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Automated Multi-Residue Pesticide Analysis in Fruits and Vegetables by Disposable Pipette Extraction (DPX) and Gas Chromatography/Mass Spectrometry

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Abstract

One of the most important aspects of reducing pesticide exposure is monitoring of pesticide residues in foods. A number of analytical methods have been developed, many of them based on traditional liquid-liquid extraction, gel-permeation or solid phase extraction in combination with GC-MS or LC-MS. Recently, the QuEChERS (quick, easy, cheap, effective, rugged and safe) sample preparation methods have been developed to help monitor pesticides in a range of food samples. These methods, however, still require many manual steps, such as centrifugation, leading to increased total analysis time. There is a need for a simple, reliable and readily automated technique to clean up QuEChERS type extracts in order to improve laboratory productivity for monitoring pesticide residues in foods.

In this study, we present a novel solid-phase extraction technique called disposable pipette extraction (DPX). The solid-phase sorbent contained in the DPX tip is loose, which

permits mixing of solutions to provide unsurpassed extraction efficiency and short equilibration times.

DPX extractions are automated using the GERSTEL MultiPurpose Sampler (MPS), enabling efficient, high-throughput sample preparation. The GERSTEL DPX-Q and the DPX-Qg with graphitized carbon black, represent the only commercially available automated QuEChERS application for multi-residue analysis of pesticides.

Introduction

DPX is a fast and efficient solid phase extraction technique used for a wide range of applications such as drugs of abuse, therapeutic drug monitoring, comprehensive screening, pharmacology studies, as well as pesticides in fruits and vegetables. The DPX process is shown schematically in Figure 1. If needed, the sorbent is conditioned with solvent prior to extraction. The sample is then drawn into the pipette tip for direct contact with the solid phase sorbent. Turbulent air mixing creates a suspension of the sorbent in the sample ensuring optimal contact and highly efficient extraction. The extracted sample is discharged, typically after 30 seconds. If needed, the sorbent can be washed to remove unwanted residue. The extract is then eluted into a vial for subsequent LC or GC analysis.

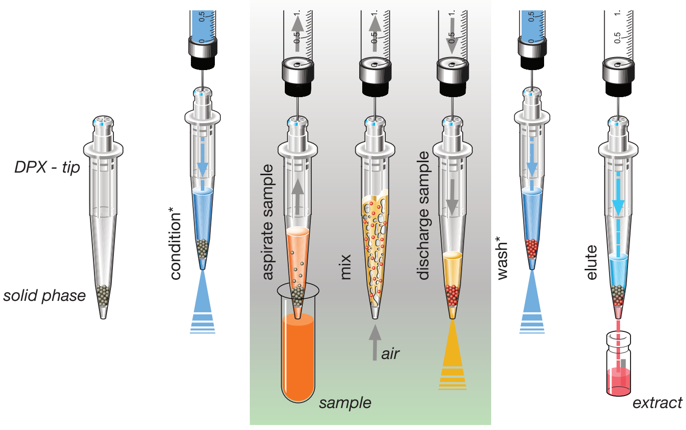

Figure 1. DPX automation process. The box depicts the extraction steps used for the DPX-QuEChERS method.

For sample cleanup methods, such as QuEChERS which focuses on removing fatty acids and water, the DPX method simply incorporates the steps of aspirating the sample solution, mixing with the sorbent, and dispensing the solution into the vial for analysis. There are no wash- or elution steps, the extractions can therefore take place in less than 1 minute. The GERSTEL MPS 2 with MAESTRO software control automates the entire process including sample introduction. In the following study, DPX-Qg tips are used to remove sample interferences from QuEChERS type extracts prior to GC/MS analysis.

Experimental

Instrumentation. Analyses were performed on a 7890 GC equipped with a 5975C MSD with triple axis detector (Agilent Technologies), PTV inlet (CIS 4, GERSTEL) and MPS 2 robotic sampler with 10 µL syringe (GERSTEL).

Analysis conditions.

