Application Note

Food Testing and Agriculture

Agilent

Trusted Answers

Analysis of Multiple Pesticide Residues in Complex Food Matrices Using High-Throughput Online Mini-SPE and GC/MS/MS

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Abstract

In this Application Note, we describe the analysis of multiple pesticides residues in complex food matrices using online sample preparation with an Agilent PAL RTC system followed by separation and detection using an Agilent 7890B GC and Agilent 7000D triple quadrupole GC/MS system. The online sample preparation method is based on mini-SPE technology and is combined with an automated workflow on the Agilent PAL RTC system.

The objective of this application is the cleanup of the typically dirty extracts from the well-known QuEChERS sample extraction process to achieve ease-of-use and extended sample throughput with less maintenance. Only one type of QuEChERS mini-SPE cartridge is necessary for the cleanup of different food sample extracts and analysis by GC/MS. It is shown that no food-specific optimization of the cleanup process is necessary, even for different kinds of food commodities. The presented online sample preparation and injection workflow executed by the Agilent PAL RTC and GC/MS system is well suited for the large-scale screening of any kind of food samples for pesticides residues. The addition of internal standards and analyte protectants is integrated into this cleanup workflow. No manual extract cleanup steps are needed. The raw extract in acetonitrile is taken directly from the centrifuged extraction tube.

It is shown that the PAL RTC mini-SPE cleanup is robust for different kind of food matrices. In quantitation, the achieved precision with the linear correlation coefficient was always greater than 0.995 for five concentration data points. The repeatability of most of the analytes was excellent at less than 10 %. The good cleanup performance is demonstrated by the comparison with the extract after cleanup in a full scan chromatogram. A high recovery could be achieved for almost all the analytes in the range of 70 to 130 % with the mini-SPE cleanup, which meets the requirements for pesticide residue analysis. The Agilent MassHunter software seamlessly controls both the Agilent PAL RTC and Agilent GC/MS systems for high sample throughput. With this data, it is evident that the cleanup performance of the mini-SPE technology is much better than the traditional manual QuEChERS dispersive SPE method.

Introduction

With the improvement of agricultural production technology, the types of pesticides and frequency of application for vegetable and fruit production is increasing. At the moment, the scope of monitoring pesticide contaminations in food according to the regulations is still not comprehensive. Rational comprehensive monitoring for food safety needs a more extensive monitoring tool. For example, in the last year, Agilent cooperation with end users advocated and developed method screening, which can monitor thousands of target analytes and basically covers all the pesticides currently used in China. After this solution was released to the public, it found immediate interest by analysts for local food control.

Nowadays, the sample preparation method of QuEChERS (Quick, Easy, Cheap, Efficient, Rugged, and Safe) for multipesticide analysis is popular worldwide [1]. With its simple sample extraction process, QuEChERS is becoming the preferred method in heavy workload laboratories. Therefore, after QuEChERS was introduced by Anastassiades et al. in 2003 [2], it has been widely used in food analysis for pesticide residues. But there is no denying that the proposed QuEChERS dispersive SPE (dSPE) step cannot deliver good cleanup performance of the sample extract for many complex food matrices, and is limited to low-fat foods. Users have to adjust the QuEChERS dSPE sorbent material composition according to the sample characteristics to achieve better chromatography and less injector maintenance in practice.

Is there a sample preparation cleanup technology that is easy, effective, and widely used? The answer is yes. In recent years, the technology using mini-SPE cartridges, which combines the traditional features of column-SPE (c-SPE), has become increasingly popular[3, 4]. The particle size in the columns is much smaller than the materials used in the original QuEChERS dSPE. The cleanup performance is much better as well since its working principle is similar to the separation of an LC column. At a low flow of only 2 µL/s delivered by the load syringe, the matrix components are retarded while the small molecule pesticide fraction is eluted. As the extract load and elution volumes are only a few hundred microliters, this method can be recognized as a green sample preparation technology. The small volumes applied in the mini-SPE technology enable the automated extract preparation with online injection on a GC/MS system.

This application used microcolumn SPE for extract cleanup with a mini-SPE cartridge from ITSP Solutions Inc. on the Agilent PAL RTC as the online sample preparation platform. Analyte protectants (AP) can be applied optionally as of user's choice [5]. Apple, orange, and lettuce were used as the food test matrices. The sample extract after cleanup was directly injected into the Agilent 7000D triple quadrupole GC/MS system. The pesticide analytes screening and quantification were performed in multiple reaction monitoring mode (MRM). The described configuration truly realized automated online sample preparation and pesticides analysis by a GC/MS system.

Experimental

Reagents and samples

- Acetonitrile, analytical grade, from Bailing Granville
- Pesticide mixed standard from AccuStandard, Inc.
- Internal standard (ISTD), triphenyl phosphate (TPP) from AccuStandard Inc.
- Analyte protectants (AP), ethylglycerol, gulonolactone, and D-sorbitol from Sigma-Aldrich

The ISTD solution was prepared by diluting TPP with ACN to 1 µg/mL and filling into a 2 mL vial.

The AP mixture standard solution was prepared by making final concentrations of 25 mg/mL ethylglycerol, 2.5 mg/mL gulonolactone, and 2.5 mg/mL D-sorbitol, containing 1.1 % formic acid, in a 3:2 (v:v) ACN:water solution, and filling into a 2 mL vial.

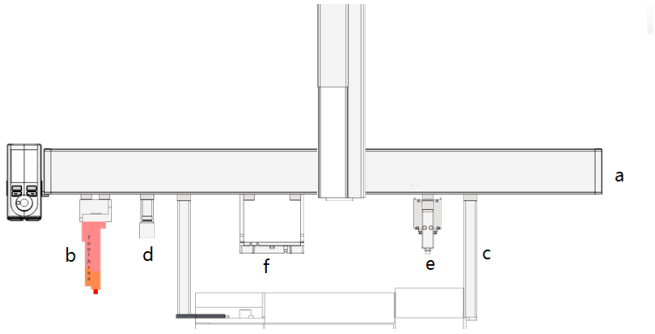
The Agilent QuEChERS extraction kit comprised 4 g magnesium sulfate, 1 g sodium chloride, 1 g sodium citrate, and 0.5 g disodium monohydrogen citrate (p/n EN 5982-5650CH).

The mini-SPE cartridge for GC/MS analysis was a green cartridge, comprising 45 mg MgSO4/primary secondary amine (PSA)/C18/CarbonX (20:12:12:1, w:w:w:w), obtained from ITSP Solutions Inc., Hartwell, GA, USA.

