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Application Note
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Environmental Series

ANALYSIS OF ORGANOPHOSPHORUS PESTICIDES USING GC/PFPD AND METHOD 8141B

Introduction

Organophosphorus pesticides were among the most widely used pesticides until the twenty-first century. They have a variety of uses in agriculture, home, garden, and veterinary practices. Thirty-six are registered in the United States, but because of their additive toxicity, many are being discontinued for use.[1] These pesticides persist in the environment and are present in many agricultural products, often at very low levels, so it is important to identify and quantify their presence using the most up-to-date methodology.

USEPA Method 8141B is often used to analyze organophosphorus (OPP) pesticides. The method specifies flame photometric detection (FPD) or nitrogen – phosphorus detection (NPD). Use of a pulsed flame photometric detector (PFPD) is an alternative to these two detectors.

The PFPD uses a pulsed flame, instead of continuous or static flame of the FPD, which adds a time-dependent variable to the analysis. The PFPD is not subject to the interferences caused by organonitrogen compounds that naturally occur in plant tissue.[2] There are several advantages in using a PFPD, including detectivity and selectivity of the phosphorus species as well as ease of use. The detector can also be configured to simultaneously detect phosphorus and sulfur, producing mutually selective chromatograms thus increasing information gathered for each analysis.[3]

While this is a mature methodology, there have been improvements in instrumentation and column technology which will be explored using new technology and showing an optimized method for OPP pesticides.

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Figure 1. 5383 Detector

Experimental

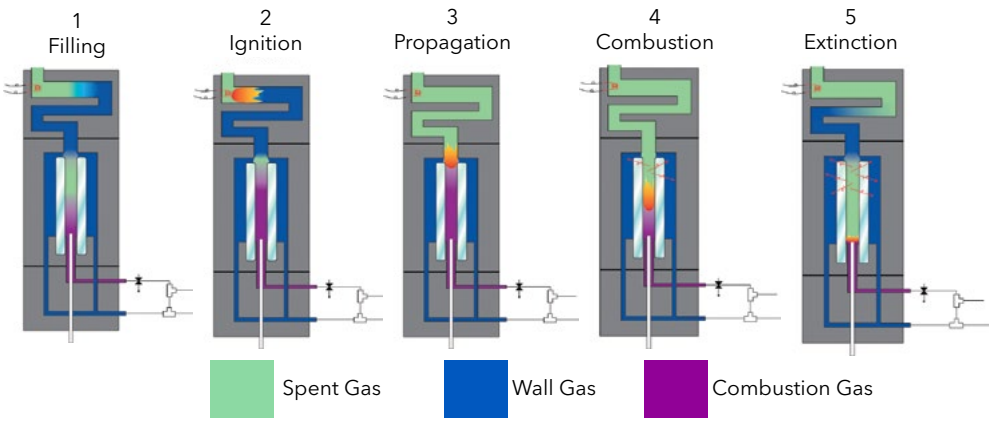
Instrumentation for this study included an OI Analytical 5383 PFPD (Figure1) mounted on an Agilent 7890A GC system with split/splitless injector and G4513A automatic liquid autosampler. See Table 1.

Table 1. Instrument Configuration & Operating Parameters

Agilent 7890A GC & OIA 5383 PFPD	
Inlet	250 °C Pulsed split 20 psi until 0.75 minutes Split ratio 20:1 Agilent Ultra Inert 4 mm precision liner with wool
GC Column	Restek Rtx® – OPPesticides2 30-m x 0.25 mm ID x 0.25 µm df Helium carrier gas, 1.0 mL / min
Oven Program (Agilent 7890A)	80 °C for 1 minute 20 °C / minute to 140 °C 40 °C / minute to 210 °C Hold for 2 minutes 30 °C / minute to 320 °C Hold for 4 minutes Total run time 31.167 minutes
Phosphorus Detection	Pulsed Flame Photometric Detector (PFPD) 3 mm combustor, GG-495 filter, R1924 PMT Detector base temperature 300 °C H_2 / air ratio tuned for optimum sulfur emission 4-11 milliseconds phosphorous gate 1-2 milliseconds hydrocarbon gate