PTV:	splitless
	25°C; 12°C/min; 280°C (3 min)
Column:	30 m DB5-MS (Agilent)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics:	He, constant flow = 1.0 mL/min
Oven:	60°C (1 min); 10°C/min; 300°C (3 min)

Standard preparation. A composite standard of organochlorine and organophosphate pesticides was prepared at a concentration of 1000 µg/L in acetonitrile. The standard was diluted to 20, 50, 100 and 250 µg/L. Twenty-five microliters of a matrix matching solution were added to the standards.

Sample preparation. Processed fruit and vegetable extracts were provided by the University of South Carolina. The pesticide standard was diluted to obtain concentrations of 20 and 200 µg/L in 500 µL of the extracts.

DPX extraction. 1 mL QuEChERS DPX tips were provided by DPX Labs, LLC. 500 µL of vegetable extract was manually transferred into a test tube. The extracts, 0.5 mL each, were drawn through the DPX tips 3 times. This process was automated using the GERSTEL MPS 2 autosampler with 2.5 mL syringe. The PrepSequence is shown in Figure 2. The extract was then transferred into a 2 mL autosampler vial. 1 µL of eluent was injected into the GC.

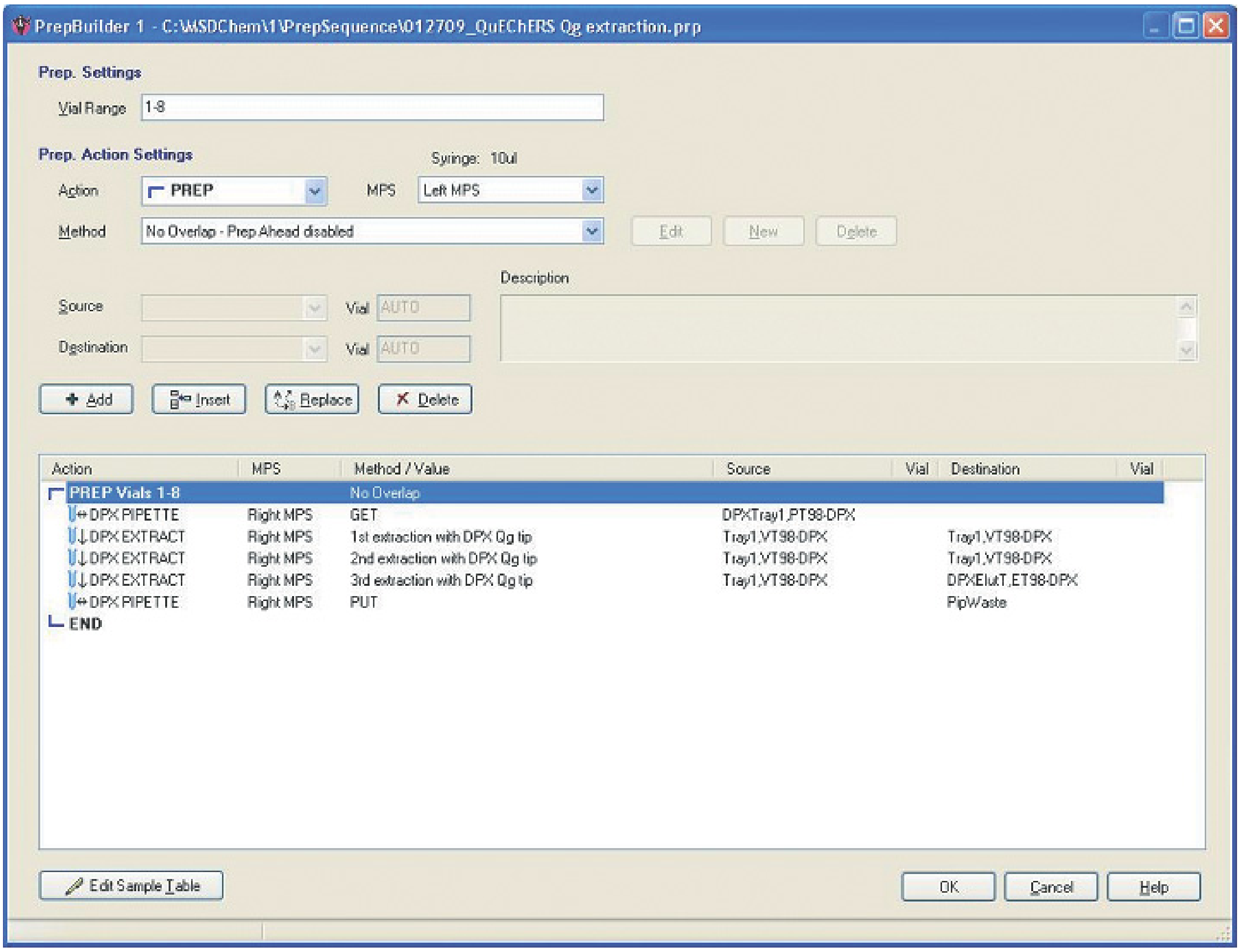

Figure 2. MAESTRO PrepSequence for automated DPX.

Results and Discussion

The spinach extract was cleaned using a DPX Qg-1TA tip and the orange extract was cleaned using both the Q-1TA and Qg-1TA tips. The Qg-1TA tips contain graphitized carbon black which is more effective in removing chlorophyll from the extracts. Figure 3 shows a photograph of the orange and spinach extracts before and after processing with the DPX tips. The green color is effectively removed from the spinach sample. The orange sample still had a mild orange tint when the Q-1TA tip was used. The Qg-1TA tip effectively removed all color and was used for all subsequent experiments.

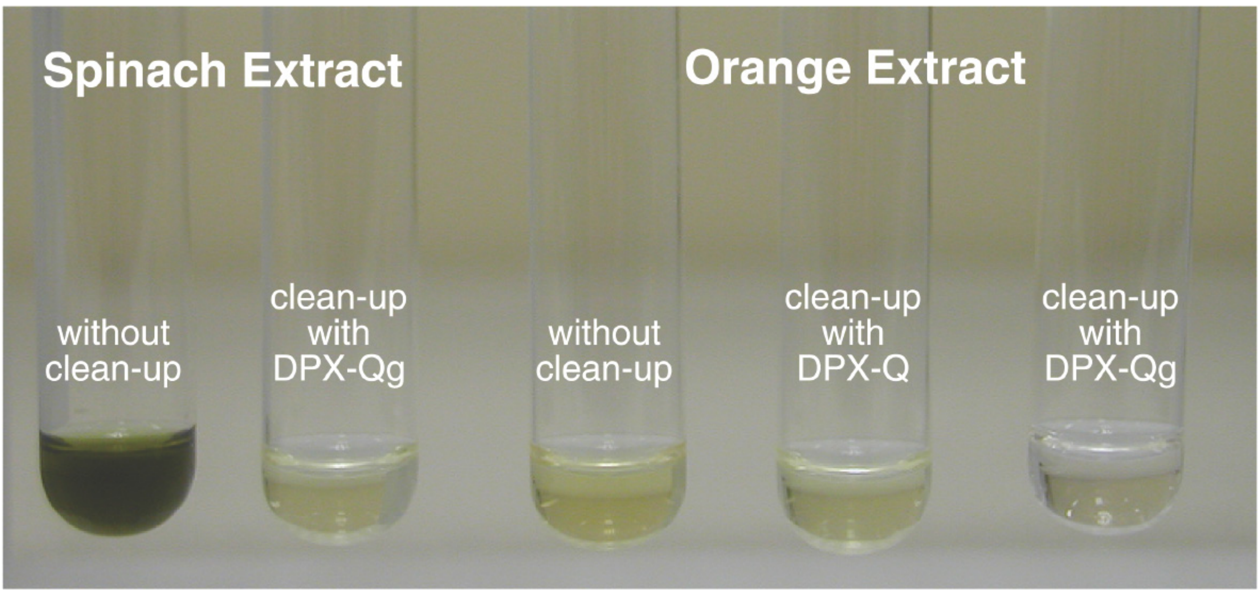

Figure 3. Picture of extracts before and after clean-up.

