Automated QuEChERS Tips for GC/MS Analysis of Fruit and Vegetables

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Abstract

An automated QuEChERS cleanup method was developed using disposable pipette extraction (DPX) tips containing $MgSO_4$, primary secondary amine (PSA) and graphitized carbon black (GCB). The tips were made for cleanup of 0.5 mL of acetonitrile extract of 5 different fruit and vegetable matrices, which included carrots, tomato, broccoli, green beans, and celery. Over 200 pesticides were spiked in these matrices at 100 to 1,000 ppb, and recoveries for all pesticides ranged from 70 to 117% with less than 12% RSDs for all matrices. The automated QuEChERS cleanup method was easy and rapid to perform and did not require a centrifuge.

Introduction

Numerous QuEChERS (which stands for Quick, Easy, Cheap, Effective, Rugged and Safe[1]) approaches for analysis of pesticides in fruit and vegetables (and other matrices) have been developed recently. The methods begin with extraction and partitioning of pesticides from blended and homogenized sample matrices into acetonitrile using high concentrations of salts. After the initial extraction, the acetonitrile extracts undergo a "cleanup method" by treatment with primary secondary amine (PSA) and $MgSO_4$ to remove fatty acids and water, respectively. Some methods also incorporate graphitized carbon black (GCB) and/or C18 to remove other matrix components such as pigments.

There are generally 2 ways to perform the cleanup method, using cartridges (similar to solid-phase extraction (SPE) products) or dispersive tubes. Dispersive tubes have been found to provide generally higher recoveries, and have therefore received much attention. With dispersive tubes, centrifugation is required to remove the solid sorbent from the acetonitrile solution, which will be subsequently analyzed by gas chromatography or liquid chromatography with mass spectrometry (GC/MS or LC/MS).

For automation of the cleanup method, the use of a centrifuge can make the method more challenging and time consuming to perform. A more practical way to perform the dispersive SPE method is to use disposable pipette extraction (DPX) tips. These tips have a screen which loosely contain the sorbent material inside the pipette tip. By incorporating $MgSO_4$ and PSA for sorbent, these tips are referred to as QuEChERS tips. The use of QuEChERS tips have been reported previously[2,3] and found to provide similar results to dispersive tubes.

In this study, automation is used to perform the cleanup method with QuEChERS tips. Analyses of over 200 pesticides spiked in 5 different fruit and vegetable matrices were performed using this method. "Just in time sample preparation" is demonstrated in which the sample extraction is performed in less time than the chromatographic analysis. In this manner, the extraction of one sample (or more) is performed while the previously extracted sample is being chromatographically separated and analyzed by GC/MS. This methodology provides the highest throughput for analysis.

Key Words

disposable pipette extraction, DPX, pesticides, GC/MS, automation

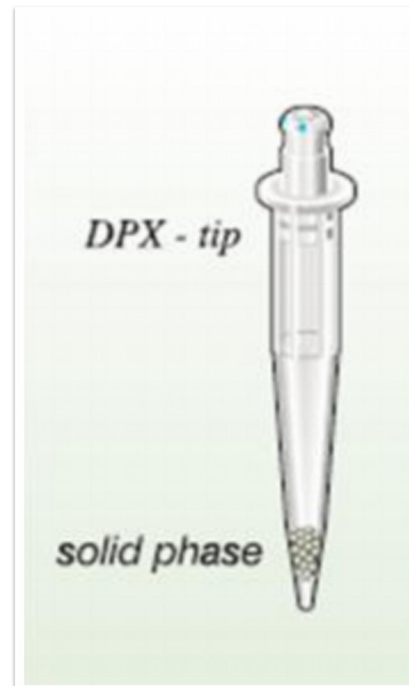

Figure 1. QuEChERS tip with MgSO4, PSA, and GCB for the solid phase sorbent, and a screen which acts as a filter to contain the sorbent material. A transport adaptor is at the upper end of the pipette tip for automation handling.

Experimental

Materials

All pesticide standards were provided by Jon Wong of the Food and Drug Administration (FDA, College Park, MD).

The QuEChERS tips (Fig. 1) were provided by DPX Labs (Columbia, SC). These tips contained 75 mg MgSO4, 25 mg PSA and 12.5 mg GCB with a transport adaptor.

Instrumentation

The analysis was performed with an Agilent Technologies GC/MS instrument (model 6890 with 5975 MSD) coupled with a dual rail multi-purpose sampler (MPS) from GERSTEL, Inc. (Linthicum, MD) as shown in Figure 2. The dual rail sampler with DPX option contained 2 syringes, one was a 2.5 mL syringe for performing automated extractions (right side) and the other was a 10 µL syringe for injection (left side) into the GC injection port.

