Pesticide Analysis in Drinking Water with Disk Extraction and Large Volume Injection

A Residue Application for GC/MS/MS Triple Quadrupole Analysis

Application Note

Food Testing and Agriculture

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Abstract

This application note describes a method based on EPA Method 525.2 [1] with modifications in conditioning, elution, and extraction steps to provide better recovery rates for 30 pesticides, including isomers and metabolites. The EPA method concentrates the final extract volume to near dryness with nitrogen flow and reconstitutes with 1 mL of ethyl acetate. This concentration step is time demanding, and could increase the risk of sample contamination. We also compare a 2 µL injection with a 50 µL large volume injection (LVI). To reduce analysis time, and eliminate the concentration step, LVI was used to inject 50 µL of extract directly to the injection port, where concentration occurred. The recovery rates for six replicates, at the limit of quantification (LOQ), ranged from 70 to 88%. RSDs were 2.2 to 18%. The LOQs for most of the 30 pesticides were 0.05 µg/L. LOQs were 0.02 µg/L for alachlor, and 0.10 µg/L for carbaryl and endosulfan sulfate. The limits of detection (LOD) ranged from 0.01 to 0.09 µg/L. The 2 µL injection method was used to evaluate 14 brands of mineral water purchased from a local supermarket.

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Introduction

Water is a pathway for pesticide dissemination into the environment. The use of pesticides and their possible effects on human and environmental health have become the target of discussion in the scientific community, because potentially contaminated water resources can be used for human consumption. Brazil is one of the largest pesticide consumers in the world, and is responsible for consumption of more than 85% of these pesticides in Latin America. Due to the possible risks from pesticide residues in water for human consumption, water quality must be monitored. Traditional methods employ liquid/liquid extraction with large volumes of organic solvent. For our method, extraction was performed using a C18 SPE disk that requires much less solvent for elution. The multimode inlet (MMI) installed on the Agilent 7890 GC with an Agilent 7000B Triple Quadrupole GC/MS was operated in hot splitless mode for 2 µL injections, and solvent elimination mode for injections of 50 µL. The two methods gave comparable recoveries and linearity, but large volume injection avoided the concentration step required for 2 µL injections. Additionally, the use of analyte protectants provided better peak shape and response for several of the pesticides. Calibration curves for each pesticide were prepared at seven levels (three replicates) to quantify pesticide residues, after the optimal analytical conditions were established.

Experimental

Reagents and solvents

Reagents included methanol and acetonitrile (HPLC grade, Tedia, Brazil), hexane, acetone, ethyl acetate, and dichloromethane (HPLC grade, J.T. Baker), and anhydrous sodium sulfate, D-sorbitol, and L-gulonolactone (Sigma-Aldrich, Corp.). Water from Milli-Q was used for preparing blanks.

Analyte protectant solution (AP)

The stock solution of L-gulonolactone (p/n 310301) was prepared by weighing 500 mg into a 10 mL volumetric flask, adding 4 mL of water, and bringing to volume with acetonitrile. D-sorbitol (p/n 240850) stock solution was prepared by weighing 500 mg into a 10 mL volumetric flask, adding 5 mL of water, and bringing to volume with acetonitrile. A composite solution containing 20 mg/mL L-gulonolactone and 10 mg/mL D-sorbitol was prepared by adding 4 mL of stock L-gulonolactone and 2 mL of D-sorbitol to a 10 mL volumetric flask, and bringing to volume with acetonitrile [2].

Standards

Forty-seven pesticides, purchased from Dr. Ehrenstorfer (Augsberg, Germany), were prepared at 1,000 µg/mL each in isooctane. Aliquots of these solutions were combined to prepare a working solution of every pesticide at 1 µg/mL in ethyl acetate. For large volume injection, the calibration curve solution was prepared by spiking the blank sample extract to give similar solvent mixtures as in the samples.

Sample preparation

The extraction of pesticides from 1 L water samples was performed using a SPEC (Agilent Technologies, Inc.) six-position manifold (p/n A712). The manifold allows the analyst to process from one to six samples simultaneously using SPEC disk holders and SPEC (C18AR, 47 mm, p/n A74819) extraction disks. The disks were conditioned with 10 mL dichloromethane, 10 mL ethyl acetate, and 10 mL of methanol.