Figures 4 and 5 show chromatographically the effectiveness of the cleanup of the samples using DPX for the orange and spinach samples, respectively. The DPX Qg-1TA tips effectively remove interferents, especially free acids in the 15-22 minute retention time window.

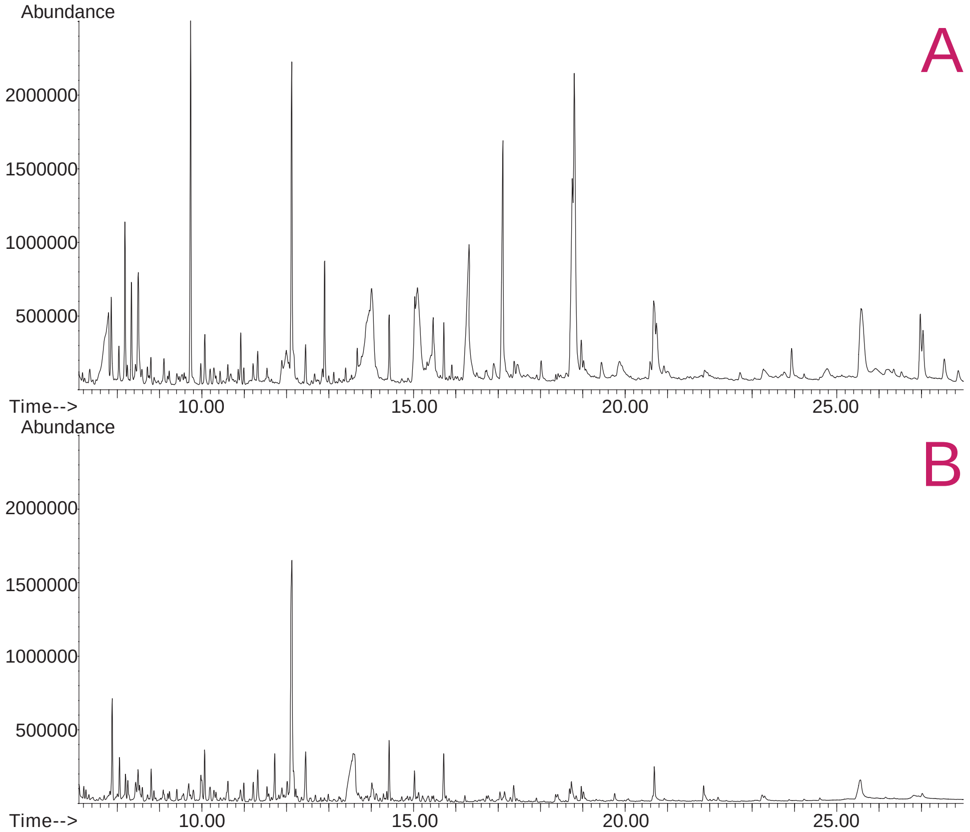

Figure 4. Chromatograms of orange extract before (A) and after (B) clean-up.