Instruments

The following instrumentation was used to perform the experiments.

Sample preparation platform	Agilent PAL RTC sample handing system
GC/MS platform	Agilent 7890B GC and Agilent 7000D GC/MS system
Centrifuge	TDL-5C, Shanghai Anting Scientific Instruments
Balance	AL104, Mettler Toledo
Pipette	Research plus, 2 – 20 µL, 10 – 100 µL, 100 – 1000 µL, Eppendorf



a: Agilent PAL RTC; b: Park station; c: 7890B GC mounting kit; d: Standard wash module; e: Fast wash module; f: Tray holder with mini-SPE configuration kits

Figure 1. Configuration of the Agilent PAL RTC sample handling system for mini-SPE cleanup

Sample preparation

Apple, orange, and lettuce leaves were used as test samples to cover simple, complex, and high-chlorophyll food matrices. Food and spiked quality control samples were extracted according to the standardized QuEChERS method (EN 15662).

The food sample was fully mixed after cutting, put into a tissue crusher, and mashed to a homogenate. 10 g of the test sample (accurate to 0.01 g) were put into a 50 mL plastic centrifuge tube, 10 mL frozen acetonitrile were added followed by adding the QuEChERS extraction kit and one ceramic homogenizer. The capped centrifuge tubes were shaken vigorously for 1 min and then centrifuged at 4200 rpm for 5 min. 1 mL of every matrix extract was transferred six times into regular 2 mL autosampler vials. Five sample vials were used for the preparation of the calibration curve, which was measured automatically by the PAL RTC system. The remaining sixth one was used for actual sample testing.

Matrix standard preparation

The food sample was fully mixed after cutting, put into a tissue crusher and mashed to a homogenate. 10 g of the test sample (accurate to 0.01 g) were put into a 50 mL plastic centrifuge tube and the target standard solution was added. The final concentrations of 5, 10, and 50 ng/mL were prepared. Six parallel samples for each concentration level were prepared. 10 mL frozen acetonitrile and the QuEChERS extraction kit and 1 ceramic proton were added. The capped centrifuge tubes were shaken vigorously for 1 min and then centrifuged at 4200 rpm for 5 min. The extract was transferred into 2 mL autosampler vials and put into the sample in the rack of PAL RTC system for the automated cleanup procedure.

Automated sample preparation cleanup workflow

In these experiments, the PAL RTC system and mini-SPE cleanup cartridges were used, see Figures 2 and 3. QuEChERS extracts were added to the 2 mL injection bottle and then placed in the PAL RTC system. By starting the sequence, fully automatic sample purification and analysis can be achieved.

As shown in Figure 4, compared with the traditional QuEChERS purification method, mini-SPE can save much time in both operation procedure and processing. Further, the PAL RTC system can automatically realize sample overlap. As shown in Figure 5, no matter how many samples there are in this test, the entire pretreatment time is only the sample pretreatment time of the first sample. Starting from the second sample, during the previous sample analysis period, the instrument can automatically calculate the start-up time of the next sample pretreatment, which can save time and improve efficiency.

Figure 2. Agilent PAL RTC sample handling system

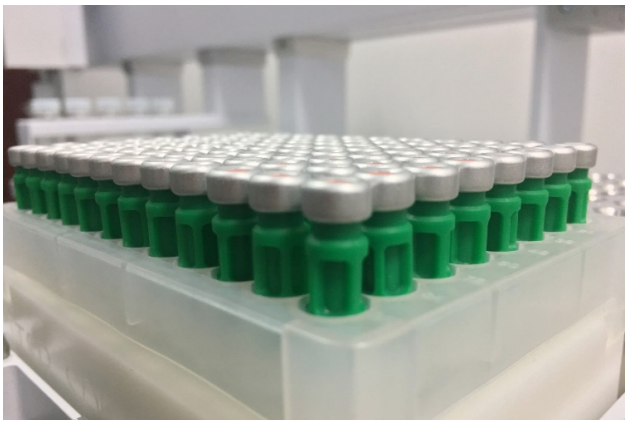


Figure 3. Mini-SPE cleanup cartridges

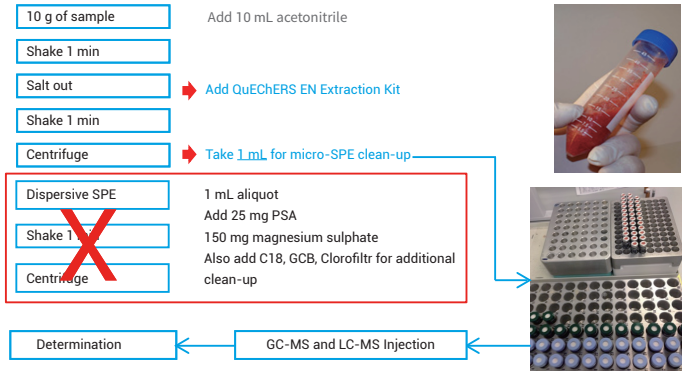


Figure 4. Workflow of mini-SPE cleanup

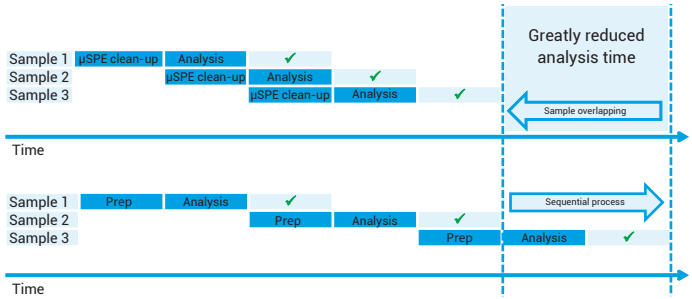


Figure 5. Sample overlap can save time and improve efficiency

Due to actual experimental demands and characteristics of pesticide analysis in food matrices, Agilent developed an automated sample preparation program for the analysis workflow, including addition of analytical protectant (to eliminate the adsorption of active substances), internal standard (to correct the fluctuation of mass spectrometry system), and preparation of a working curve (to eliminate matrix effect). The detailed work procedure is shown step-by-step in Table 1.