The sample was adjusted to < pH 2, and 5 mL of methanol was added, then it was transferred to a 1 L flask and filtered, controlling the flow so that the sample would finish passing through the disk in about 20 minutes at a 50 to 100 mL/min constant flow rate. Disks were dried on the vacuum manifold for about 20 minutes. The pesticides retained in the disk were extracted using 3 mL of methanol, three 5 mL aliquots of ethyl acetate, and then three 5 mL aliquots of dichloromethane. The extract was filtered using 5 to 7 g anhydrous sodium sulfate to remove any water residue with the aid of two 3 mL aliquots of dichloromethane. After this, two injection methods were applied. For 2 a µL injection, the solution was concentrated to near dryness and adjusted with ethyl acetate to 1 mL. For large volume injection, the extract was adjusted to 30 mL with ethyl acetate to have a consistent final volume, then injected without any concentration. Figure 1 summarizes the extraction process.

Use of analyte protectant

A common problem in GC is analyte losses or peak tailing due to undesired interactions with active sites in the inlet and column. Analytes that give poor peak shapes or degrade have higher detection limits, are more difficult to identify and integrate, and are more prone to interferences than stable analytes that give narrow peaks [4]. To overcome this problem, a composite solution of 20 mg/mL L-gulonolactone and 10 mg/mL D-sorbitol was prepared as AP. For a large volume injection, 40 µL of this solution was added to 1,160 µL of final extract, resulting in a final volume of 1,200 µL. For 2 µL injections, the analyte protectant solution was transferred to a 2 mL vial and positioned at the L2 position of the autosampler. Using the sandwich injection function of the Agilent 7693 GC Autosampler, the syringe was programmed to take an aliquot of 0.2 µL of AP solution from the L2 position and then 2 µL of sample, injecting them together so that mixing occurred in the injection port. The advantage of this procedure is the ease of method setup. However, care must be taken to avoid contaminating samples by exchanging the AP vial often. Moreover, washing the syringe with two solvents, isooctane as solvent A and ethyl acetate as solvent B, is essential to keep the needle free of contamination.

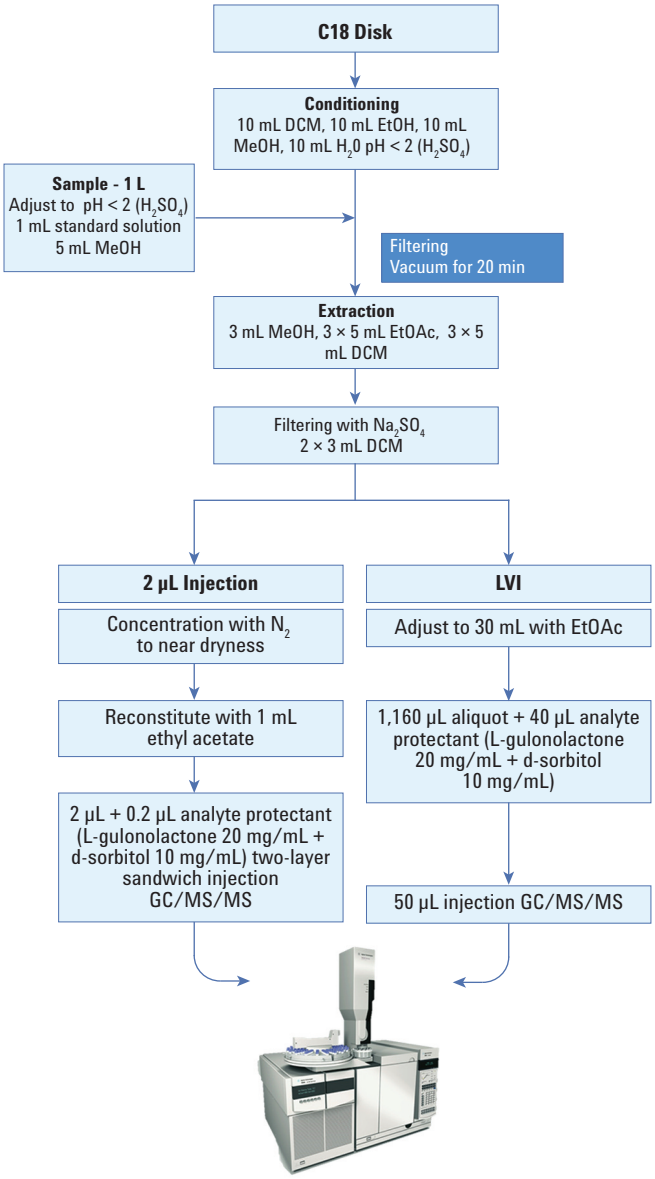

Figure.1 Flow diagram for pesticide extraction from water.

