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Reduced Cost for Pesticides Residues Analysis by GC/MS/MS Using Mini-QuEChERS and a High Efficiency Source

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Introduction

Laboratories responsible for ensuring food safety seek to reduce the cost per analysis without compromising the accuracy and reliability of their results. A promising approach involves miniaturization of the QuEChERS extraction method and the use of smaller sample injection volumes. We found cost savings of >40% due to reductions in solvent, sorbent and labeled ISTD. Use of a High Efficiency Source and only 0.5 µL injection further reduces sample cost through decreased maintenance while still enabling lower LOQs. In carrot, tomato and celery matrix, recovery-based LOQs for 86-90% of the 126 pesticides analyzed were 1 ng/g, and 95-98% of the pesticides had LOQs ≤ 5 ng/g, or half the default MRL of 10 ng/g. Challenging captan and folpet residues were quantified at 5 and 1 ng/g, respectively, by employing the commercially available ISTDs captan-d6 and folpet-d4 for only $0.04 per sample.

Method

Refer to GC/MS/MS "Pesticide Analysis Reference Guide", Agilent Technologies publication 5991-2389EN.

Sample Preparation: Extraction/Partitioning (AOAC)

2 g of sample, 2 ceramic homogenizers
2 mL ACN (1% HAc), vortex
1 g of Agilent Bond Elut AOAC salts; shake and centrifuge

Dispersive SPE:

Transfer 1 mL of extract to 2 mL Agilent Bond Elut dSPE: General fruit & veg [PSA] or Universal [PSA, C18, GCB]
vortex and centrifuge
transfer 250 uL to vial for analysis

QC samples were fortified with a 1 µg/mL pesticide stock solution (126 pesticides) yielding concentrations of 1, 5, 10, and 50 ng/g. A 10 µL volume of internal standard spiking solution (10 µg/mL of Parathion-d10, DDT, p,p-13C12, TPP, captan-d6 and folpet-d4) was added to all samples except the control blank to yield a 50 ng/g concentration in each sample. Calibration standards were prepared by spiking the extracted blank at 0.5, 1, 5, 10, and 50 ng/g.

Analysis by GC/MS/MS

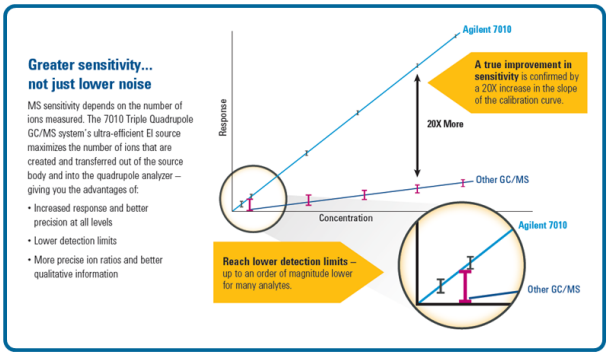
An Agilent 7890 GC coupled to a 7010 Triple Quadrupole GC/MS system with High Efficiency Source was used. The GC system was equipped with a Multi-Mode Inlet (MMI) with air cooling and a back flushing system based on a Purged Ultimate Union controlled by an AUX EPC module. Agilent Mass Hunter Software was used for instrument control, and for qualitative and quantitative data analysis.

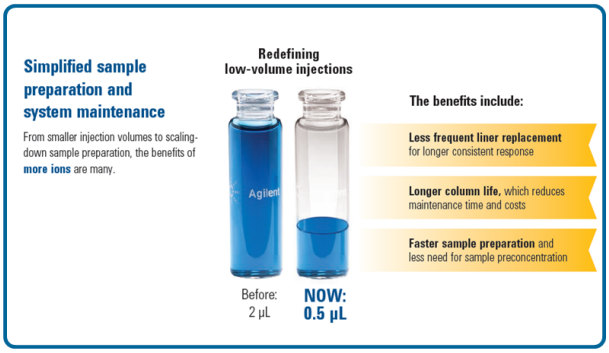
Method Transfer– No Re-optimization

What is new to this method:

- ***2 g QuEChERS sample instead of 15 g sample***
- ***0.5 µL injected instead of 2 µL***

The GC/MS/MS analysis method, with no change except injection volume, was seamlessly transferred to the 7010 GCMS with its High Efficiency Source, which maximizes ion production and leads to greater sensitivity.