Table 1. Mini-SPE cleanup workflow for GC/MS

Step	Description	Time
1	Clean the 1 mL liquid syringe with acetonitrile (2 times, 1 mL each).	60 s
2	Aspirate 150 µL raw sample form rack 1 with the 1 mL liquid syringe.	60 s
3	Transfer the mini-SPE cartridge from rack 4 to the top of rack 2 with the 1 mL liquid syringe (needle transport).	10 s
4	Load the sample into the mini-SPE cartridge with a flow of 2 µL/s (cleanup procedure).	80 s
5	Transfer the used cartridge back to the original position.	10 s
6	Clean the 1 mL liquid syringe with ACN (2 times, 0.2 mL each).	25 s
7	Aspirate 100 µL ACN with formic acid from the standard wash 3 position with the 1 mL liquid syringe.	45 s
8	Transfer the used mini-SPE cartridge from rack 4.	10 s
9	Load 100 µL ACN with formic acid into the vial in rack 2 with flow 2 µL/s (elution step).	85 s
10	Change to the 25 µL liquid syringe, clean the syringe with ACN (2 times, 25 µL each).	75 s
11	Add 20 µL AP solution into the collection vial with insert in rack 2.	30 s

Step	Description	Time
12	Clean the 25 µL liquid syringe with ACN/MeOH/water 1:1:1 (2 times, 25 µL each).	25 s
13	Clean the 25 µL liquid syringe with ACN (2 times, 25 µL each).	25 s
14	Add 5 µL ISTD solution into the collection vial and insert in rack 2.	65 s
15	Clean the 25 µL liquid syringe with ACN (2 times, 25 µL each).	20 s
16	Add 20 µL ACN into the collection vial and insert in rack 2.	30 s
17	Add 0 µL target standard intermediate solution to the collection vial and insert in rack 2 (for samples this step is skipped).	35 s
18	Clean the 25 µL liquid syringe with ACN (2 times, 25 µL each).	25 s
19	Change the 25 µL syringe to a 1 mL syringe.	50 s
20	Mix the solvent in the collection vial using the 1 mL liquid syringe and insert in rack 2.	100 s
21	Clean the 1 mL liquid syringe with ACN (2 times, 0.3 mL each).	30 s
22	Change the 1 mL liquid syringe to a 10 µL liquid syringe.	55 s
23	Aspirate 1 µL collected cleaned sample extract from rack 2 and inject into GC with MMI inlet.	35 s
24	Clean the 10 µL liquid syringe with ACN (3 times, 10 µL each).	25 s
Total time		16.83 min

It is general analytical practice to avoid matrix effects for quantitation by using a matrix-added standard calibration. The PAL RTC system also supports this function. In the workflow outlined in Table 1, it is performed in step 17. This step could be executed automatically or manually. For the target standard, acetonitrile volume, and addition concentration, refer to Table 2.

Table 2. Target standard, acetonitrile volume, and addition concentration

Target concentration (ng/mL)	ACN volume (µL)	Target standard intermediate solution volume (µL)	Target standard intermediate solution concentration (ng/mL)
0	20	0	0
5	14.5	5.5	200
10	9	11	200
20	15.6	4.4	1000
50	9	11	1000
100	9	11	2000

GC parameters

Instrument	Agilent 7890B GC
GC column	HP-5MS UI capillary column, 30 m × 0.25 mm, 0.25 µm, p/n 19091S-433UI
Programmed temperature	Initial temp 60 °C, hold 1 min 40 °C/min to 120 °C 5 °C/min to 310 °C
Carrier gas	Helium, constant flow, 1.0 mL/min
Inlet	MMI inlet, inert liner with glass wool, p/n 5190-2293
Inlet temperature	280 °C
Injection mode	Splitless injection
Injection volume	1.0 µL
Transfer line temperature	280 °C

MS parameters

MS detector	Agilent 7000D triple quadrupole GC/MS system
Ion source	Electrospray ionization (EI), 70 eV
Ion source temperature	280 °C
Quadrupole temperature	150 °C
Solvent delay	4.5 min
EM voltage	Gain 10
Detection mode	MRM, creating the 667 pesticides MRM screening method based on Agilent G9250 pesticides and contaminants database
Collision gas	Nitrogen, 1.5 mL/min
Quenching gas	Helium, 2.25 mL/min

Results and Discussion

Comparison of the cleanup performance between mini-SPE and QuEChERS dSPE

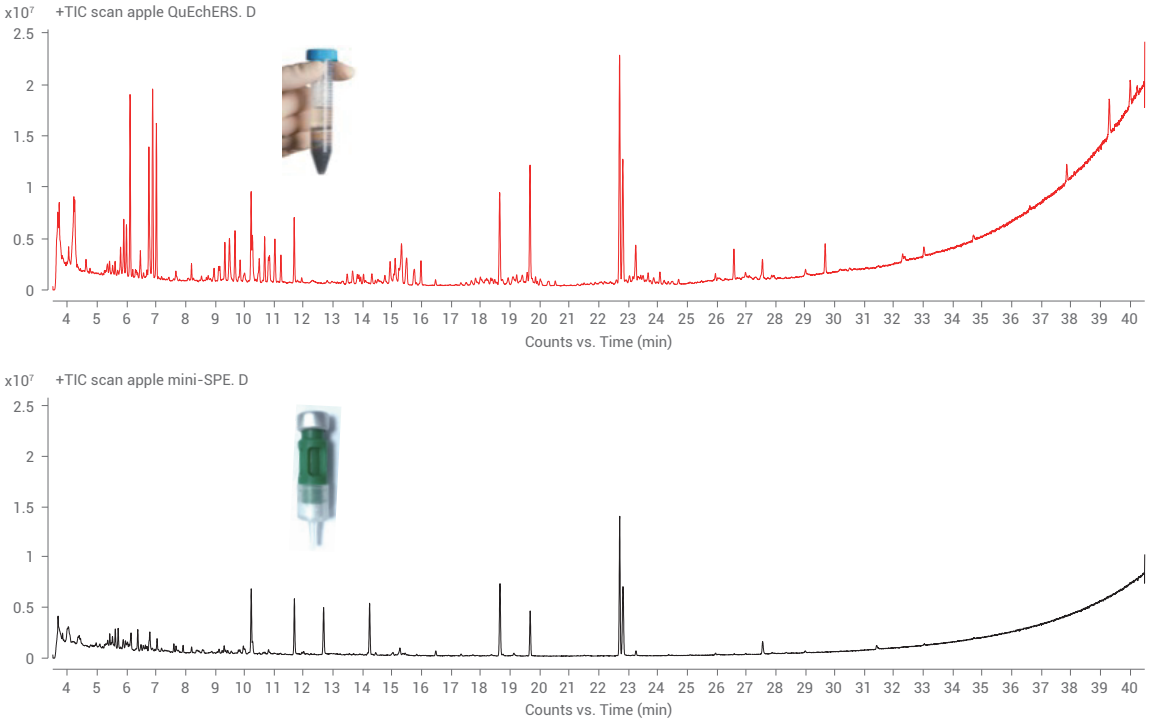


Fig 6. Full-scan chromatogram (TIC) of apple QuEChERS extract (red) and mini-SPE cleaned extract (black)