Instrumentation

The analyses were done on an Agilent 7890 GC with an Agilent 7000B Triple Quadrupole GC/MS/MS system. An Agilent J&W HP-5ms Ultra Inert GC column (p/n 19091S-433UI) and Ultra Inert splitless liner (p/n 5190-3167) were used to provide an inert flow path from the inlet to the detector. Tables 1 and 2 show the experimental conditions for the two different types of injection.

Table 1. Instrument parameters for the Agilent GC/MS/MS system for 2 µL injection with sandwich injection of analyte protectants.

Parameter	Value		
GC	Agilent 7890 Series		
Autosampler	Agilent 7693A Automatic Liquid Sampler and sample tray		
	Syringe size 5 µL		
	Injection volume 2 µL		
	Pre- and postinjection solvent A (isooctane), 5		
	Pre- and postinjection solvent B (ethyl acetate), 5		
	Sample pumps 6		
	Injection type: two-layer sandwich		
	L2 volume: 0.2 µL (analyte protectant solution)		
Inlet	Multimode inlet (MMI)		
Injection mode	Splitless		
Inlet temperature	280 °C		
Oven profile		70 °C	2 min
	25 °C/min	150 °C	0
	3 °C/min	200 °C	0
	8 °C/min	280 °C	5 min
Column	Agilent J&W HP-5ms Ultra Inert, 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)		

Table 2. Instrument parameters for the Agilent GC/MS/MS system for 50 µL injections with analyte protectants added to the sample.

Parameter	Value		
GC	Agilent 7890 Series		
Autosampler	Agilent 7693A Automatic Liquid Sampler and sample tray		
	100 µL syringe		
	Injection volume, 50 µL		
	Pre- and postinjection solvent A (isooctane), 5		
	Pre- and postinjection solvent B (ethyl acetate), 5		
	Sample pumps, 6		
	Injection type, standard		
Inlet	Multimode inlet		
Injection mode	Solvent vent		
MMI temperature		90 °C	0.25 min
	600 °C/min	325 °C	5 min
Purge flow to split vent	60 mL/min at 2.75 min		
Vent flow	100 mL/min until 0.25		
Vent pressure	5 psi		
Oven profile		70 °C	2 min
	25 °C/min	150 °C	0
	3 °C/min	200 °C	0
	8 °C/min	280 °C	5 min

LVI method development and optimization on the MMI were based on the solvent elimination calculator in the instrument control software [3]. MRMs of the compounds were selected using the Agilent G9250AA Pesticide and Environmental Pollutants MRM database.

Results and Discussion

The experiment started with validation of the 2 µL injection method and analysis of mineral water purchased from a local supermarket. The calibration curve was tested with and without use of analyte protectants to check efficiency for this application. Figures 2 to 4 show the benefits of using AP for some compounds, significantly improving peak shape and calibration curve.

