An Automated Solution for QuEChERS: Determination of Pesticide Residues in Cranberry Juice

Application Note

By: Tyler Trent

Abstract

The QuEChERS (Quick-Easy-Cheap-Effective-Rugged-Safe) sample extraction method was developed for the determination of pesticide residues in agricultural commodities. Since its development, QuEChERS has been modified to accommodate many other matrices such as fruit juice. The rise in popularity and ease of the QuEChERS has driven the need for automation for this manual extraction technique. By using the AutoMate-Q40, it streamlines the two part QuEChERS method from the liquid extraction to the cleanup step.

The aim of this project is to evaluate the performance and versatility of the AutoMate-Q40. Liquid Chromatography coupled to a triple-quadrupole mass spectrometry (LC-QqQ) was employed for the analysis of the LC-amenable pesticides in cranberry juice. Quantification was based on matrix-matched calibration curves with the use of internal standard to ensure method accuracy. By using the AutoMate-Q40 to streamline the QuEChERS method, this provides us with good analytical results falling in the method guidelines (range of 70-120% and RSD <20%) for the majority of the target compounds.

Introduction

Recent regulations on food analysis require screening for pesticides using confirmation techniques, such as LC-QqQ. With the ever increasing amounts of pesticides being employed, 500 or more pesticides must be analyzed on a wide range of commodities[1,2,3].

The goal of this work is to utilize the AutoMate-Q40, an automated QuEChERS extraction platform, for the determination of pesticides in Cranberry Juice. Quantification was based on matrix-matched calibration curves with the use of internal standard to ensure method accuracy. QC samples were evaluated at levels of 10.0, 50.0 and 100.0 ng/mL to ensure the precision and accuracy of the AutoMate-Q40.

Experimental Instrument Conditions

Organic cranberry juice was purchased from a local organic market in Ohio. For this method development a pesticide free cranberry juice was used to establish the method validation. The sample was stored at 4˚C until the time of extraction.

Sales/Support: 800-874-2004 • **Main**: 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Figure 1 shows the sample preparation and extraction steps utilized for this analysis. The AutoMate-Q40 used a modified AOAC multiresidue analysis[2]. For this analysis, the AutoMate-Q40 used 5.0 g of AOAC QuEChERS extraction salts ($MgSO_4$ and NaOAc). The AutoMate-Q40 also used the AOAC version of $MgSO_4$ (1200.0 mg), and PSA (400.0 mg) for the dSPE cleanup step.

Sample analysis was conducted using a Shimadzu Nexera UHPLC system coupled to an AB Sciex 4500 QTrap tandem mass spectrometer (QqQ) via electrospray ionization (ESI). For separation of the compounds of interest, a Phenomenex Kinetex 2.6um Biphenyl (50 x 2.1mm) column was used. Table I and Table II demonstrate the optimized LC-MS/MS analysis parameters for both the chromatographic separation and optimal analyte transitions. Figure 2 shows the scheduled MRM chromatogram spiked at 400.0 ng/mL.