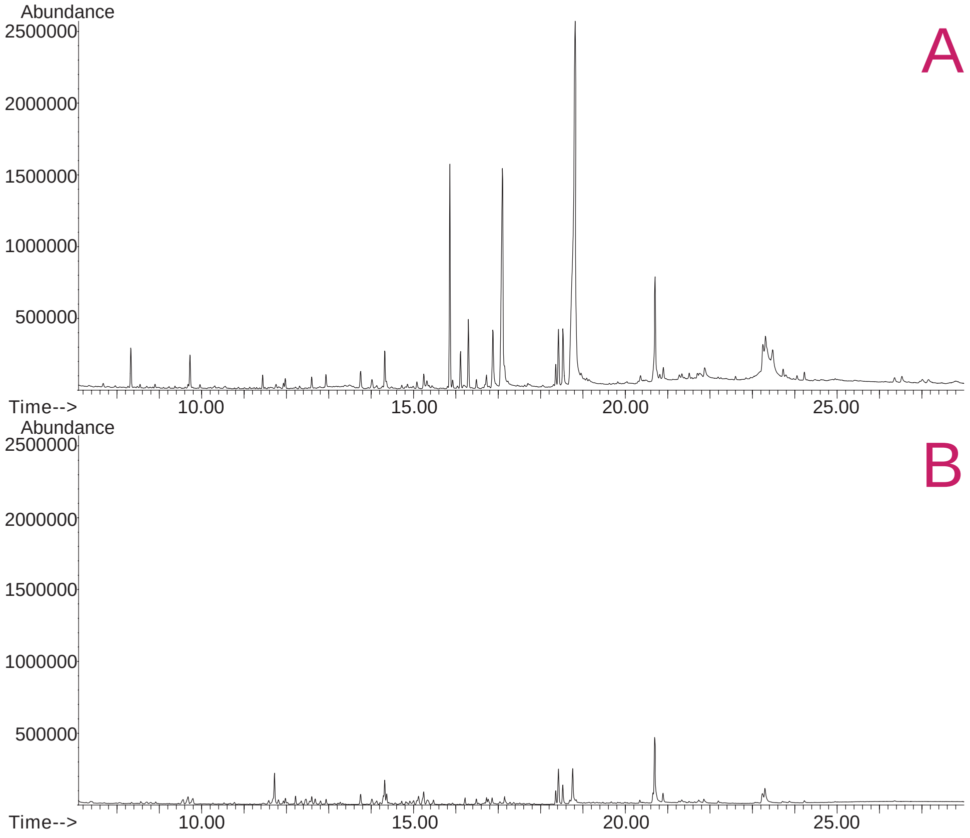

Figure 5. Chromatograms of spinach extract before (A) and after (B) clean-up.

Each extract type was spiked at 20 and 200 ppb in triplicate and cleaned up using DPX. An example chromatogram for a spinach extract spiked at 200 ppb is shown in Figure 6. Table 1 shows the results for the DPX cleanup.