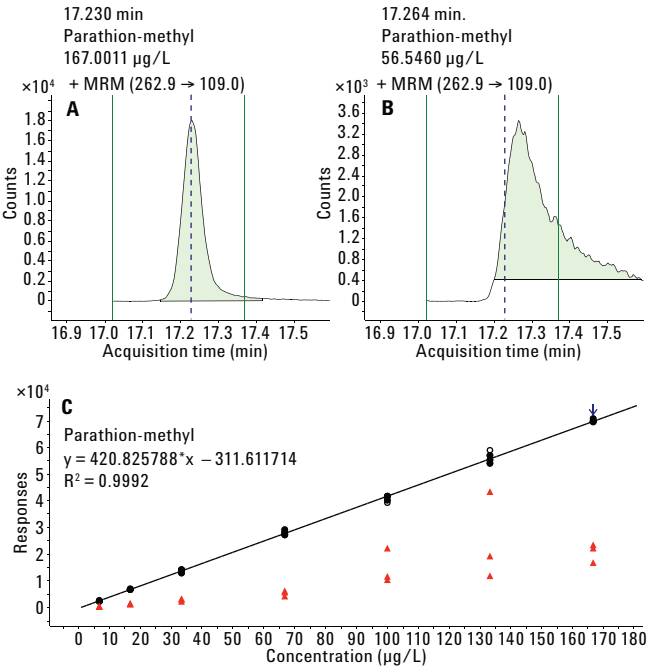

Figure 2. Parathion-methyl peak injected with (A) and without (B) analyte protectants, (C) calibration curve of parathion-methyl using analyte protectant. The red triangles are injections without protectant.

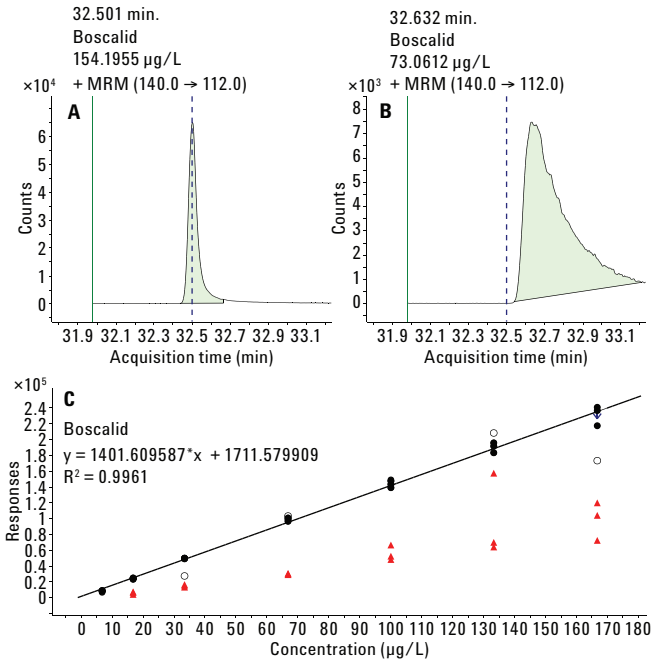

Figure 3. Boscalid peak injected with (A) and without (B) analyte protectants. C) Calibration curve of boscalid using analyte protectant. The red triangles are injections without protectant.

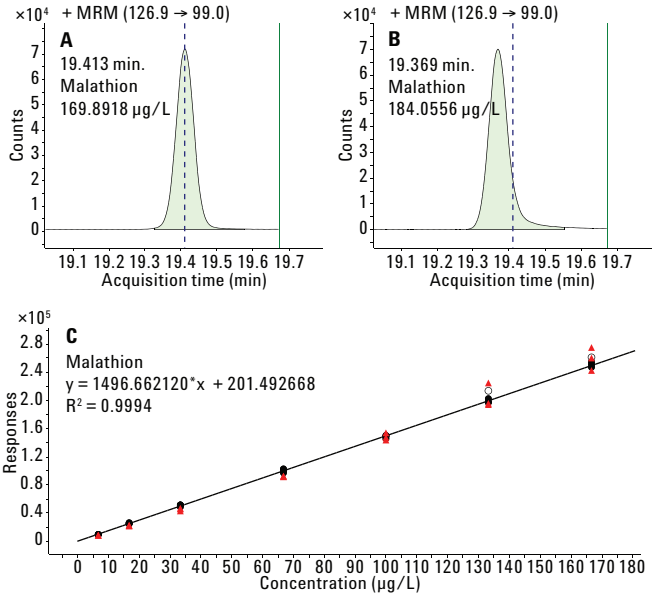

Figure 4. Malathion peak injected with (A) and without (B) analyte protectants. C) calibration curve of malathion using analyte protectant. The red triangles are injections without protectant.