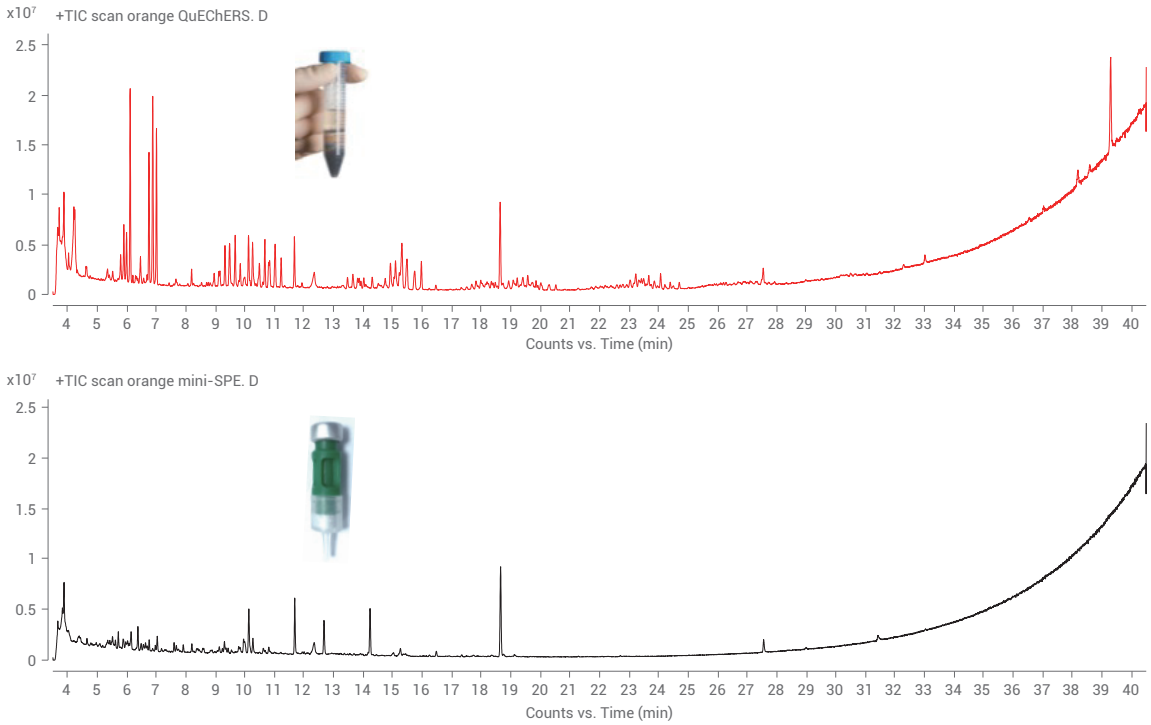


Fig 7. Full-scan chromatogram (TIC) of orange QuEChERS extract (red) and mini-SPE cleaned extract (black)