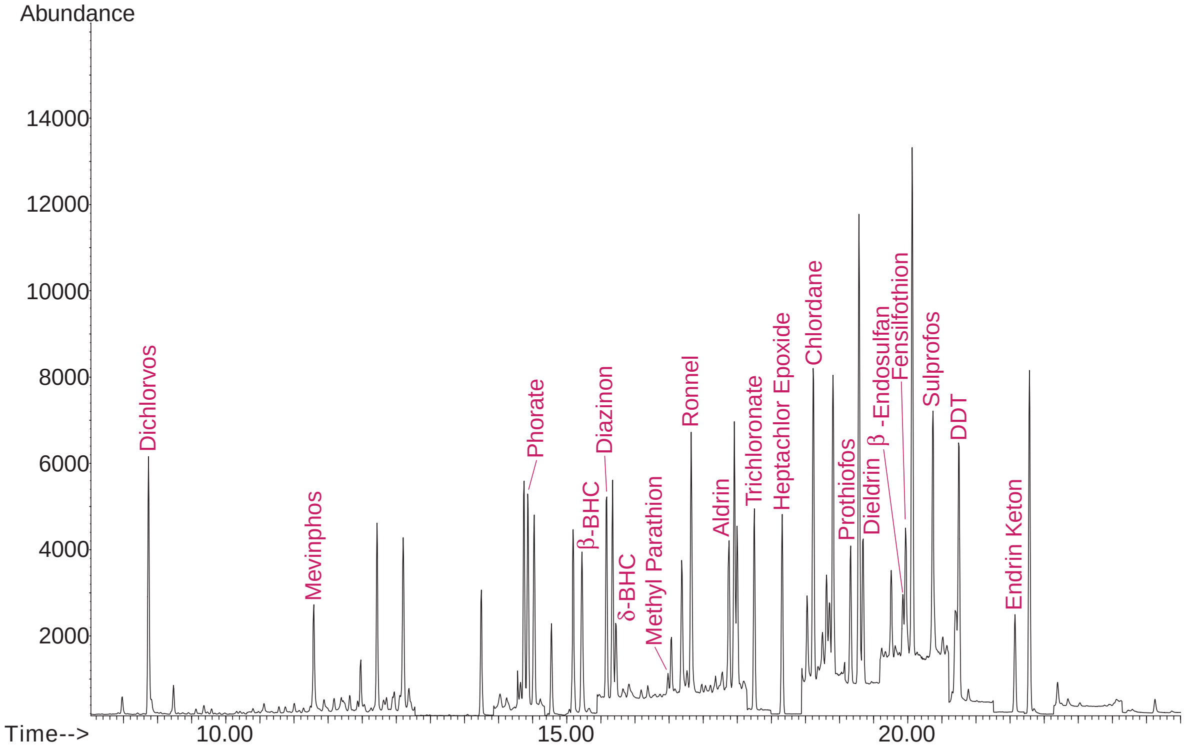

Figure 6. Chromatogram of spinach extract, spiked with 200 ppb, after DPX clean-up.

Table 1. Pesticide recoveries and % RSD.

Analyte	Orange Extracts				Spinach Extracts			
	% Recovery		% RSD		% Recovery		% RSD	
	20 ppb	200 ppb	20 ppb	200 ppb	20 ppb	200 ppb	20 ppb	200 ppb
Dichlorvos	139	80	14	15	92	51	8.3	15
Mevinphos	89	68	15	10	60	34	8.3	15
Phorate	68	122	16	3.7	16	93	32	5.2
α-BHC	100	113	5.9	4.4	47	76	16	6.2
δ-BHC	126	89	6.3	8.2	105	51	17	24
Diazinon	151	116	5.1	4.4	117	96	2.5	3.9
Methyl Parathion	263	104	7.9	12	165	54	20	14
Ronnel	97	75	5.5	5.8	95	63	11	9.8
Aldrin	173	138	5.2	3.4	148	124	1.9	3.3
Trichloronate	119	74	26	3.6	152	87	8.3	6.8
Heptachlor Epoxide	142	135	4.3	3.0	120	102	4.2	3.4
t-chlordane	147	140	4.9	2.7	135	116	3.7	3.5
Prothiofos	131	98	1.9	4.0	162	104	4.7	6.3
Dieldrin	168	137	5.2	2.4	128	123	9.0	3.2
Endrin	167	149	6.5	4.0	142	118	5.4	3.9
ß-Endosulfan	156	134	4.7	2.9	138	102	12	7.4
Fensulfothion	121	142	6.9	5.1	63	88	4.6	11
Sulprofos	196	136	3.6	4.3	200	122	4.3	6.4
DDT	213	179	4.5	11	208	117	6.9	7.3
Endrin Ketone	174	144	2.6	3.8	138	97	2.1	7.7
Average	147	119	7.6	5.7	122	91	9.1	8.2

The recoveries were calculated from an external six point calibration plot for each analyte. The external standards were matrix matched. The results show good recoveries for the mix of OC and OP pesticides used in this study. The average % RSDs (n=3) are less than 10 % for both matrices at both 20 and 200 ppb spike levels. The recoveries at the 200 ppb level range from 68-179 % with an average value of 119 % for the orange extracts and range from 34-124 % and average 91 % for the spinach extracts. These values could be improved with further optimization of the DPX automation method (number of extracts and aspiration speeds) and the use of internal standards in the GC/MS method.

The recoveries with and without DPX cleanup are shown in Table 2 for the spinach and orange extracts, clearly showing the elimination of matrix interferences with the DPX Qg-1TA tip.

Figure 7 shows an overlay of 3 replicates of an orange sample spiked with 200 ppb and processed using a DPX Qg-1TA tip. The inset shows the excellent precision which can be obtained using DPX extraction.

