A Rapid Method for Trace Analysis of Organophosphorus Pesticides in Drinking Water

Application Note

Environmental

Authors

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Abstract

A simple and quick method for the determination of organophosphorus pesticides (OPs) in drinking water has been developed. After sample extraction with methylene chloride, analysis was directly carried out without further treatment using GC with a specific detector FPD on a DB-1701P column. A linear relationship between concentration and peak area was obtained within the range of 0.005 to 0.500 ng with correlation coefficients greater than 0.999 and detection limits less than 0.03 µg/L. Recoveries of six OPs at spiked levels of 0.50, 2.50, and 4.50 µg/L ranged from 88 to 104% These OPs were reproducibly detected well below the maximum residue limits (MRLs) of EPA Method 525 and European Union regulations for pesticide residues in drinking water.

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Introduction

Organophosphorus pesticides (OPs) are among the most common pesticides used in industrialized countries. These compounds are very toxic when absorbed by human organisms because of acetylcholinesterase deactivation. Due to their universal application in agriculture, OPs represent an important source of environmental contamination. Maximum residue limits (MRLs) have been established for pesticides in foodstuff and drinking water in most countries to avoid any adverse impact on public health. U.S. Environmental Protection Agency (EPA) Method 525 has a maximum allowable risk level for OPs in drinking water ranging from 0.001 to 0.25 mg/L [1]. In the European Union (EU), a maximum allowable concentration of 0.0001 mg/L for each individual pesticide in drinking water is in force. For evaluation of environmental waters and water sources for preparation of drinking water, highly sensitive methods for the determination of OPs in surface water, ground water, and drinking water are required.

Most analytical methods for pesticide analysis of OPs in aqueous samples are based on chromatographic techniques. Gas chromatography (GC) with nitrogen-phosphorus detection [2] (NPD), mass spectrometry [1] (MS), and flame photometric detection [3] (FPD) has traditionally been the method of choice for the analysis of OPs. FPD is a highly selective and sensitive detector that works by measuring the emission of phosphorus- (or sulfur-) containing species, which will minimize interferences from materials that do not contain phosphorus. Since the chromatograms of extracts were free from interfering peaks, no cleanup was needed. For the OPs analysis, FPD is a potentially efficient detector for monitoring water samples.

OPs are active compounds that can be adsorbed onto active sites throughout the sample flow path, including the injection port, liner, golden seal, capillary column, and any metal detector parts. A capillary column is one of the major sources of active sites owing to its large surface area and the long residence time of an analyte in the column. Peak tailing, response loss, and compound degradation will occur for these active compounds when the column is not inert.

The DB-1701P column was specially designed for the analysis of pesticides [4]. It has a better inertness for active compounds, which offers improved resolution, better selectivity, and higher sensitivity for OPs analysis. This application note presents a sensitive method developed on a DB-1701P column using GC/FPD for the analysis of OPs in drinking water.

Experimental

Instrument

An Agilent 7890 GC equipped with split/splitless capillary inlets and FPD was used for this work. The inlets were fitted with a long-lifetime septa (P/N 5183-4761) and single-taper helix liner (P/N 5188-5397). Injections were done using 10-µL syringes (P/N 9301-0714).

Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination and are silanized. Columns should be installed and maintained properly.

GC Conditions

Column	DB-1701P, 30 m × 0.32 mm × 0.25 µm (P/N 122-7732)
Carrier gas	Helium, constant pressure mode, 25 psi
Inlet	Split/splitless @ 270 °C, splitless
Oven temperature	60 °C (1 min); 30 °C/min to 180 °C (7 min); 15 °C/min to 220 °C (3 min)
Detector	250 °C, FPD in phosphorus mode
Detector gas	H2 75 mL/min, air 100 mL/min, makeup (N2) 60 mL/min
Injection size	1 µL

Standard Solution

Six OP stock solutions (see Table 1) were purchased from China National Standards Research Center. These six OPs are commonly used in agriculture and are strictly monitored. A mix stock solution (10 mg/L) of OPs was prepared in acetone. Six calibration standards solutions were prepared by diluting the stock solution with acetone. The calibration standard solutions should be stored in tightly sealed bottles at temperatures below 5 °C.