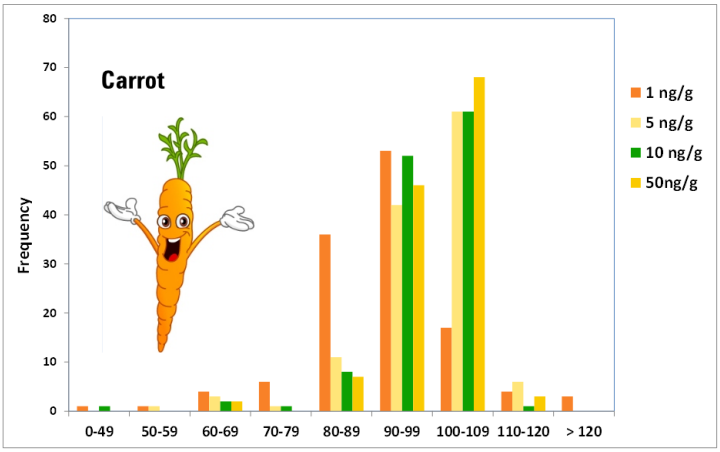
Results

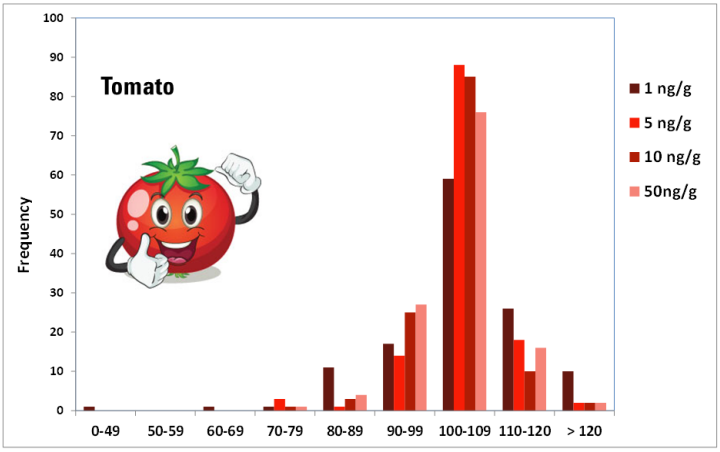
LOQs are based on %RSD ≤ 20 for n=6 Recovery Samples, where Average Recovery is in the range of 70 ≤≥ 120%

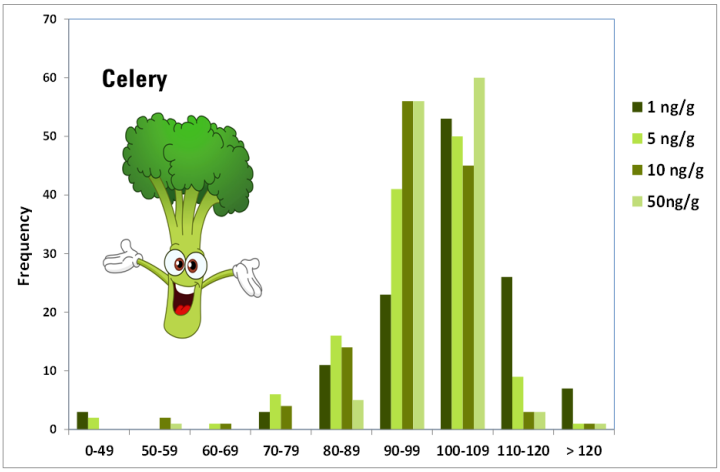
LOQs of 5 ng/g or lower were reached for 95, 98 and 97% of the 126 pesticides analyzed in carrot, tomato and celery, respectively.
In the case of carrot, 86% of the pesticides had LOQs of 1 ng/g. For tomato, 89% had LOQs of 1 ng/g and for celery 90% of the 126 pesticides had LOQs of 1 ng/g.

Recovery-Based LOQs are 1 ng/g For 86-90% of Residues

Distribution of Average Recoveries (n=6) for 126 Pesticides Spiked at 1, 5, 10 and 50 ng/g in Carrot, Tomato and Celery