The linearity of the calibration curves is slightly better with AP. However, the accuracy for the first two levels of the calibration curve makes a difference in the calculated concentration. Table 3 shows the calculated concentrations for malathion and parathion-methyl at each calibration level based on calibration curves generated from samples with and without AP. Even for malathion, where the correlation coefficients are similar (R^2 = 0.9982 with AP and 0.9914 without AP), there is a substantial difference at the lowest calibration level. The effect is even larger for parathion-methyl (R^2 = 0.9985 with AP and 0.9604 without AP). Clearly, analyte protectants improve calibration accuracy for these compounds, especially at the lowest levels. Peak shape improvements for most chlorinated compounds were much less because they were less affected by active sites in the flow path. Overall, the use of analyte protectants offers a more consistent response throughout the injection sequence, and better calibration accuracy.

The 14 brands of mineral water were analyzed with the 2 µL injection and analyte protectant method. None of the samples evaluated contained any of the target pesticides above the limit of quantification (LOQ).

Table 3. Comparison of calibration accuracy between calibration curves with and without analyte protectants.

		With AP		Without AP
Expected concentration (pg/µL)	Accuracy (%)	Calculated concentration (pg/µL)	Accuracy (%)	Calculated concentration (pg/µL)
	Malathion			
6.67	101.10	6.74	138.60	9.24
16.67	100.00	16.66	104.80	17.46
33.33	101.90	33.98	100.30	33.43
66.67	100.70	67.16	94.10	62.72
100.00	99.30	99.25	101.70	101.68
133.33	100.20	133.59	95.60	127.40
166.67	100.80	167.98	101.60	169.37
	Parathion-methyl			
6.67	105.00	7.01	178.90	11.93
16.67	101.30	16.88	112.70	18.79
33.33	98.30	32.76	99.80	33.25
66.67	100.00	66.66	87.80	58.55
100.00	99.40	99.40	106.00	106.05
133.33	99.40	132.49	97.90	130.53
166.67	100.20	167.01	98.30	163.83

After verifying the importance of using analyte protectants, calibration curves were prepared for large volume injection to compare the response with the 2 µL injection calibration curve. The calibration curve solution was prepared to have the same mass of compounds introduced in the column as the 2 µL injection. The first level of the curve, for example the 2 µL injection, was 6.67 pg/µL. Therefore, 13.33 pg was injected on the column. Thus, for the first calibration level of a large volume injection, a solution containing each of the pesticides at 0.27 pg/µL was prepared so that the same mass would be injected with the 50 µL method as with the 2 µL method. To achieve this concentration, we used 960 µL of blank extract, 200 µL of pesticide working solutions, and 40 µL of analyte protectant, as shown in Table 4.

Table 4. Preparation of a set of standards in blank extract for large volume injection.

Standard	Pesticide working solution		Blank extract	AP solution
Concentration (pg/µL)	Concentration (pg/µL)	Volume (µL)	Volume (µL)	Volume (µL)
0.27	1.6	200	960	40
0.67	4.0	200	960	40
1.33	8.0	200	960	40
2.67	16.0	200	960	40
4	24.0	200	960	40
5.33	32.0	200	960	40
6.67	40.0	200	960	40

Table 5 compares the recovery for both injection techniques with calibration curves prepared as mentioned. Compounds that had improved peak shape with the use of protectant (marked with *). The benefit in peak shape is mostly seen for the more unstable compounds while more stable compounds, such as malathion, show little effect.

Table 5. Multiple reaction monitoring (MRM) transitions, retention time (RT), limit of detection (LOD), limit of quantification (LOQ), and recovery rate (REC) for large volume and 2 µL injections.