The GC/MS instrument contained a 30 m and 0.25 mm ID Rtx-5 ms column with 0.2 µm film (Restek Corp., Bellefonte, PA). Carrier gas was He at constant flow of 1 mL/min. Oven temp started at 105 °C for 2 min, ramp at 15 C°/min to 130 °C, increased to 240 °C at 3 °C/min, then ramp at 20 °C/min for 7 min (50 min total). The inlet temperature was 250 °C. Injection was 2 µL splitless.

Selected ion monitoring (SIM) was used for analysis, which incorporated at least 3 ions for each analyte comprising a total of well over 600 ions. Tables for these transitions are available upon request.

Methods

Samples (15 g) of carrots, tomato, celery, broccoli and green beans were chopped and blended 1:1 with acetonitrile (15 mL). The extracts were mixed vigorously with $MgSO_4$ and NaCl to salt out the acetonitrile layer according to the QuEChERS protocol.[1] These solutions were subsequently spiked to give concentrations of 100 ppb to 1,000 ppb for subsequent automated cleanup using QuEChERS tips.

Figure 2. Dual rail MPS system on top of the GC/MS instrument for "just in time sample preparation" using automated QuEChERS tips.

Using just 0.5 mL of the acetonitrile extract, the solutions were placed on the tray of the MPS system and the prep sequence was started. The automated prep sequence performed the steps of aspirating, mixing and dispensing the solutions in and out of the QuEChERS tips. The steps were repeated 2 times, and the final step eluted the solution directly into sealed (with a thick septum slit capped vial) GC vials. An additional 0.2 mL of acetonitrile was added to the top of the QuEChERS tips and passed through the sorbent to remove any bound pesticides. The final volume of solution in the GC vials was approximately 0.5 mL.

Results & Discussion

The spiked sample matrices were analyzed using automated QuEChERS tips. Representative chromatograms are shown in Figure 3, with blank matrices plotted on the left side and spiked pesticides (100 ppb) plotted to the right. It is noted that some pesticide residues were detected in some of the samples.

Table 1. Recovery and reproducibility data for the first (alphabetically listed) 24 pesticides spiked in carrot, tomato and green beans at 100 ppb.

Pesticides	%Recovery (%RSD)		
	Carrot	Tomato	Bean
Acrinathrin	95.71 (8.73)	105.63 (3.05)	81.35 (7.94)
Akton,	72.69 (11.03)	74.14 (3.640	72.05 (7.71)
Alachlor	82.91 (9.24)	79.21 (4.23)	75.51 (10.63)
Aldrin	75.37 (2.00)	71.27 (3.41)	72.60 (10.44)
Allethrin	84.96 (9.33)	80.83 (2.25)	78.38 (5.67)
Allidochlor	75.13 (10.29)	82.43 (7.00)	79.49 (11.49)
Aspon	85.39 (5.94)	77.55 (4.65)	82.26 (6.15)
Azemethiphos	98.16 (4.27)	79.09 (8.63)	99.31 (4.29)
Azinphos oxon	79.38 (5.67)	101.89 (6.28)	102.15 (9.53)
Azinphos-ethyl	82.99 (2.26)	109.84 (9.42)	98.87 (1.74)
Azinphos-methyl	88.50 (5.30)	71.72 (8.42)	71.78 (6.39)
α-BHC	82.68 (8.61)	63.35 (3.75)	60.06 (8.42)
β-BHC	78.36 (2.41)	77.05 (8.56)	75.71 (5.83)
δ-BHC	71.06 (2.67)	78.22 (4.15)	59.28 (1.11)
Bifenthrin	80.21 (6.72)	74.73 (5.05)	75.10 (4.85)
Biphenyl	74.34 (9.85)	68.44 (4.62)	71.90 (6.66)
Bromophos	64.62 (7.62)	66.80 (4.98)	57.47 (8.71)
Bromophos-ethyl	58.94 (9.44)	56.63 (3.38)	59.44 (5.19)
Bromopropylate	89.12 (7.99)	88.04 (4.57)	90.05 (4.42)
Butachlor	84.25 (9.15)	85.51 (3.34)	81.48 (7.98)
Butralin	92.77 (5.84)	92.93 (2.12)	90.92 (4.50)
Captafol	95.28 (8.75)	93.63 (9.20)	101.61 (9.56)
Captan	97.20 (2.06)	94.10 (9.52)	93.23 (4.13)
Carbophenothion	78.91 (7.21)	73.60 (9.46)	72.08 (10.41)