Table 1. Six Organophosphorus Pesticides Solutions

Compound	Molecular formula	Molecular weight	Standard solution (mg/mL) in methanol
1 Dichlorvos	$C_4H_7Cl_2O_4P$	220.98	0.89
2 Dimethoate	$C_5H_{12}NO_3PS_2$	229.28	1.00
3 Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	350.59	1.00
4 Methylparathion	$C_8H_{10}NO_5PS$	263.63	1.00
5 Malathion	$C_{10}H_{19}O_6PS_2$	330.36	1.02
6 Parathion	$C_{10}H_{14}NO_5PS$	291.26	1.00

Sample Preparation

100 mL of water sample was transferred to a 250-mL separatory funnel. After adding 20 mL of methylene chloride, the separatory funnel was sealed and then shaken vigorously for 1 to 2 minutes with periodic venting to release excess pressure. Once the funnel was still for 10 minutes, the extract for the organic layer was collected. The extraction was repeated twice, using fresh portions of solvent. The resulting three portions of the extracts were combined and dried with anhydrous sodium sulfate, then evaporated to near dryness. The residue was dissolved with 1 mL of acetone and transferred into the sample vial for GC analysis.

Results and Discussion

The separation of six OPs is illustrated in Figure 1. As you can see, all OPs can be baseline separated with highly efficient and symmetrical peaks on the DB-1701P column, which demonstrated significantly reduced peak tailing and adsorption for these challenging analytes.

Linearity and Reproducibility

FPD is a selective detector for sulfur and phosphorus compounds in complex mixtures. The response of the FPD is linear in phosphorus mode. Table 2 shows the linearity range, r^2 values for six OPs calculated from the study. The calibration curve was constructed from data obtained by 1-µL injections of standards at six levels. All the OPs exhibit a wide linear range from 0.005 to 0.500 ng, with r^2 values higher than 0.999, suggesting a good linearity range for low-level OP quantification in drinking water.

Table 2. Linearity and Limit of Detection (S/N = 3)

Compound		Linearity (ng)	Correlation coefficient (R^2)
1	Dichlorvos	0.004 ~ 0.445	0.9993
2	Dimethoate	0.005 ~ 0.500	0.9991
3	Chlorpyrifos	0.005 ~ 0.500	0.9994
4	Methylparathion	0.005 ~ 0.500	0.9993
5	Malathion	0.005 ~ 0.510	0.9993
6	Parathion	0.005 ~ 0.500	0.9993

The reproducibility of the method was investigated by replicate analysis of three levels of OPs (0.050, 0.250, and 0.450 ng) in Table 3. The relative standard deviation (RSD) of the retention time (RT) of the six OPs was lower than 0.017%. Peak areas were reproducible with an RSD of less than 4.0%. Good RT and peak area repeatability ensure reliable qualitative and quantitative analyses.

Table 3. Reproducibility of Peak area and Retention time (n ≥ 10)

		RSD (%) (n ≥ 10)					
Compound		0.050 ng		0.250 ng		0.450 ng	
		Area	RT	Area	RT	Area	RT
1	Dichlorvos	3.364	0.011	1.680	0.007	1.620	0.011
2	Dimethoate	3.904	0.015	1.497	0.017	1.752	0.011
3	Chlorpyrifos	1.303	0.008	1.476	0.010	1.196	0.009
4	Methylparathion	1.963	0.011	1.642	0.009	1.169	0.008
5	Malathion	1.084	0.009	1.842	0.005	1.426	0.006
6	Parathion	1.750	0.006	1.666	0.008	1.300	0.007

