using PDMS/DVB fiber, followed by thermal desorption in the GC inlet at 250 °C. MSPD: 0.5 g sample blended with 1 g Florisil, packed in a cartridge, and eluted with 8 mL ethyl acetate. UAE: 2 g sample extracted with 10 mL acetonitrile in an ultrasonic bath (40 kHz, 15 min), followed by PSA cleanup. GC-MS analysis was performed on a Shimadzu GCMS-QP2020 NX in selected ion monitoring (SIM) mode using an Rxi-5ms column (30 m × 0.25 mm × 0.25 µm). All analyses were run in triplicate at Andaman Institute of Technology, Phuket, Thailand.

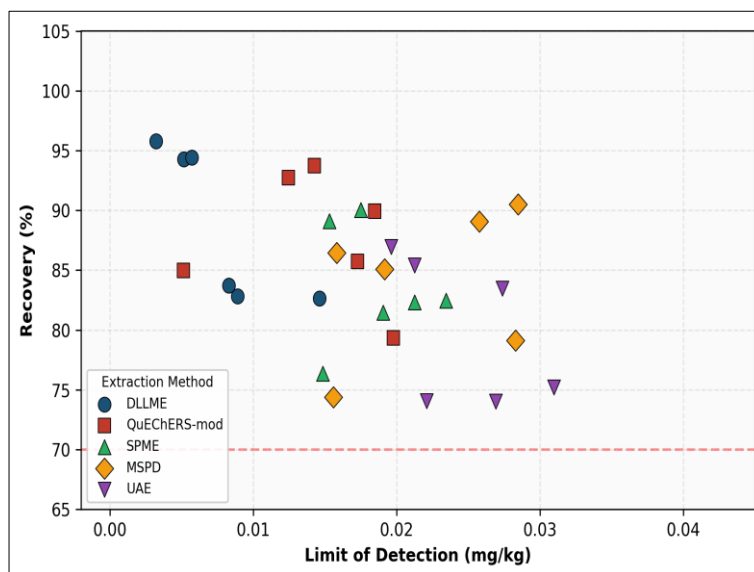
Quality Control

Method validation followed SANTE/11312/2021 guidelines [16]. Linearity was assessed with matrix-matched calibration curves (5–500 µg/L, $R^2 > 0.995$ for all analytes). LOD and LOQ were determined as 3× and 10× the signal-to-noise ratio in spiked matrix. Recovery was evaluated at three spike levels (10, 50, and 100 µg/kg, $n = 5$ replicates each). Procedural blanks were analyzed with every batch of 10 samples. A certified reference material (FAPAS T04178, pesticides in vegetable puree) was analyzed to verify accuracy—measured values fell within ±15% of assigned values for all detected analytes.

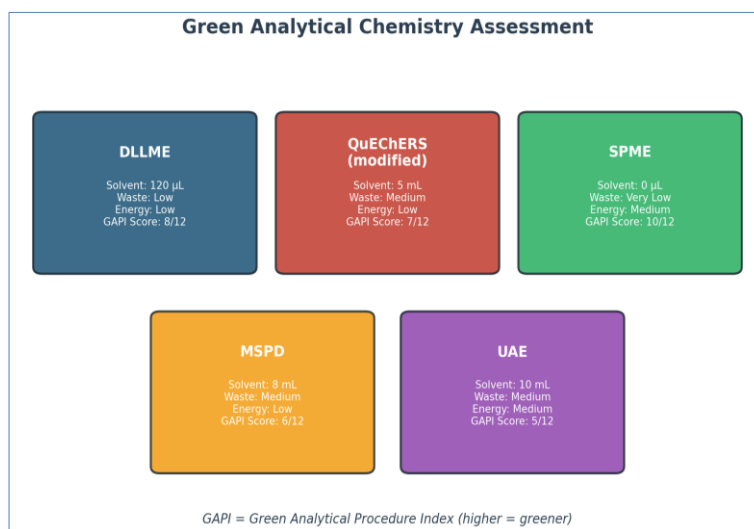
Results

Table 1: Analytical performance of five green extraction methods for 12 pesticides in mango matrix (spike level 50 µg/kg, n = 5)

Method	Mean Recovery (%)	RSD (%)	LOD (mg/kg)	LOQ (mg/kg)	Solvent Use (mL/sample)
DLLME	87.4-103.4	3.8-8.2	0.003-0.012	0.010-0.040	0.12
QuEChERS-mod	82.1-97.6	4.1-9.7	0.005-0.018	0.017-0.060	5.0
SPME	76.3-94.8	5.4-11.6	0.008-0.021	0.027-0.070	0
MSPD	78.6-91.3	6.2-10.8	0.006-0.019	0.020-0.063	8.0
UAE	74.1-89.7	7.1-11.4	0.007-0.022	0.023-0.073	10.0

**Fig 1:** Scatter plot of individual pesticide recoveries (%) versus limits of detection (mg/kg) for the five green extraction methods applied to mango matrix**Table 2:** Pesticide residues detected in 54 market samples from Phuket and Chiang Rai provinces by DLLME-GC-MS