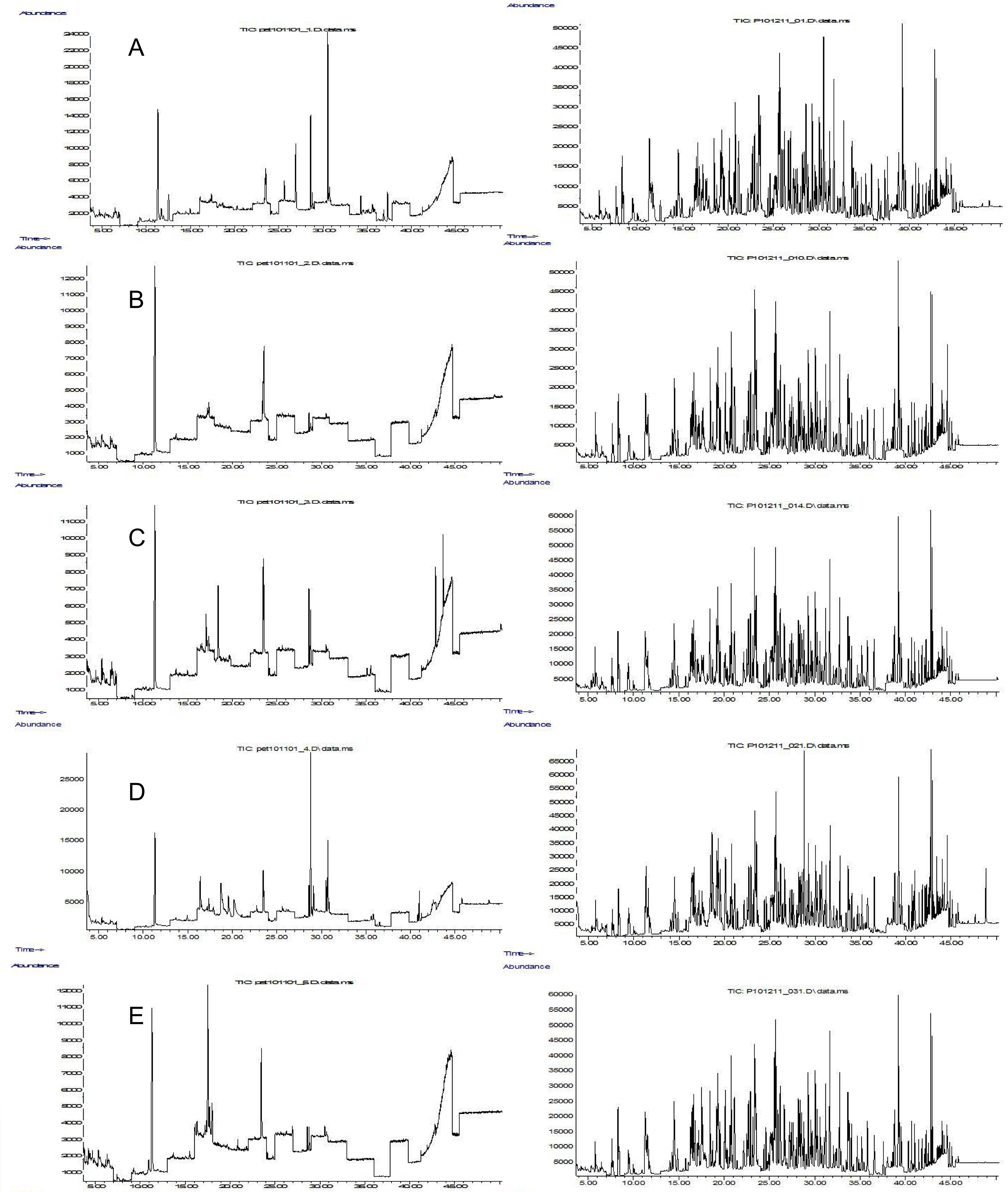

Figure 3. Total ion chromatograms of the QuEChERS extracts of blank (left) and spiked pesticides at 100 ppb (right) in carrots (A), tomato (B), green beans (C), broccoli (D) and celery (E).

Recoveries were found to be in the range of 70-117% for most pesticides in all 5 matrices. Representative results are shown in Table 1 for the first 24 pesticides in 3 sample matrices. Complete tables of the results are available upon request. It is noted that the use of GCB will result in decreased recoveries for some pesticides. However, the losses were low (probably due to the additional elution step) and the results were very reproducible because of the automation.

Conclusions

Automated cleanup was successfully utilized with QuEChERS tips for analyzing 210 pesticides from carrots, tomato, green beans, broccoli and celery. Results were reproducible with %RSDs of less than 12% for most of the pesticides in all 5 matrices at 100 ppb and 1,000 ppb.

Acknowledgements

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References

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