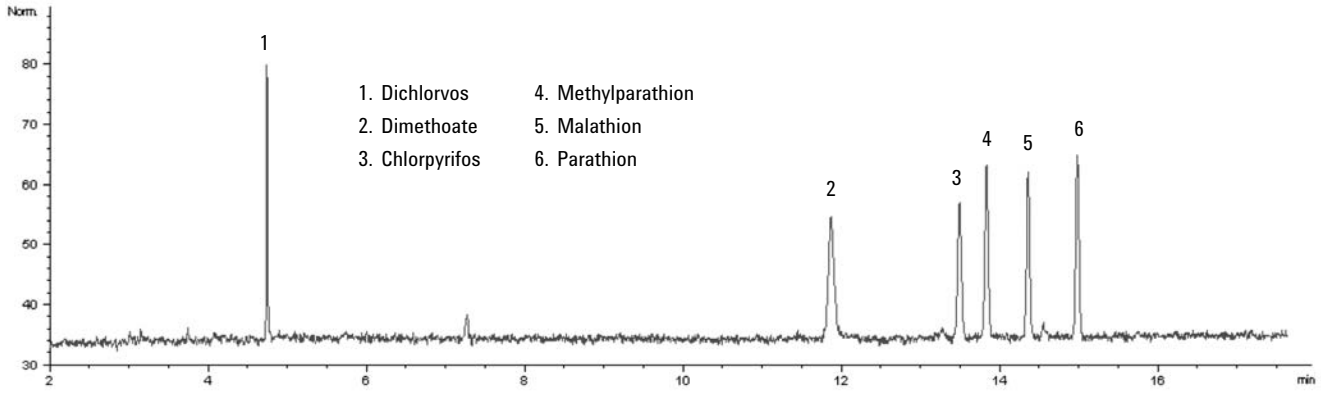

Figure 1. Chromatograms of six OPs standard solution on DB-1701P column.

Recovery and Limit of Detection (LOD)

Table 4 presents the recoveries for spiked water samples. Replicate samples of 100-mL ultrapure water were spiked with OPs at 0.50, 2.50, and 4.50 µg/L. During the study, no target OPs were found in the ultrapure water, so it is regarded as blank water. The spiked samples were treated according to the procedure described in the sample preparation. Excellent recoveries were obtained for all the compounds, ranging from 88 to 104%. Duplicate samples were analyzed and demonstrated that the method has a good repeatability at trace levels (see Figure 2).

Table 4. Recovery of Three Levels of OPs

		Recovery (%)		
Compound		**0.50 µg/L**	**2.50 µg/L**	**4.50 µg/L**
1	Dichlorvos	88.7	90.0	91.2
2	Dimethoate	103.5	98.5	100.7
3	Chlorpyrifos	90.3	90.4	91.0
4	Methylparathion	92.8	92.5	91.6
5	Malathion	92.2	91.6	92.5
6	Parathion	91.8	90.4	91.8

Table 5 lists the LODs of the method and the MRLs of EPA Method 525. The LODs were determined at a signal-to-noise ratio of 3. It demonstrates the high sensitivity of FPD for trace analysis of OPs. The developed method enables quantitative determination of OPs in water solutions at concentration levels lower than 0.03 µg/L, which is about 100 times lower than the MRLs in EPA Method 525. It also meets the requirement of EU limits (0.1 µg/L) in drinking water.

Table 5. Limit of Detection in 100-mL Water Sample

Compound		**LOD (µg/L)**	**MRLs* (µg/L)**
1	Dichlorvos	0.012	1
2	Dimethoate	0.030	80
3	Chlorpyrifos	0.027	30
4	Methylparathion	0.021	20
5	Malathion	0.023	250
6	Parathion	0.020	3

* MRLs in EPA Method 525

Real Sample

In order to check the applicability of the proposed method to real matrices, tap water samples and ultrapure water samples were collected. A 100-mL aliquot of each sample was analyzed following the procedure described in the sample preparation section. Peak areas were used for quantitation. The use of FPD eliminates the interferences that do not contain phosphorus. None of the samples gave peaks that interfered with the determination of the six OPs (Figure 3). In these samples, no OPs were found above the method's LOD.