					LVI mode				Splitless mode 2 µL		
	Compound	MRM Transitions		RT	LOD (µg/L)	LOQ (µg/L)	REC (RSD)(%)	RSDINJ (%)	LOD (µg/L)	LOQ (µg/L)	REC (RSD)(%)
1	Trifluralin	305.9 → 264.0	264.0 → 160.1	12.2	0.02	–	65.1 (6.0)	1.1	0.03	–	57.1 (9.5)
2	BHC-*alpha*	216.9 → 181.0	218.9 → 183.0	12.7	0.01	0.05	88 (3.0)	1.5	0.03	0.05	78 (10.5)
3	Carbofuran*	181.0 → 145.0	216.9 → 181.1	13.9	0.01	0.05	81 (3.5)	1.3	0.03	0.05	80 (10.8)
4	BHC-*beta*	164.2 → 149.1	149.1 → 121.1	13.7	0.01	0.05	85 (3.5)	1.5	0.03	0.05	88 (8.9)
5	Clomazone*	125.0 → 89.0	204.1 → 107.1	13.9	0.01	0.05	80 (2.2)	1.4	0.03	0.05	94 (8.5)
6	BHC-*gamma*	216.9 → 181.0	181.0 → 145.0	14.1	0.01	0.05	83 (4.6)	1.5	0.03	0.05	84 (9.4)
7	Terbufos	230.9 → 175.0	230.9 → 129.0	14.4	0.01	–	67.2 (4.3)	1.3	0.11	–	17.4 (36.9)
8	BHC-*delta*	181.1 → 145.1	217.0 → 181.1	15.2	0.01	0.05	85 (3.4)	0.7	0.02	0.05	91 (8.0)
9	Chlorothalonil*	263.8 → 168.0	263.8 → 229.0	15.4	0.01	–	49.9 (3.2)	1.4	0.03	0.05	97.2 (9.8)
10	Propanil *	161.0 → 99.0	161.0 → 90.0	16.9	0.02	0.05	73 (6.0)	4.7	0.04	0.05	107 (12.3)
11	Parathion-methyl*	144.0 → 115.1	144.0 → 116.1	17.5	0.01	0.05	78 (4.0)	2.8	0.04	0.05	88 (11.7)
12	Vinclozolin*	271.7 → 236.9	273.7 → 238.9	17.4	0.01	0.05	85 (2.9)	1.4	0.02	0.05	91 (8.0)
13	Heptachlor	262.9 → 109.0	125.0 → 47.0	17.2	0.03	–	55.4 (11.6)	3.3	0.03	–	54.9 (10.7)
14	Carbaryl*	187.0 → 124.0	197.9 → 145.0	17.3	0.01	0.10	73 (4.3)	1.5	0.03	0.10	96 (11.6)
15	Alachlor	188.1 → 160.2	160.0 → 132.1	17.7	0.02	0.02	81 (5.8)	1.7	0.05	0.02	73 (17.7)
16	Malathion	126.9 → 99.0	172.9 → 99.0	19.4	0.01	0.05	76 (3.7)	1.3	0.03	0.05	85 (11.4)
17	Chlorpyrifos	196.9 → 169.0	198.9 → 171.0	19.8	0.01	0.05	71 (2.7)	1.1	0.03	0.05	75 (8.8)
18	Parathion*	138.9 → 109.0	290.9 → 109.0	19.9	0.01	0.05	81 (3.6)	1.9	0.03	0.05	79 (10.5)
19	Bentazone*	119.0 → 92.0	198.0 → 119.0	20.5	0.01	–	63.4 (4.1)	4.1	0.04	0.05	70.3 (13.3)
20	Heptachlor exo	182.9 → 154.9	182.9 → 118.9	21.5	0.04	0.05	76 (14.6)	2.2	0.02	0.05	86 (7.5)
21	Heptachlor endo	352.8 → 262.9	354.8 → 264.9	21.2	0.02	0.05	77 (6.9)	1.6	0.02	0.05	78 (7.8)
22	Pendimethalin	251.8 → 162.2	251.8 → 161.1	21.5	0.01	0.05	75 (4.0)	4.3	0.03	0.05	70 (9.8)
23	Fipronil*	366.8 → 212.8	350.8 → 254.8	22.4	0.01	0.05	85 (4.6)	7.2	0.03	0.05	92 (11.1)
