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New practical approach for using an analyte protectant for priming in routine gas chromatographic analysis

Soparat Yudthavorasit [a], Wanisa Meecharoen [b], Natchanun Leepipatpiboon [a,*]

[a] Chromatography and Separation Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[b] Central Laboratory (Thailand) Co., Ltd., Bangkok 10900, Thailand

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ABSTRACT

A new practical approach of using an analyte protectant (AP) for priming a gas chromatography (GC) system has been investigated for routine pesticide residue analysis. Matrix co-extractives are known to cause signal improvement, called the "matrix-induced chromatographic response enhancement effect". APs are known to provide advantages of signal enhancement independent of the matrix, but it takes time in routine applications to follow the common approach of adding APs to every extract. It is faster and easier to compensate for matrix effects by injecting an AP solution to coat active sites in the GC system at the beginning of the analytical sequence. In this study, 100 pesticides in highly pigmented QuEChERS extracts of chili were evaluated in the AP priming approach using GC–tandem mass spectrometry (MS/MS) over the course of many injections. The AP priming approach presented significantly more consistent results (87% of pesticides met RSD criteria) compared with injection sequences without the use of APs (42% of pesticides met RSD criteria). Also, AP priming with 300 ng D-sorbitol was found to display a similar trend to mixed AP in priming effect. We demonstrated that this approach is fit-for-purpose in routine analysis.

1. Introduction

Nowadays, the use of pesticides is considered to be a common agricultural practice in order to increase worldwide food production and crop yields. Their extensive application inevitably leaves residues in all parts of the food-production chain, such as in soil and water resources, and especially in derived foods; this poses risks to public health and the environment in both the short and long term (González-Rodríguez, Rial-Otero, Cancho-Grande, Gonzalez-Barreiro, & Simal-Gándara, 2011). Due to food safety issues, many countries have enacted legislation to establish the maximum residue levels (MRLs) of pesticides in foods. Gas chromatography (GC) coupled with various detection methods is typically employed as a qualitative and quantitative analytical tool for multi-residue pesticides (González-Rodríguez, Rial-Otero, Cancho-Grande, & Simal-Gándara, 2008a, 2008b; Martınez Vidal, Arrebola, & Mateu-Sánchez, 2002).

Matrix effects (MEs) are a common problem that complicates analysis because it induces greater random and systematic errors leading to less accurate results. In addition, MEs also lead to more frequent instrument maintenance needs. In gas chromatography (GC), the term "matrix-induced chromatographic response enhancement effect" was first described to explain the phenomenon in which the analyte concentration was overestimated in sample matrix compared to calibration standards in pure solvent (Erney, Gillespie, Gilvydis, & Poole, 1993). The sample matrix enhanced the transfer of analytes to the analytical column by masking the active sites (silanols, metal ions, and other active sites produced by thermally decomposed components of samples) in GC injector and column leading to greater signal (Maštovská, Lehotay, & Anastassiades, 2005). When there is no sample matrix, the detected signal is lower because susceptible analytes tends to be retained or decomposed on the active sites. The important factors affecting MEs in GC include the number and types of active sites, analyte structure (hydrogen bonding capability) and concentration, amount and type of matrix, and instrument conditions (Anastassiades, Maštovská, & Lehotay, 2003). Despite commercial claims of inert materials for use in GC, new actives sites are formed during long analytical sequences by the deposited non-volatile

* Corresponding author. Tel.: +66 2 2187608; fax: +66 2 2541309.
E-mail address: natchanun.l@chula.ac.th (N. Leepipatpiboon).

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Table 1
Average retention times (RTs), elution time range, and multiple reaction monitoring (MRM) transitions for each pesticide.