Figure 1 AutoMate-Q40 Extraction Parameter

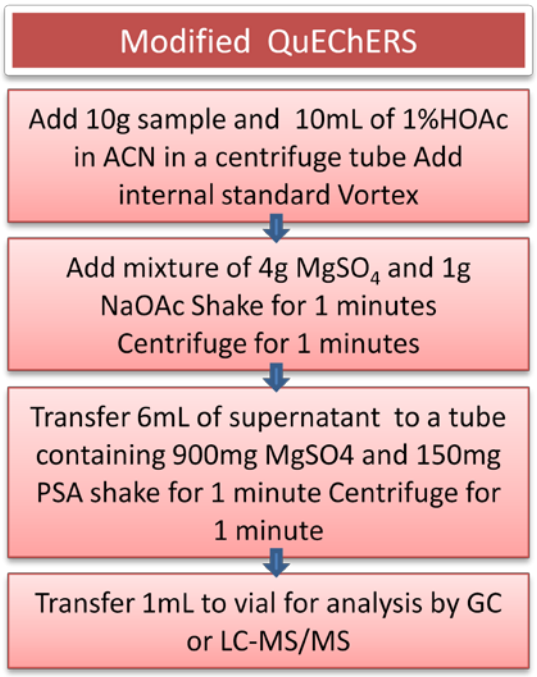
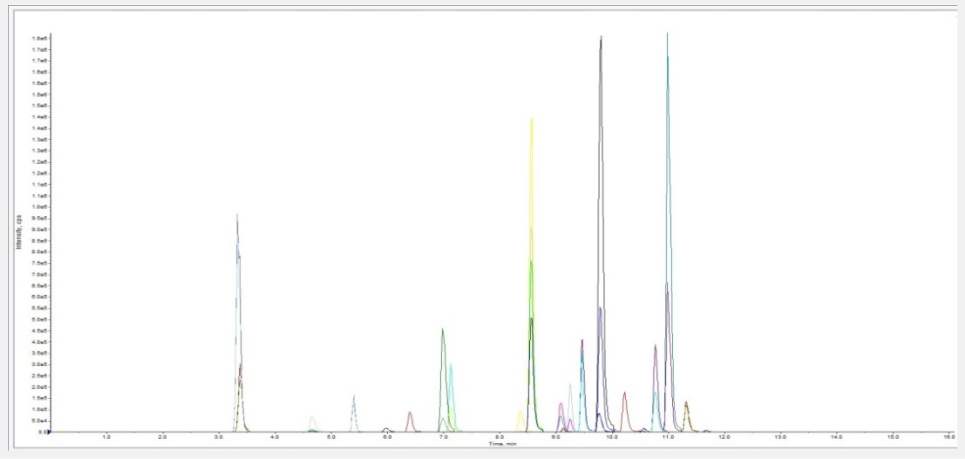


Table I UHPLC-MS/MS Parameters	
Shimadzu Nexera	
Column	Kinetix 2.6u Biphenyl 100Å
Column Temp	40˚C
Column Flow	0.450mL/min
Mobile Phase	A: 5mM Ammonium Acetate in Water B: 5mM Ammonium Acetate in Methanol
Injection Volume	10 uL
AB Sciex 4500 QTrap	
Curtain Gas	30
Ion Spray (V)	4500
Temperature (˚C)	500
GS1	50
GS2	60

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Table II LC-QqQ Transitions		
Compound	**Q1 Mass**	**Q3 Mass**
Azoxystrobin	404.0	371.9
Atrazine	216.0	173.9
Boscalid	342.9	307.0
Buprofezin	306.0	201.0
Carbaryl	202.0	144.9
Carbendazim	192.0	159.9
Chlorpyrifos	349.8	197.8
Cyprodinil	226.0	93.1
Imazalil	296.9	158.9
Imidacloprid	255.9	208.9
Iprodione	329.9	244.8
Malathion	330.9	126.9
Metalaxyl	280.0	220.0
Methiocarb	225.9	168.9
Methomyl	163.0	87.9
Metolachlor	284.0	252.0
Metribuzin	214.9	187.0
Monocrotophos	223.9	192.8
Myclobutanil	288.9	192.8
Profenofos	372.9	302.7
Pyrimethanil	200.0	107.0
Simazine	202.0	131.9

Figure 2 Cranberry Juice Spiked at 400 ng/mL



Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Results

Automating the QuEChERS extraction enables an easy, reliable and more reproducible extraction. The AutoMate-Q40 offer significant labor savings, while it improves the repeatability and consistency between the samples.

A precision and accuracy study was performed using the AutoMate-Q40. A 2.0 µg/mL stock pesticide solution was used to fortify the cranberry juice samples. Using the AutoMate-Q40, the system is able to spike samples with 50.0, 100.0 and 200 µL of the pesticide standard that yielded a 10.0, 20.0 and 40.0 ng/mL check samples. These QC samples were quantitated against their corresponding matrix matched calibration curve.