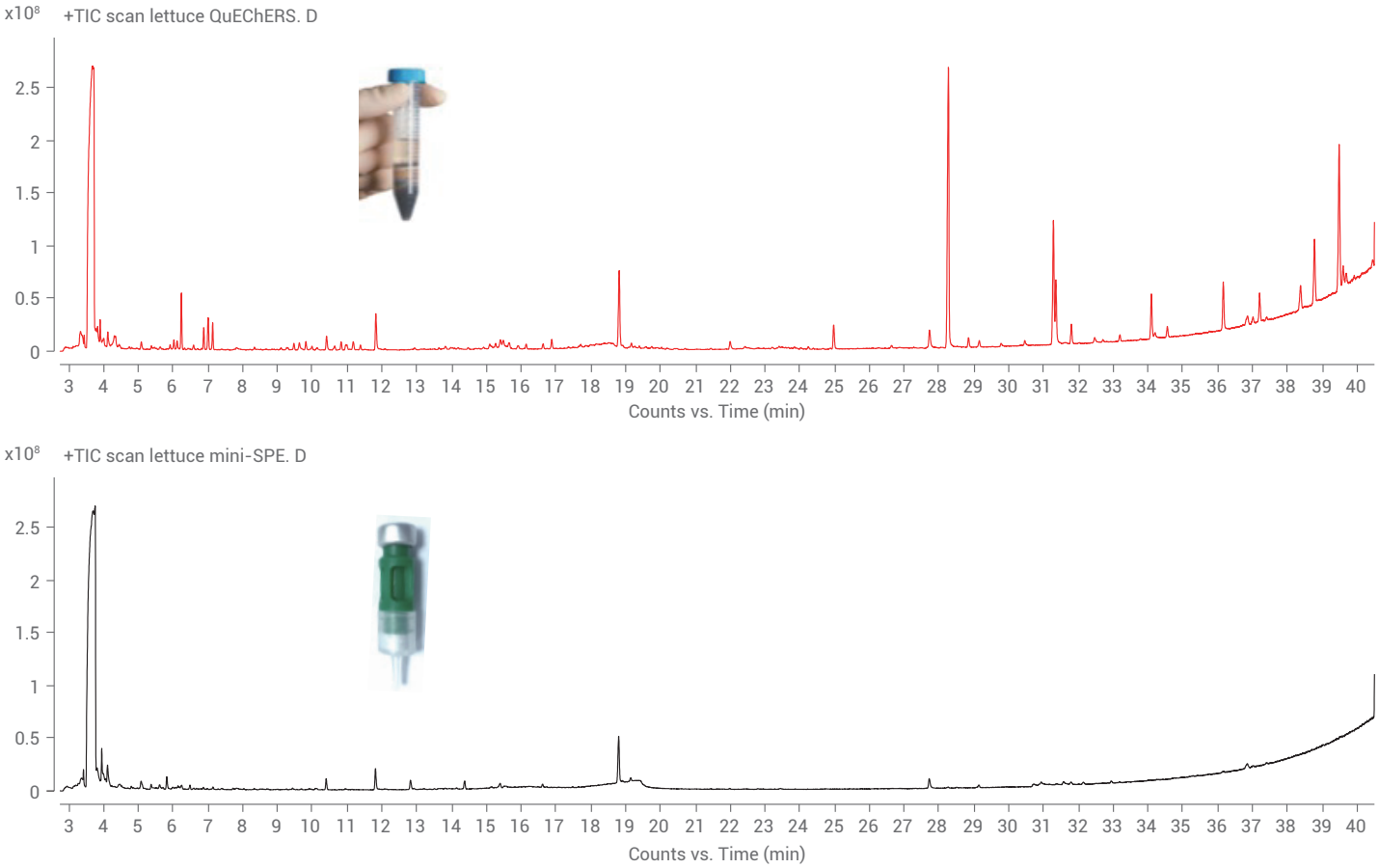


Fig 8. Full-scan chromatogram (TIC) of lettuce QuEChERS extract (red) and mini-SPE cleaned extract (black)

Two controlled experiments were performed to demonstrate the different cleanup performance between the automated mini-SPE and the traditional manual QuEChERS dSPE procedure. From Figures 6, 7, and 8, the cleaning effect of mini-SPE is better than the traditional manual QuEChERS dSPE procedure. The mini-SPE cleaning method showed longer uptime for increased sample throughput and less maintenance.

Traditional QuEChERS dSPE cleanup

The apple and orange sample were fully mixed after cutting, put into the tissue crusher and mashed into homogenate. 10 gram of the sample (accurate to 0.01 g) was put into 50 mL plastic centrifuge tubes and 10 mL frozen acetonitrile was added followed by the QuEChERS extraction kit (p/n 5982-5650CH). The capped centrifuge tubes were shaken vigorously for 1 min and centrifuged at 4200 rpm for 5 min.

After centrifugation, 6 mL of the acetonitrile raw extract was transferred into the 15 mL plastic centrifuge tube with the dSPE QuEChERS kit (p/n 5982-5056), vortexed for 1 min and centrifuged at 4200 rpm for 5 min. The upper solvent layer was then transferred into 2 mL autosampler vials for GC/MS injection.

Mini-SPE cleanup on the PAL RTC system

The apple, orange, and lettuce samples were fully mixed after cutting, put into the tissue crusher and mashed into homogenate. 10 grams of the sample (accurate to 0.01 g) was put into 50 mL plastic centrifuge tubes and 10 mL frozen acetonitrile was added followed by the QuEChERS extraction kit (p/n 5982-5650CH). The capped centrifuge tubes were shaken vigorously for 1 min and centrifuged at 4200 rpm for 5 min.

The upper solvent layer was then transferred into 2 mL autosampler vials and put into the sample rack of PAL RTC system for mini-SPE cleanup sample preparation.

The cleanup performance of both methods was evaluated by a full-scan GC/MS analysis. From the recorded chromatograms of the apple and orange samples in Figure 6, 7, and 8, we conclude that cleanup with mini-SPE achieves better response and shows significantly fewer interference peaks than traditional dSPE cleanup.

Although mini-SPE cartridge material is much less than used in traditional QuEChERS dSPE method, results show that the capacity of the mini-SPE cleanup is better. This solution realizes the automatic extract cleanup and improves the overall performance of the QuEChERS sample preparation.

PAL RTC screening for positive pesticide results

This GC/MS screening solution is based on the 667 pesticides MRM screening method of the Agilent G9250 pesticides and contaminants database. This file contains the pesticides method information of more than 1100 analytes, creating directly the acquisition and quantification method. The performed screening and quantification runs included three blank samples and matrix standard spiked samples.

For the evaluation of the overall cleanup and screening performance, this application uses 133 target pesticides (see Table 3), and evaluates the screening results and standard addition recovery results of the three matrices apple, orange, and lettuce leaves.

Table 3. Pesticides used for matrix standard addition

No.	Compound Name	CAS	No.	Compound Name	CAS
1	Dimefox	115-26-4	68	Pendimethalin (Penoxaline)	40487-42-1
2	Methamidophos	10265-92-6	69	Terbufos sulfone	56070-16-7
3	Dichlorvos	62-73-7	70	Captan	133-06-2
4	Acephate	30560-19-1	71	Heptachlor endo-epoxide (isomer A)	1024-57-3
5	Heptenophos	23560-59-0	72	Chlorfenvinphos	470-90-6
6	Omethoate	1113-02-6	73	Quinalphos	13593-03-8
7	Thionazin	297-97-2	74	Folpet	133-07-3
8	Propoxur	114-26-1	75	Triadimenol	55219-65-3
9	Demeton-S-methyl	919-86-8	76	Chlordane-trans (gamma)	5103-74-2
10	Ethoprophos (Ethoprop)	13194-48-4	77	Methoprene	40596-69-8
11	Chlordimeform	6164-98-3	78	Methidathion	950-37-8
12	Naled	300-76-5	79	DDE-o,p'	3424-82-6
13	Trifluralin	1582-09-8	80	Endosulfan I (alpha isomer)	959-98-8
14	Benfluralin	1861-40-1	81	Vamidothion	2275-23-2
15	Cadusafos	95465-99-9	82	Chlordane-cis (alpha)	5103-71-9
16	Phorate	298-02-2	83	Tetrachlorvinphos	961-11-5
17	BHC-alpha	319-84-6	84	Flumetralin	62924-70-3
18	Monocrotophos	6923-22-4	85	Fenamiphos (Phenamiphos)	22224-92-6
19	Hexachlorobenzene	118-74-1	86	Napropamide	15299-99-7
20	Dicloran (Dichloran)	99-30-9	87	Prothiofos	34643-46-4
21	Dimethoate	60-51-5	88	Isoprothiolane	50512-35-1
22	Carbofuran	1563-66-2	89	Profenofos	41198-08-7
23	BHC-beta	319-85-7	90	DDE-p,p'	72-55-9
24	Clomazone	81777-89-1	91	Dieldrin	60-57-1
25	Schradan	152-16-9	92	Uniconazole	83657-22-1
26	BHC-gamma	58-89-9	93	DDD-o,p'	53-19-0
27	Terbufos	13071-79-9	94	Myclobutanil	88671-89-0
28	Fonofos	944-22-9	95	Endrin	72-20-8
29	BHC-delta	319-86-8	96	Nitrofen	1836-75-5
30	Diazinon	333-41-5	97	Endosulfan II (beta isomer)	33213-65-9
31	Disulfoton	298-04-4	98	Chlorobenzilate	510-15-6