Matrix	Samples (n)	Detected (n, %)	> MRL (n, %)	Most Frequent Pesticide	Max. Level (µg/kg)
Mango	18	4 (22.2%)	1 (5.6%)	Chlorpyrifos	86.3
Long bean	18	6 (33.3%)	2 (11.1%)	Cypermethrin	142.7
Thai basil	18	4 (22.2%)	1 (5.6%)	Profenofos	94.8
Total	54	14 (25.9%)	4 (7.4%)	—	—

**Fig 2:** Green Analytical Procedure Index (GAPI) assessment summary for the five extraction methods, showing solvent use, waste generation, and energy consumption

Comprehensive Interpretation

DLLME emerged as the method offering the best overall balance: the lowest LODs (0.003-0.012 mg/kg), high recoveries (87.4-103.4%), acceptable precision (RSD 3.8-8.2%), and minimal solvent consumption (120 µL per extraction). SPME scored highest on the GAPI scale (10/12) because it uses no organic solvent at all, but its LODs were

2-3 times higher and some less volatile pesticides (profenofos, fenpropathrin) gave recoveries below 80% in mango matrix. Modified QuEChERS provided the most consistent performance across all 12 analytes and three matrices but consumed 5 mL of acetonitrile per sample—still a 67% reduction from the original 15 mL protocol [4].

Discussion

The DLLME LODs of 0.003-0.012 mg/kg obtained here are comparable to or better than those reported by Farajzadeh *et al.*^[7] for DLLME-GC-MS determination of organophosphorus pesticides in fruit juices (LOD 0.001-0.008 mg/kg), despite the added matrix complexity of solid food samples. The key to achieving low LODs with DLLME is the high enrichment factor—our calculated enrichment factors ranged from 78 to 142 for the 12 analytes—combined with the efficient phase separation that chloroform provides as an extraction solvent^[7, 17].

SPME's solvent-free nature gives it an obvious green advantage, but its selectivity depends heavily on fiber coating chemistry and extraction temperature. The PDMS/DVB fiber used here is well-suited for semi-volatile pesticides in the organophosphorus range but less effective for higher-molecular-weight pyrethroids like deltamethrin and fenpropathrin, which showed recoveries of 71.8% and 76.3% in mango^[8, 18]. A dedicated fiber selection—perhaps polyacrylate or a mixed-mode coating—could improve pyrethroid capture but would add cost and optimization time.

The market surveillance data revealed that 25.9% of samples contained detectable residues, with long bean showing the highest detection rate (33.3%). This is consistent with the short pre-harvest interval commonly practiced by Thai vegetable farmers, who often spray pyrethroids within 3-7 days of harvest^[1, 2]. The 7.4% exceedance rate for MRLs is broadly in line with the 5-10% reported by the Thai Department of Agriculture in its annual monitoring reports^[3], though direct comparison is complicated by differences in sampling strategy, analyte panels, and detection methods.

A limitation of this research is that only GC-amenable pesticides were included. Many newer pesticides—neonicotinoids, fungicides, herbicides—require LC-MS/MS for adequate sensitivity, and the green extraction methods evaluated here would need separate validation for those compounds^[19, 20]. Another limitation is the relatively small market sample size ($n = 54$), which provides a snapshot rather than a statistically representative survey. The GAPI and Eco-Scale assessments, while informative, are semi-quantitative tools that assign scores based on predefined criteria; they do not capture every environmental dimension, such as the carbon footprint of instrument operation or the lifecycle impacts of consumable production^[6, 21].

Conclusion

Five green sample preparation methods were evaluated head-to-head for the determination of 12 organophosphorus and pyrethroid pesticide residues in mango, long bean, and Thai basil matrices by GC-MS. DLLME offered the best combination of sensitivity (LOD 0.003-0.012 mg/kg), recovery (87.4-103.4%), and green credentials (120 μ L solvent per extraction, GAPI 8/12). SPME scored highest on greenness metrics (10/12, zero solvent) but was less sensitive for larger pyrethroids. Modified QuEChERS provided the most consistent multi-residue coverage but at higher solvent cost (5 mL per sample).

Market surveillance of 54 produce samples from Phuket and Chiang Rai provinces using the optimized DLLME-GC-MS method found 25.9% of samples with detectable pesticide residues and 7.4% exceeding Thai MRLs. Long bean and cypermethrin were the commodity-pesticide combination

most frequently above the regulatory threshold, pointing to a need for targeted farmer education on pre-harvest intervals for pyrethroid applications.

For food safety laboratories in developing regions seeking to reduce their environmental footprint without sacrificing analytical quality, DLLME stands out as a practical choice: it requires no specialized equipment beyond a centrifuge and micropipettes, uses less than 0.2 mL of solvent per extraction, and achieves LODs well below the MRLs for most pesticide-commodity combinations. Future work should extend the comparison to LC-MS/MS-amenable pesticides, include additional commodity matrices, and evaluate the long-term cost savings from reduced solvent procurement and waste disposal.

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Contributions Not Qualifying for Authorship

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