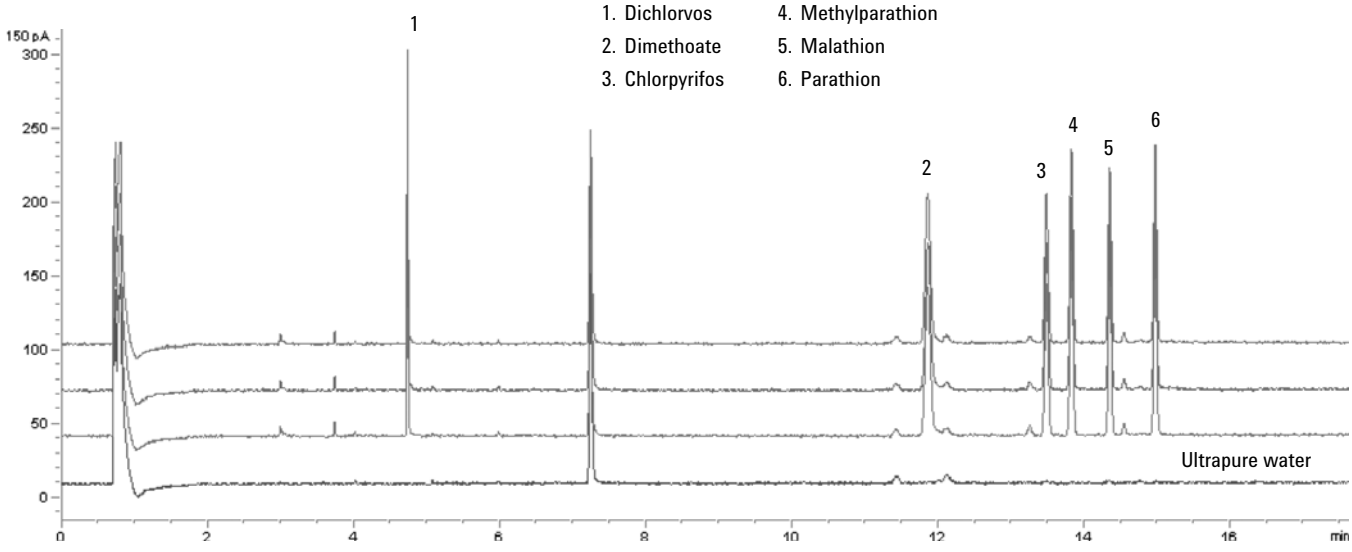

Figure 2. Overlay chromatogram of 0.50-µg/L spiked samples on DB-1701P column.

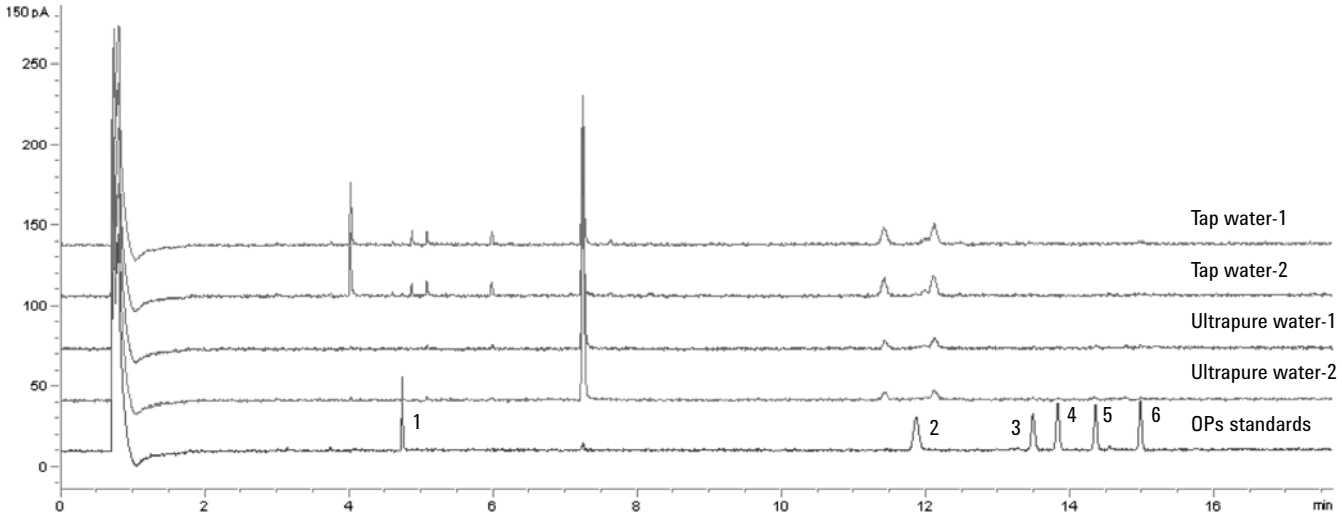

Figure 3. Chromatogram of real water samples on DB-1701P column.

Conclusions

This application note describes a method for the quantification of OPs in drinking water samples. After liquid-liquid extraction and concentration, the sample extracts were directly analyzed on a DB-1701P column using an Agilent 7890 Series GC with FPD. The method provides good linearity, repeatability, and high recovery. It is adequate to determine OPs LODs lower than 0.03 µg/L, which is in full compliance with the MRLs in EPA Method 525 and EU regulations in drinking water. The local drinking water samples were determined to be free of OP contamination.

It is a fast, simple, and economic method to analyze OPs at micro-trace levels. Therefore, it is suitable to control the water quality for OPs according to the MRLs specified in the regulations.

References

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Published in the USA
November 13, 2008
5990-3158EN

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