24	Procymidone*	96.0 → 67.1	96.0 → 53.1	22.5	0.01	0.05	74 (5.0)	2.3	0.03	0.05	92 (9.6)
25	DDE-*o,p'*	246.0 → 176.2	248.0 → 176.2	22.9	0.03	–	58.1 (10)	1.8	0.03	–	65.1 (10)
26	Endosulfan	194.9 → 159.0	194.9 → 160.0	23.0	0.01	0.05	83 (3.7)	1.3	0.03	0.05	82 (8.9)
27	Dieldrin	235.0 → 165.2	237.0 → 165.2	24.6	0.01	0.05	78 (3.9)	2.2	0.03	0.05	80 (11.6)
28	Profenofos*	246.1 → 176.2	315.8 → 246.0	24.3	0.01	0.05	72 (3.6)	2.9	0.03	0.05	89 (8.7)
29	DDE-*p,p*	262.9 → 193.0	277.0 → 241.0	24.2	0.03	–	58.2 (9.7)	2.2	0.03	–	63.4 (10.7)
30	DDD-*o,p'*	207.9 → 63.0	338.8 → 268.7	24.3	0.02	0.05	70 (5.9)	2.1	0.02	0.05	77 (8.2)
31	Endosulfan II	136.9 → 102.0	246.9 → 227.0	25.5	0.07	0.05	71 (18.0)	2.5	0.05	0.05	89 (9.4)
32	Endrin	234.9 → 165.1	236.9 → 165.2	25.9	0.01	0.05	81 (3.7)	1.7	0.03	0.05	97 (15.4)
33	Chlorfenapyr	206.9 → 172.0	194.9 → 158.9	25.4	0.01	–	66.7 (4.8)	3.0	0.02	0.05	76.3 (8.5)
34	DDD-*p,p'*	262.8 → 193.0	244.8 → 173.0	25.4	0.02	0.05	71 (5.7)	4.8	0.02	0.05	80 (7.6)
35	DDT-*o,p*	235.0 → 165.2	237.0 → 165.2	25.9	0.03	–	53.3 (10.4)	5.1	0.03	–	54.2 (8)
36	Endosulfan sulfate	235.0 → 165.2	237.0 → 165.2	27.1	0.01	0.10	81 (3.4)	1.7	0.03	0.10	99 (10.4)
37	DDT-*p,p'*	271.9 → 237.0	273.8 → 238.9	26.9	0.03	–	52.5 (10.4)	0.7	0.02	0.05	71.6 (9.4)
38	Iprodione*	187.0 → 124.0	243.9 → 187.0	28.4	0.07	0.05	74 (4.5)	4.0	0.03	0.05	104 (7.8)
39	Bifenthrin	181.2 → 166.2	181.2 → 165.2	28.8	0.06	–	48.9 (21.2)	1.6	0.02	–	50.9 (13.4)
40	Methoxychlor, *p,p'*-	227.0 → 169.1	227.0 → 141.1	28.8	0.03	–	63.9 (8.5)	4.8	0.03	0.05	87.8 (8.6)
41	Tetradifon*	158.9 → 131.0	226.9 → 199.0	29.3	0.05	0.05	72 (15.3)	3.5	0.04	0.05	96 (8.0)
42	Cyhalothrin	208.0 → 181.0	197.0 → 141.0	30.3	0.06	–	49.1 (20.5)	1.9	0.03	–	47.9 (11.2)
43	Permethrin I	183.1 → 168.1	183.1 → 165.1	31.2	0.07	–	45.5 (21.7)	1.3	0.03	–	51.5 (12.4)
44	Permethrin II	182.9 → 168.1	182.9 → 155.1	31.4	0.07	–	47 (23.8)	3.6	0.04	–	53.5 (11.5)
45	Boscalid*	140.0 → 112.0	140.0 → 76.0	32.5	0.01	0.05	73 (4.5)	3.1	0.05	0.05	112 (8.4)
46	Fenvalerate I*	167.0 → 125.1	208.9 → 141.1	33.9	0.06	–	47.7 (21.1)	2.2	0.04	–	49.3 (11.9)
47	Fenvalerate II*	181.0 → 152.1	224.9 → 119.0	34.3	0.06	–	43.2 (21.3)	4.2	0.05	–	51.6 (17.5)