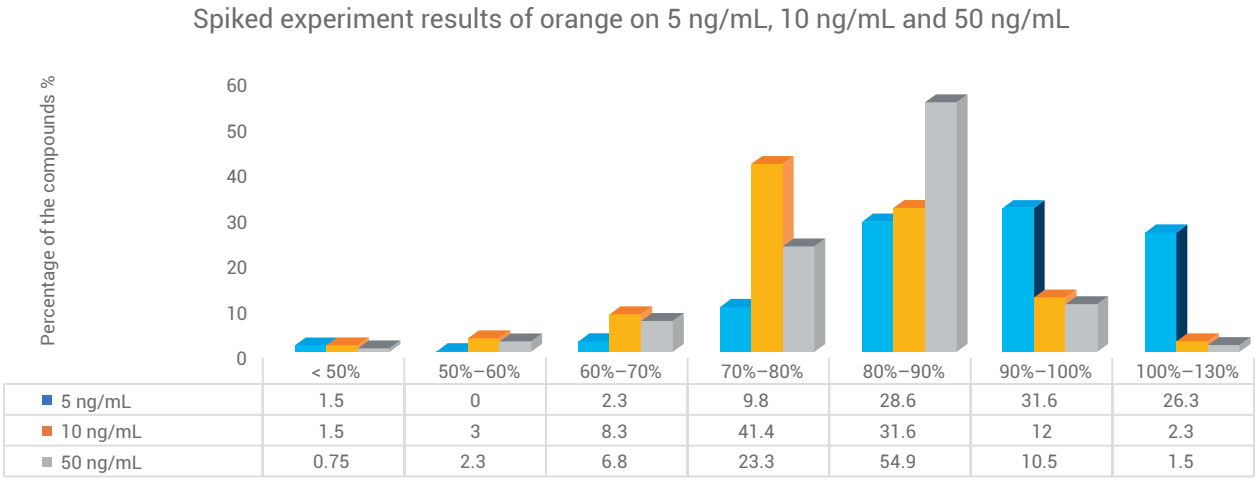
No.	Compound Name	CAS	No.	Compound Name	CAS
32	Phosphamidon	13171-21-6	99	Fensulfothion	115-90-2
33	Chlorothalonil	1897-45-6	100	Fenthion sulfoxide	3761-41-9
34	Mexacarbate	315-18-4	101	DDD-p,p'	72-54-8
35	Isazofos (Miral, Isazophos)	42509-80-8	102	DDT-o,p'	789-02-6
36	Tefluthrin, cis-	79538-32-2	103	Fenthion sulfone	3761-42-0
37	Iprobenfos	26087-47-8	104	Oxadixyl	77732-09-3
38	Formothion	2540-82-1	105	Ethion	563-12-2
39	Pirimicarb	23103-98-2	106	Triazophos	24017-47-8
40	Chlorpyrifos-methyl	5598-13-0	107	Chlornitrofen	1836-77-7
41	Parathion-methyl	298-00-0	108	Benalaxyl	71626-11-4
42	Acibenzolar-S-methyl	135158-54-2	109	Endosulfan sulfate	1031-07-8
43	Carbaryl	63-25-2	110	DDT-p,p'	50-29-3
44	Heptachlor	76-44-8	111	Fenamiphos sulfone	31972-44-8
45	Alachlor	15972-60-8	112	EPN	2104-64-5
46	Metalaxyl	57837-19-1	113	Bifenthrin	82657-04-3
47	Ronnel (Fenchlorphos)	299-84-3	114	Methoxychlor, p,p'-	72-43-5
48	Methiocarb sulfone	2179-25-1	115	Tetradifon	116-29-0
49	Demeton-S-methyl sulfon	17040-19-6	116	Azinphos-methyl	86-50-0
50	Fenitrothion	122-14-5	117	Phosalone	2310-17-0
51	Methiocarb	2032-65-7	118	Leptophos	21609-90-5
52	Bromacil	314-40-9	119	Mirex	2385-85-5
53	Pirimiphos-methyl	29232-93-7	120	Cyhalothrin (lambda)	91465-08-6
54	Aldrin	309-00-2	121	Azinphos-ethyl	2642-71-9
55	Malathion	121-75-5	122	Pyrazophos	13457-18-6
56	Metolachlor	51218-45-2	123	Benfuracarb	82560-54-1
57	Fenthion	55-38-9	124	Permethrin (cis-)	61949-76-6
58	Parathion	56-38-2	125	Cyfluthrin	68359-37-5
59	Chlorpyrifos	2921-88-2	126	Cypermethrin	52315-07-8
60	Triadimefon	43121-43-3	127	Flucythrinate	70124-77-5
61	DCPA (Dacthal, Chlorthal-dimethyl)	1861-32-1	128	Fenvalerate	51630-58-1
62	Bromofos	2104-96-3	129	Difenoconazole	119446-68-3
63	Butralin	33629-47-9	130	Deltamethrin	52918-63-5
64	Diphenamid	957-51-7	131	Azoxystrobin	131860-33-8
65	Isopropalin	33820-53-0	132	Famoxadone	131807-57-3
66	Heptachlor exo-epoxide (isomer B)	28044-83-9	133	Dimethomorph	110488-70-5
67	Penconazole	66246-88-6			