Table III documents the AutoMate-Q40's ability to extract pesticide residues from cranberry juice with all recoveries falling within 70-120%. These spike recoveries fall well within the recommended values in Document N° Sanco/12495/2011[5] which states the mean recoveries must fall within 70.0% to 120.0% and a RSD <20%. The AutoMate-Q40 also demonstrated great precision with an average of 4.9%RSD for the spiked QC samples.

Table III Cranberry Juice Method Validation

Compound	Low Level Spike 10ng/mL		Medium Spike 20ng/mL		High Spike Level 40ng/mL	
	% CV	Mean Accuracy (%)	% RSD	Mean Accuracy (%)	% RSD	Mean Accuracy (%)
Azoxystrobin	2.87	90.55	0.81	89.60	0.98	88.79
Atrazine	5.84	102.13	1.72	96.45	1.80	91.91
Boscalid	9.68	96.24	8.79	92.34	6.50	90.79
Buprofezin	9.54	94.45	4.44	93.65	0.76	94.98
Carbaryl	3.22	106.97	2.68	98.64	2.77	92.72
Carbendazim	1.49	94.86	1.01	91.99	1.21	89.33
Chlorpyrifos	2.35	108.15	1.49	94.61	1.50	88.29
Cyprodinil	19.15	86.92	11.00	86.55	5.59	84.32
Imazalil	2.21	101.93	1.16	91.78	1.94	87.00
Imidacloprid	8.52	101.58	6.75	91.42	1.86	88.44
Iprodione	21.74	74.22	15.79	87.99	3.96	79.15
Malathion	13.58	82.92	6.55	82.98	7.35	84.25
Metalaxyl	6.4.0	82.10	3.36	88.34	0.98	94.21
Methiocarb	1.69	92.44	0.72	91.44	0.58	90.59
Methomyl	3.54	86.18	2.04	88.65	0.97	89.25
Metolachlor	7.37	88.87	1.59	90.85	1.88	91.75
Metribuzin	6.67	105.01	4.23	99.15	1.22	88.63
Monocrotophos	3.67	91.41	3.85	87.10	0.44	88.08
Myclobutanil	10.16	95.83	4.41	93.64	2.85	88.90
Profenofos	17.13	91.64	9.16	86.76	4.71	90.85
Pyrimethanil	4.97	106.75	3.21	96.58	2.08	91.62
Simazine	4.73	109.45	7.15	90.08	2.92	87.60
Average	7.57	95.03	4.63	91.39	2.49	89.16

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Conclusion

This study demonstrates the Automate-Q40's ability to successfully process cranberry juice samples for pesticide residue by the QuEChERS extraction method. By automating the liquid handling, addition of salt/buffers, sample mixing, pipetting, and liquid level sensing using the patent pending VialVision™, the AutoMate-Q40 frees the scientist from a labor-intensive extraction method and exposure to unhealthy chemicals.

The automated extraction process enables an easy, reliable and more reproducible extraction. This enables time and labor savings, while improving consistency and reproducibility of the extraction. As shown above in Table III the combined pesticide spike recoveries for all levels had a 91.86% recovery, with an average RSD of 4.89% exceed the requirement outlined in The Document N˚ Sanco/12495/2011. These numbers indicate superb precision and accuracy thus validating the performance of the AutoMate-Q40 to adequately perform the QuEChERS pesticide extraction method for juice.

Reference

1. European Committee for Standardization/Technical Committee CEN/TC275 (2008), Foods of plant origin: Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/ partitioning and cleanup by dispersive SPE QuEChERS-method.
2. 2. AOCA Official Method 2007.07 Pesticide Residues in Food by Acetonitrile Extraction and Partitioning with Magnesium Sulfate. Gas Chromatography/Mass Spectrometry and Liquid Chromatography/Tandem Mass Spectrometry, First Action 2007
3. 3. M. Anastassiades: QuEChERS a mini-multiresidue method for the analysis of pesticide residues in low-fat products
4. 4. Method Validation and Quality Control Procedure for Pesticide Residues Analysis in Food and Feed (Document N˚ SANCO/12495/2011)

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com