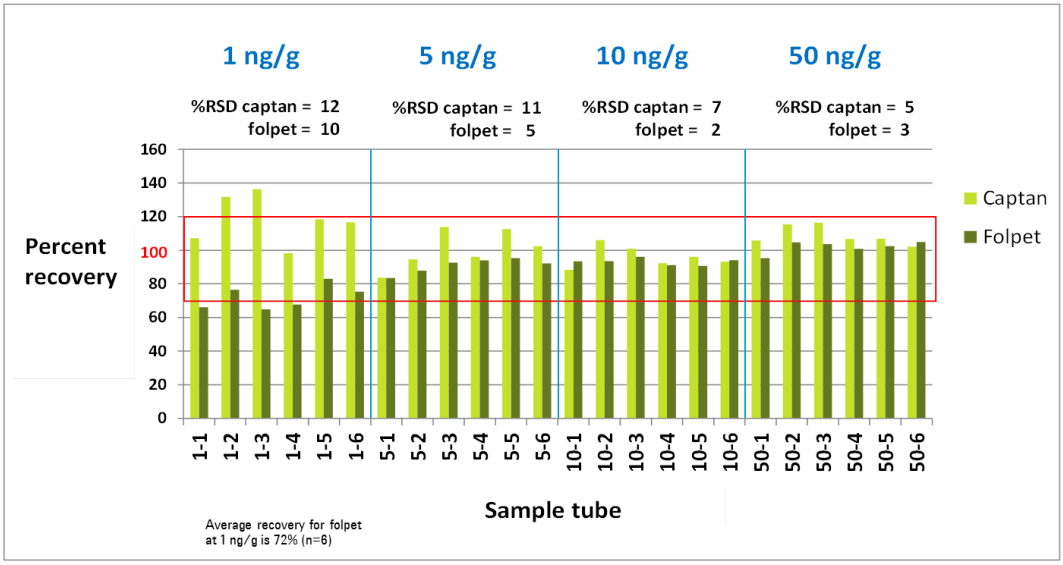


Some Challenging Pesticides Monitored in Carrot, Tomato and Celery:
A Partial List of Recovery-based LOQs (ng/g)

	Carrot	Tomato	Celery
Bifenthrin	1	1	1
Bupirimate	1	1	1
Captan	5	5	1
Chlorothalonil	1	1	1
Chlorpropham	1	1	1
Clomazone	1	1	1
Cypermethrin	1	1	1
Cyprodinil	1	5	1
DDE-p,p'	1	1	1
Diazinon Results	1	1	1
Dicloran	1	1	1
Dieldrin	1	1	1
Difenoconazole I	1	1	1
Diphenylamine	1	1	1
Endosulfan I	5	1	1
Endosulfan II	1	1	1
Endosulfan Sulfate	1	1	1
Endrin	1	1	1
Etridiazole	1	1	5
Fenpropathrin	1	1	1
Fenvalerate	1	1	1
Fludioxonil	1	1	1
Folpet	1	1	1
Fuberidazole	5	5	1
Iprodione	1	1	1
Lenacil	1	1	1
Lindane (gamma-BHC)	1	1	5
Linuron	1	1	5
Metalaxyl	1	1	1
Methoxychlor-p,p	1	1	1
Nuarimol	1	1	1
Parathion-ethyl	1	1	1
Penconazole	1	1	1
Pendimethalin	1	1	1
Permethrin I	1	5	5
Permethrin II	1	1	1
Phenothrin I and II	1	1	1
Phosmet	1	1	1
Pirimicarb	1	1	1
Pirimiphos-methyl	1	1	1
Prochloraz	1	1	1
Pyridaben	1	1	5
Pyriproxyfen	1	1	1
Quinalphos	1	1	1
Resmethrin I and II	50	5	>50
Secbumeton	1	1	1
Tebuconazole	1	1	1
Tebufenpyrad	1	1	1
Tecnazene (TCNB)	1	1	1
Tefluthrin	1	1	1
Terbuthylazine	1	1	1
Tetrachlorvinphos, E-isomer	1	1	5
Tetraconazole	1	1	1
THPI	1	5	1
Triadimefon	1	1	1
Triadimenol	1	1	1
Trifluralin	1	1	1

Precision Maintained With 2 g Sample and 0.5 µL Injection

Individual Recoveries of Captan and Folpet Spiked in Celery, 2g sample



Captan and folpet are base-sensitive compounds and are often the most problematic in terms of recovery when using QuEChERS and precision during analysis. Miniaturization allowed for 100 ng each of captan-d6 and folpet-d4 ISTD to be added to a 2 g sample at a cost of $0.012 and $0.028 per tube ($0.04 total). Resulting LOQs for captan and folpet are 1 ng/g in celery (MRLs are 50 ng/g for each commodity). Results are shown above.

LOQs for captan in carrot and tomato are 5 ng/g (%RSD 8 and 15, respectively) and 1 ng/g for folpet (%RSD 10 and 13, respectively). MRLs are 100 µg/g for captan and 20 ppb for folpet in carrot and 3 µg/g for both in tomato. Additional labeled compounds such as captan-d6 and folpet-d4 could be included without significant cost increase per sample (below).

Reduce Sample Prep Costs by Over 40%

Cost Breakdown and Cost Savings for Sample Preparation with QuEChERS and Mini-QuEChERS Technique

Sample Preparation Cost/Sample	Centrifuge Tube	ACN	Salts	Internal Standards: Captan-d6, Folpet-d4	dSPE General F&V or Universal	Total Cost/Sample	Cost Savings
QuEChERS	$0.43	$1.50	$2.96	$0.30	$1.32/$1.96	$6.51/$7.15	-
Mini-QuEChERS	$0.42	$0.20	$0.80	$0.04	$1.32/$1.96	$2.78/$3.42	**43%/48%**

Conclusion

Significant cost savings were realized through both scaled down sample prep and decreased instrument maintenance. This was made possible by using a miniaturized QuEChERS method and a High Efficiency Source for GC/MS/MS analysis. LOQs for the majority of challenging pesticides in carrot, tomato and celery were 1 ng/g despite injecting less sample to improve ruggedness of the overall method.