Recovery (n = 5) (REC), relative standard deviation (RSD), precision of the LVI injection instrument method at 4 µg/L (n = 5) (RSD INJ).

*Compounds that had improvement in peak shape with the use of analyte protectants.

The calibration curve injected by large volume injection (50 µL) with seven levels and three replicates in sequence gave a linearity of $R^2 > 0.9900$ for most compounds, except bentazone ($R^2 = 0.9895$) and endrin ($R^2 = 0.9766$). These results were even better than 2 µL injection, which produced $R^2 > 0.99$ for most of the compounds, except:

- Carbofuran ($R^2 = 0.9688$)
- Propanil ($R^2 = 0.9874$)
- Carbaryl ($R^2 = 0.9549$)
- Alachlor ($R^2 = 0.8115$)
- Bentazone ($R^2 = 0.9808$)
- Dieldrin ($R^2 = 0.9476$)
- Endrin ($R^2 = 0.9818$)
- Endosulfan II ($R^2 = 0.9771$)
- Bifenthrin ($R^2 = 0.9774$)
- Boscalid ($R^2 = 0.9698$), and
- Fenvalerate ($R^2 = 0.9842$).

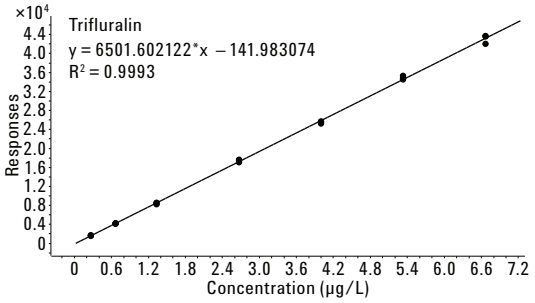

Figure 5. Calibration curve of trifluralin performed by large volume injection with three replicated injections.

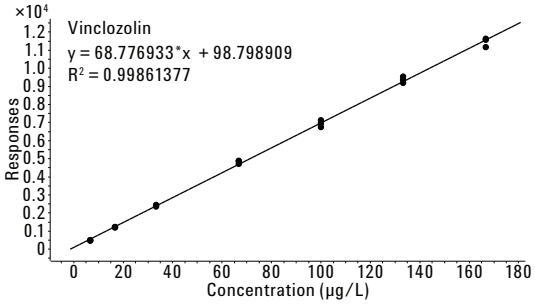

Figure 6. Calibration curve of vinclozolin performed by large volume injection with three replicated injections.

All had acceptable linearity in the calibration curve for quantification after selecting points from replicated injections. The better linearity for a large volume injection can be explained by the use of analyte protectant added to the sample solution, compared to a 2 µL sandwich injection. The addition of analyte protectant to the sample vial produced more homogenous mixtures, thus, sealing the active sites more efficiently, and increasing the response of target compounds and resolution of chromatographic peaks. Figures 5 and 6 demonstrate the excellent linearity of calibration curves from large volume injection.

From the 47 pesticides analyzed, 31 had recovery from about 70 to 88% for LVI, and about 70 to 112% for 2 µL injections. Five compounds (chlorothalonil, bentazone, chlorfenapyr, DDT-p,p', and methoxychlor-p,p') had more than 70% recovery only for a 2 µL injection. The compounds we could not recover with the 2 µL also were not recovered through the LVI method. For these compounds, the extraction method should be optimized by selecting a more appropriate solvent and optimizing the volume used. The lower recovery for LVI may be improved by increasing the concentration of AP. At the concentrations used, relatively stable compounds, such as heptachlor, gave increased response even with its long residence time inside the liner. The lower recovery for methoxychlor may be due to the degradation of the standard, since it is light sensitive.

To check the precision of the 50 µL LVI injection method, a sample containing all 47 pesticides at 4 ppb was injected six times. RSD% is shown in Table 5 in the column labeled RSDINJ. Only eight compounds had RSD values above 4%, and all were below 6%, as shown in Table 5. The use of internal standards could increase precision even more, making possible the use of a large volume injection for pesticide analysis. This technique can also lower the detection limit if needed.

The LOQs were considered to be the lowest level of concentration spiked, with acceptable recovery and precision, for each compound. The LODs were calculated from the RSD% of the concentration at LOQ multiplying by three and dividing by 1,000, with values between 0.01 to 0.07 µg/L for LVI, and 0.02 to 0.05 µg/L for the 2 µL injection.

Conclusions

The analysis of water using SPE disk extraction is a technique that reduces solvent consumption, making it economically and environmentally a better choice. Combining large volume injection and using analyte protectants for improvement of chromatographic resolution, 30 pesticides showed good recoveries with this fast extraction procedure. This study demonstrates the suitability of the method for analyzing selected pesticides in drinking water, the importance of using analyte protectants, and the possibility of replacing the traditional concentration step with large volume injection. In addition, the method was applied to 14 brands of bottled mineral water to evaluate the products. None contained any of the target pesticides above the LOQ.

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Printed in the USA
June 18, 2015
5991-6008EN

Agilent Technologies