Sample screening results

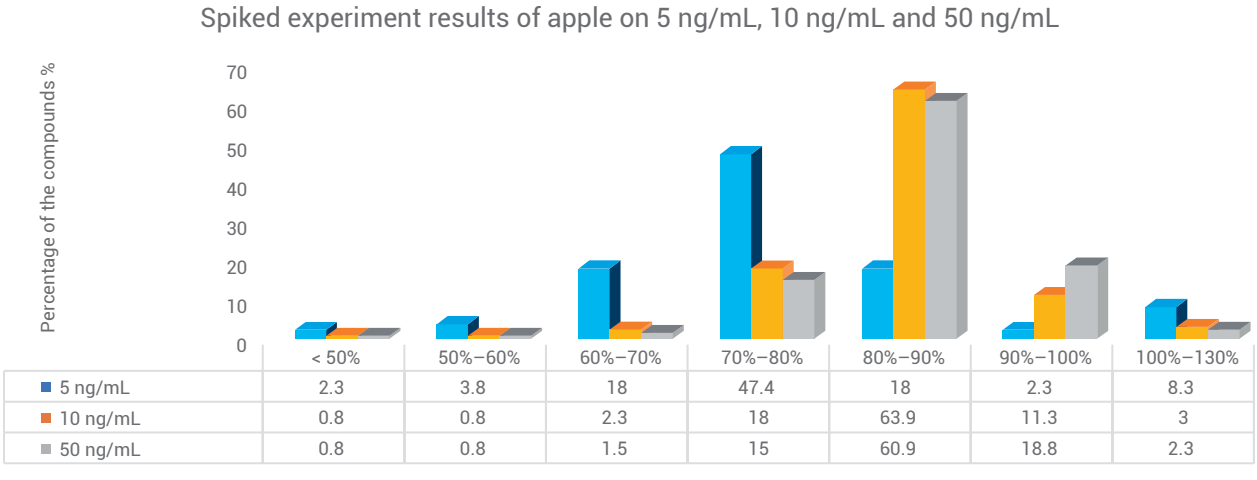
Using the Agilent method for GC/MS, a total of 133 pesticide analytes could be screened successfully. For the evaluation of the deployed mini-SPE cleanup, the three matrices samples were spiked with three different concentrations of 5, 10, and 50 ng/mL of the target analytes. For quantification by GC/MS, the sample standard addition recovery and repeatability were determined.

Figure 9 shows the method recovery results using the mini-SPE cleanup with the number of pesticides found at different recovery rates. For the chosen matrices apple, orange, and lettuce leaves, the analyte recoveries for most of the pesticides were in the range of 70 to 130 % with all the three standard addition levels 5, 10, and 50 ng/mL.

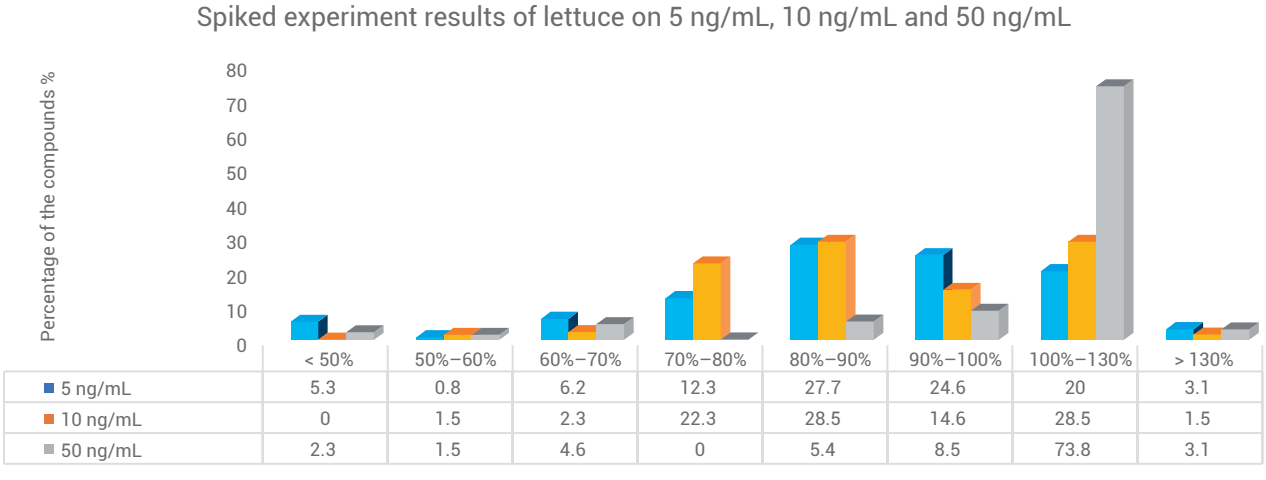
Figure 10 shows the repeatability results. Six spiked samples were cleaned with the mini-SPE and measured using GC/MS. The method showed good robustness. For the chosen matrices apple, orange, and lettuce leaves, the repeatability precision was lower than 10 % for most of the pesticides with all the three standard addition levels 5, 10, and 50 ng/mL.



	< 50%	50%–60%	60%–70%	70%–80%	80%–90%	90%–100%	100%–130%
5 ng/mL	1.5	0	2.3	9.8	28.6	31.6	26.3
10 ng/mL	1.5	3	8.3	41.4	31.6	12	2.3
50 ng/mL	0.75	2.3	6.8	23.3	54.9	10.5	1.5