Table 2. Pesticide recoveries with and without DPX clean-up; spike level = 200 ppb

Compound	Orange		Spinach	
	No DPX	DPX	No DPX	DPX
Dichlorvos	128	80	120	51
Mevinphos	179	68	145	34
Phorate	180	122	170	93
α-BHC	158	113	150	76
δ-BHC	213	89	170	51
Diazinon	162	116	160	96
Methyl Parathion	483	104	300	54
Ronnel	196	75	195	63
Aldrin	204	138	210	124
Trichloronate	242	74	245	87
Heptachlor Epoxide	198	135	155	102
t-chlordane	167	140	175	116
Prothiofos	257	98	265	104
Dieldrin	198	137	260	123
Endrin	197	149	195	118
ß-Endosulfan	192	134	180	102
Fensulfothion	197	142	165	88
Sulprofos	246	136	250	122
DDT	224	179	195	117
Endrin Ketone	168	144	155	97
Average	209	119	193	91

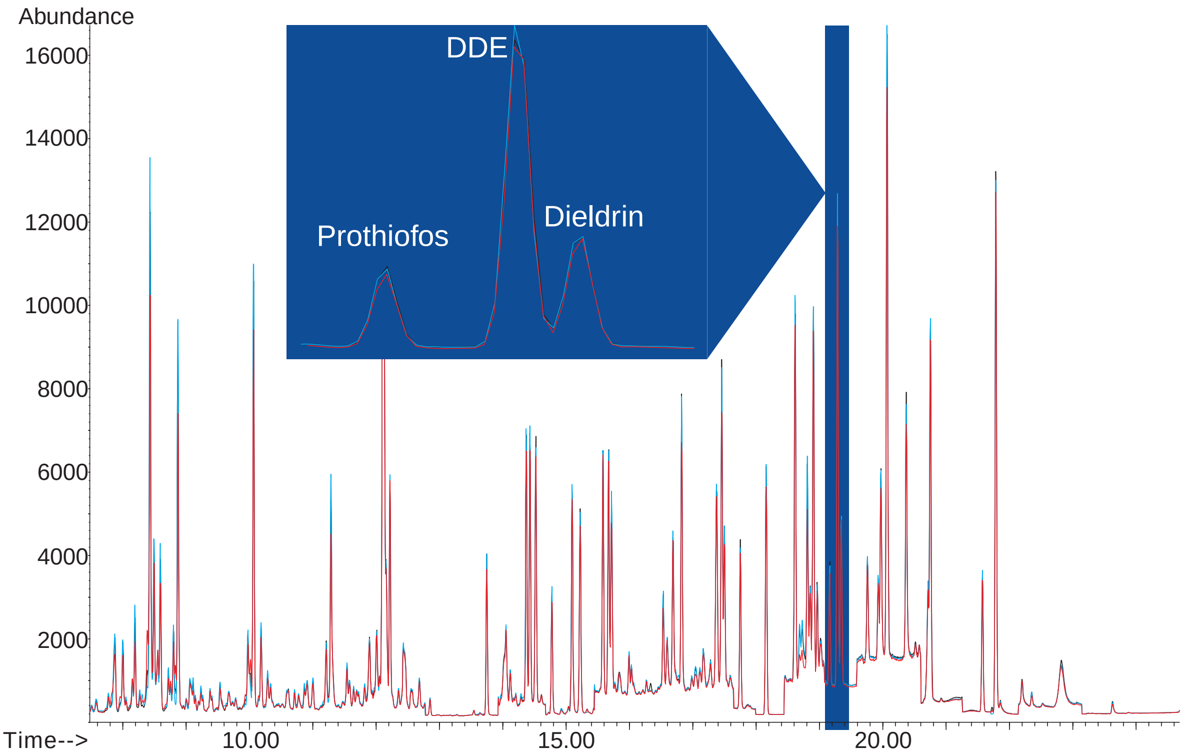

Figure 7. Overlay chromatograms of 3 replicate DPX clean-up steps and injections of an orange sample spiked with 200 ppb.

Conclusions

This study demonstrates the feasibility of using the DPX Qg-1TA for cleanup of QuEChERS type extracts prior to GC/MS analysis. The DPX tips remove matrix interferents, leading to better analyte recovery and reducing the need for maintenance since there is less build-up of non-volatile material in the GC inlet. Full automation of the sample cleanup and injection is accomplished using the GERSTEL MPS 2.

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