No.	Pesticide	RT (min)	Elution time range[a]	MRM transitions (*m/z*)			
				Quantifier	CE (V)	Qualifier	CE (V)
1	Dichlorvos	8.744	1	185 > 93	10	185 > 109	20
2	Dichlobenil	10.358	1	171 > 136	15	171 > 100	10
3	Etridiazole	12.229	1	211 > 183	10	211 > 140	25
4	Methacrifos	13.102	1	125 > 79	5	208 > 93	15
5	Heptenophos	14.583	1	124 > 89	30	215 > 89	15
6	Fenobucarb	15.188	1	150 > 121	16	150 > 103	24
7	Ethoprophos	15.665	1	158 > 97	18	158 > 114	10
8	Trifluralin	16.488	1	306 > 264	10	306 > 206	15
9	Dicrotophos	16.498	1	127 > 109	15	127 > 95	18
10	Monocrotophos	16.834	1	127 > 109	15	127 > 95	18
11	Phorate	16.857	1	231 > 129	25	231 > 175	15
12	alpha-BHC	17.069	1	181 > 145	15	219 > 183	10
13	Hexachlorobenzene	17.338	1	284 > 249	20	282 > 212	30
14	gamma-BHC	18.341	1	181 > 145	15	219 > 183	10
15	beta-BHC	18.345	1	181 > 145	15	219 > 183	10
16	Terbufos	18.464	1	231 > 129	20	231 > 175	20
17	Fonofos	18.629	1	246 > 109	18	246 > 137	18
18	Pyrimethanil	18.879	1	198 > 118	35	198 > 156	25
19	Diazinon	18.958	1	304 > 179	10	179 > 137	20
20	delta-BHC	19.353	1	219 > 183	10	219 > 147	15
21	Tefluthrin	19.357	1	177 > 127	15	177 > 87	25
22	Pentachloraniline	20.113	2	265 > 194	25	265 > 230	15
23	Phosphamidon	20.463	2	264 > 127	15	227 > 127	15
24	Malaoxon	20.849	2	127 > 99	10	127 > 109	15
25	Tolclofos-methyl	20.939	2	265 > 250	15	265 > 220	20
26	Heptachlor	20.992	2	272 > 237	20	274 > 239	20
27	Metalaxyl	21.269	2	206 > 132	20	206 > 162	10
28	Fenchlorphos	21.309	2	285 > 270	10	285 > 240	25
29	Fenitrothion	21.834	2	277 > 260	5	277 > 109	20
30	Pentanochlor	21.924	2	141 > 106	15	141 > 77	30
31	Malathion	22.220	2	158 > 125	10	173 > 99	25
32	Aldrin	22.286	2	263 > 193	40	263 > 191	40
33	Metolachlor	22.423	2	162 > 133	15	238 > 162	15
34	Fenpropimorph	22.479	2	128 > 70	10	303 > 128	10
35	Fenthion	22.550	2	278 > 109	20	278 > 125	18
36	Dimethylvinphos	22.591	2	295 > 109	20	297 > 109	20
37	Chlorpyrifos	22.596	2	314 > 258	15	314 > 286	5
38	Parathion-ethyl	22.647	2	291 > 109	10	291 > 81	25
39	Chlorthal-dimethyl	22.793	2	332 > 301	10	301 > 223	18
40	Isobenzan	22.905	2	311 > 275	10	375 > 275	10
41	Pirimiphos-ethyl	23.414	2	290 > 125	25	290 > 151	25
42	Cyprodinil	23.608	2	224 > 208	18	224 > 118	40
43	Metazachlor	23.785	2	209 > 132	15	209 > 117	30
44	Penconazole	23.896	2	248 > 157	25	248 > 192	15
45	Chlorfenvinphos	24.160	2	267 > 159	20	323 > 267	25
46	Phenthoate	24.265	2	274 > 121	10	274 > 125	20
47	gamma-Chlordane	24.664	2	373 > 266	30	373 > 301	10
48	Methidathion	24.761	2	145 > 85	10	145 > 58	15
49	Bromophos-ethyl	24.794	2	359 > 303	28	359 > 331	10
50	o,p′-DDE	24.851	2	246 > 176	30	248 > 176	30
51	Tetrachlorvinphos	25.092	2	329 > 109	20	331 > 109	25
52	alpha-Chlordane	25.172	2	373 > 266	30	373 > 301	10
53	Iodofenphos	25.612	2	377 > 362	20	377 > 250	25
54	Prothiofos	25.677	2	267 > 239	10	309 > 239	10
55	Profenofos	25.825	2	337 > 267	15	339 > 269	10
56	p,p′-DDE	25.948	2	246 > 176	30	248 > 176	30
57	Oxadiazon	26.108	2	258 > 175	10	258 > 112	25
58	o,p′-DDD	26.296	2	235 > 165	25	237 > 165	20
59	Endrin	26.867	2	263 > 193	30	281 > 245	10
60	Chlorfenapyr	27.008	2	247 > 227	15	247 > 200	25
61	Chloropropylate	27.228	2	251 > 139	10	251 > 111	30
62	o,p′-DDT	27.591	2	235 > 165	15	237 > 165	15
63	p,p′-DDD	27.591	2	235 > 165	20	237 > 165	20
64	Ethion	27.719	2	231 > 129	25	231 > 203	10
65	Triazophos	28.196	2	257 > 162	10	257 > 119	25
66	Ofurace	28.416	2	232 > 158	20	281 > 232	5
67	Cyanofenphos	28.529	2	169 > 141	5	185 > 157	10
68	Quinoxyfen	28.558	2	307 > 237	20	307 > 272	20
69	Endosulfan sulfate	28.561	2	272 > 237	15	387 > 253	10
70	p,p′-DDT	28.704	2	235 > 165	20	237 > 165	20
71	Trifloxystrobin	28.718	2	116 > 89	15	190 > 130	10
72	Spiromesifen	29.654	3	272 > 254	5	272 > 209	10
73	Pyridaphenthion	29.825	3	340 > 199	10	340 > 109	20