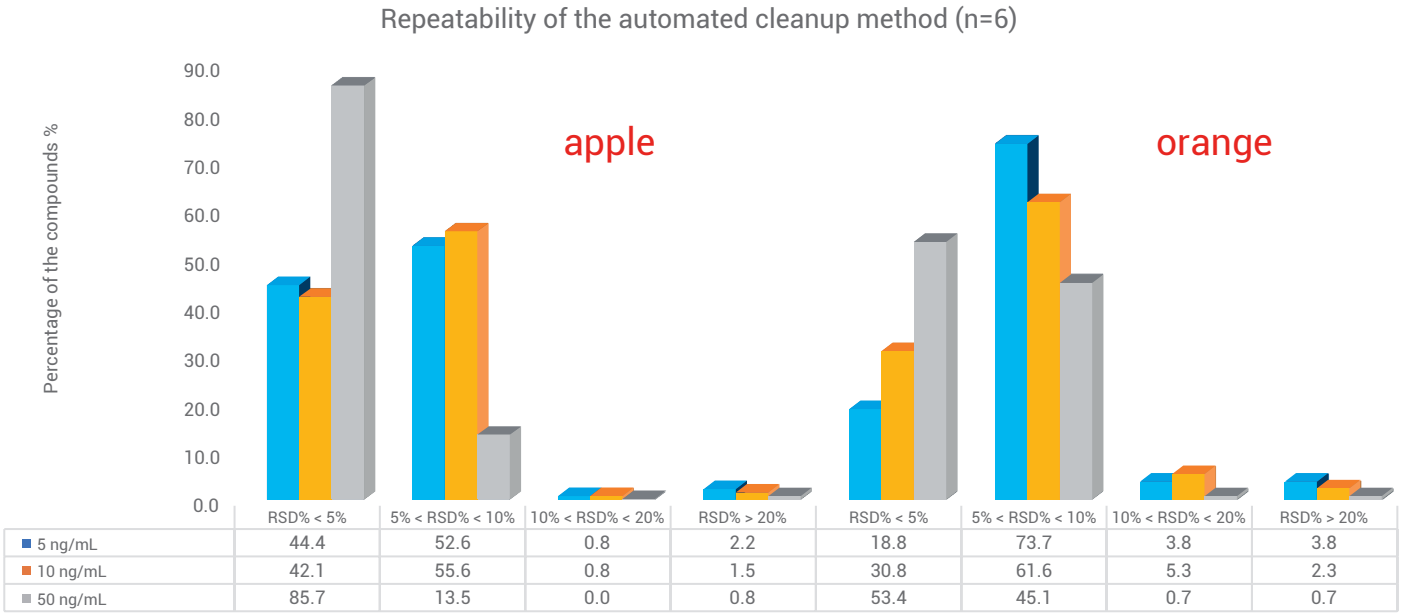


	< 50%	50%–60%	60%–70%	70%–80%	80%–90%	90%–100%	100%–130%
5 ng/mL	2.3	3.8	18	47.4	18	2.3	8.3
10 ng/mL	0.8	0.8	2.3	18	63.9	11.3	3
50 ng/mL	0.8	0.8	1.5	15	60.9	18.8	2.3

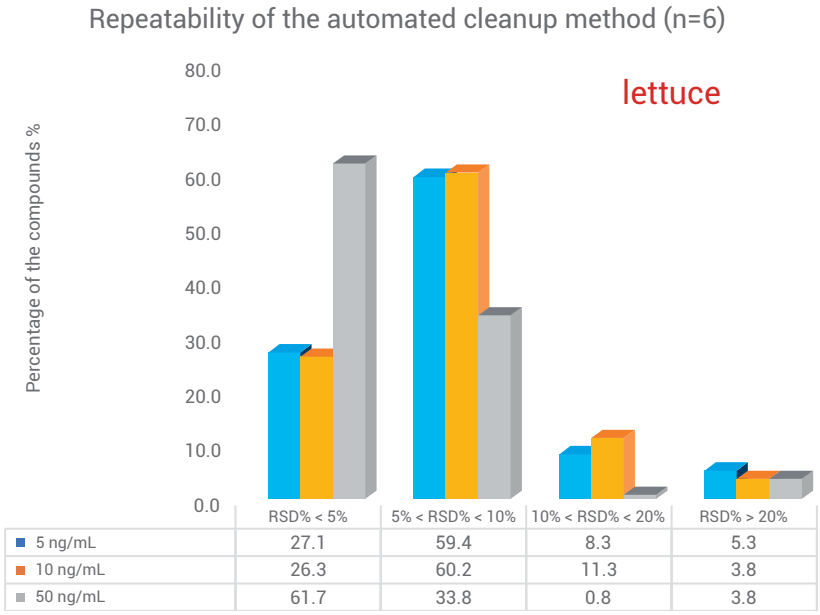


	< 50%	50%–60%	60%–70%	70%–80%	80%–90%	90%–100%	100%–130%	> 130%
5 ng/mL	5.3	0.8	6.2	12.3	27.7	24.6	20	3.1
10 ng/mL	0	1.5	2.3	22.3	28.5	14.6	28.5	1.5
50 ng/mL	2.3	1.5	4.6	0	5.4	8.5	73.8	3.1

Figure 9. Method recovery results using the mini-SPE cleanup



	RSD% < 5%	5% < RSD% < 10%	10% < RSD% < 20%	RSD% > 20%	RSD% < 5%	5% < RSD% < 10%	10% < RSD% < 20%	RSD% > 20%
5 ng/mL	44.4	52.6	0.8	2.2	18.8	73.7	3.8	3.8
10 ng/mL	42.1	55.6	0.8	1.5	30.8	61.6	5.3	2.3
50 ng/mL	85.7	13.5	0.0	0.8	53.4	45.1	0.7	0.7



	RSD% < 5%	5% < RSD% < 10%	10% < RSD% < 20%	RSD% > 20%
5 ng/mL	27.1	59.4	8.3	5.3
10 ng/mL	26.3	60.2	11.3	3.8
50 ng/mL	61.7	33.8	0.8	3.8

Figure 10. PAL RTC repeatability results using the mini-SPE cleanup

Suitability of PAL RTC sample pretreatment platform method

133 pesticide compounds were used to validate the method. In this test, benfuracarb, shown in Figure 11, exhibited specific adsorption on the mini-SPE column, which resulted in the recovery of the compound being 0 at three different substrates and three different levels (5, 10, and 50 ng/mL), while the recovery of the target compound would not be affected by the pretreatment process using QuEChERS as a control. At present, the specific adsorption reason has not been effectively confirmed. In view of this, it is necessary to test the applicability of the compound in the application of mini-SPE technology to test the pesticide target to ensure that the scheme is effective.

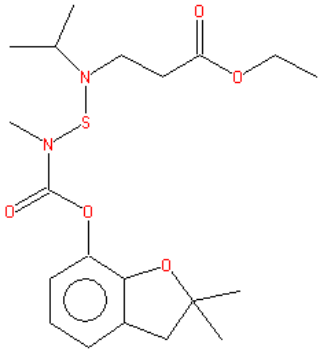


Figure 11. Structure of benfuracarb

Conclusions

The described pesticides analysis workflow uses the Agilent PAL RTC sample handling system with mini-SPE cleanup cartridges. With this setup, it is possible to run online sample cleanup and injection to the GC/MS system. This solution realizes fully automated pesticides extract cleanup, screening, and quantification.

- One mini-SPE cartridge can serve for all the matrices in food, represented here with simple, complex, and high-chlorophyll food matrix types. There is no need for a specific cleanup method development for different matrices.
- The cleanup procedure is true green chemistry. Significantly less solvent is needed. Only 150 µL sample volume is required with an additional elution solvent volume 100 µL.
- Mini-SPE cartridges achieve a significantly better cleanup performance than traditional QuEChERS dSPE, shown with the full-scan chromatogram comparison.
- The mini-SPE cleaning method has higher uptime for increased sample throughput and reduced maintenance. The method achieves high productivity.
- The automated pesticides analyses workflow is robust and mature. Most of the analyte recoveries were between 70 to 130 % with RSDs below 10 %. This meets the requirements for pesticide residue analysis in foods.
- The automated workflow is highly economical and optimizes the GC/MS duty cycle. While the sample sequence is running the prep-ahead function of the PAL RTC System starts the preparation of the next sample during the current chromatographic run. This saves precious sample preparation time and increases sample throughput in the routine laboratory.
- The PAL RTC system runs robustly to support a 24/7 work schedule for unattended operation.

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