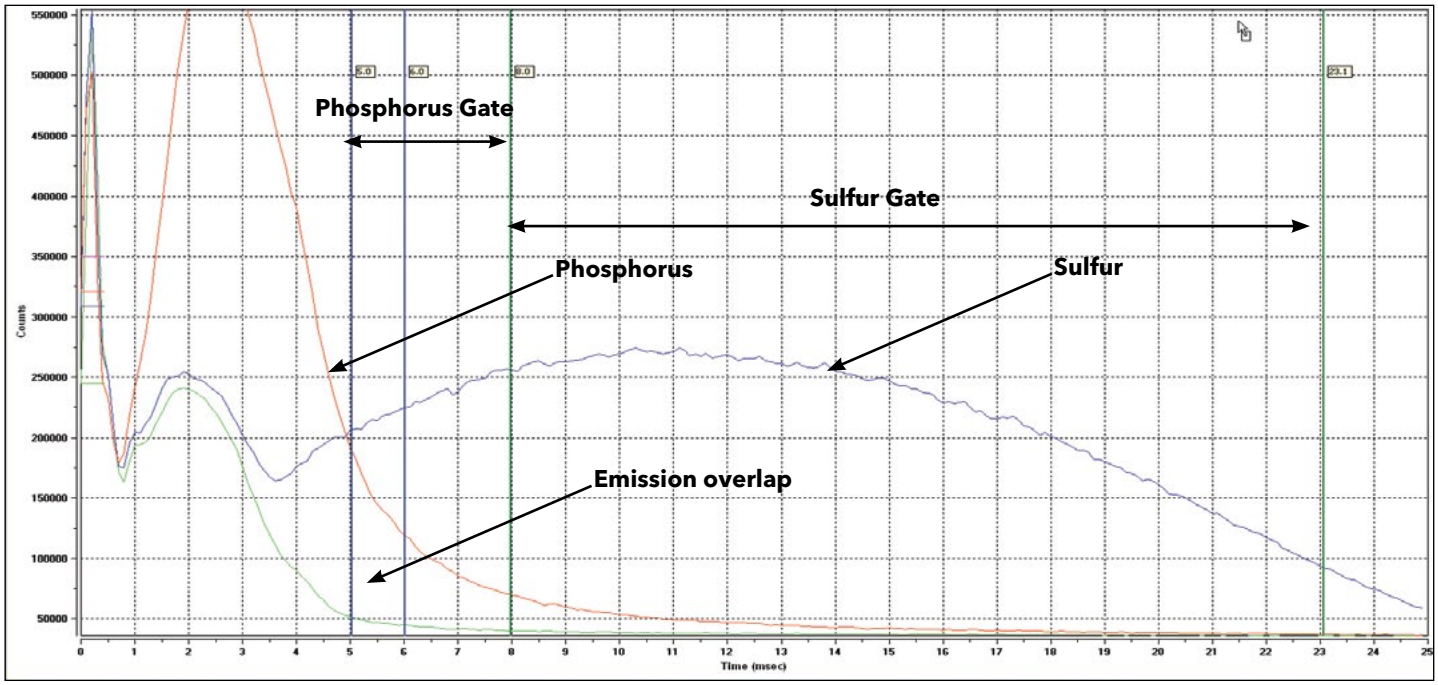
The PFPD uses a hydrogen and air mixture at a flow rate that does not support continuous combustion. The combustor is filled with the ignitable gas mixture; the flame is ignited, then propagates through the combustor, and burns out when all fuel is consumed. See Figure 2.

Figure 2. Flame Propogating Cycle



The cycle is repeated continuously at a rate of 3-4 hertz. As a result of the flame pulsing, the PFPD adds a time dimension to the emission analysis in addition to the wavelength selectivity in a conventional FPD. By analyzing a specific time slice of the emitted light, the selectivity of the detector is significantly enhanced. Furthermore, since the time separation of the emissions adds selectivity, wider band-pass filters can be used, permitting more light to be detected resulting in an increased sensitivity for the PFPD vs. the FPD. Please see Figure 3 for emissions.

Figure 3. Sulfur and Phosphorus Emission



Standards were obtained and diluted with Hexane. An eight-point calibration of 0.05-2.5 ppm was run for most of the compounds. Great care must be taken with standards because of some compound's reactivity and instability. Standards were prepared in amber vials and stored at less than 10 °C. The chromatographic system must also be well maintained as performance will degrade with time especially in the inlet. The Agilent GC ChemStation OpenLab Data System was used to generate calibration curves using linear weighted calibration.

Method detection limit (MDL) studies at 0.04 ppm and 0.4 ppm (TEPP and Monocrotophos) were conducted over a three-day period. Initial demonstrations of capability (IDOC) were run at 1 ppm.

Real world samples and associated QC were also run.

Results

Calibration criteria of r2 linear regression >0.99 was met. Criteria for MDL and IDOC were also met before running samples. Method criteria for both IDOC's and MDL's were also met before running samples. Please see Table 2 and Table 3.

Table 2. Calibration Data

Analyte	Compound	Calibration Range(ppm)	Response Factor	Linear Regression
1	Dichlorvos (DDVP)	0.05-1.0	102K	0.992
2	Mevinphos	0.05-2.0	72.8K	0.996
3	TEPP	0.5-2.5	50.1K	0.998
4	Demeton-o	0.017-0.85	8.06K	0.998
5	Tributylphosphate(SS)	0.05-2.0	80.6K	0.997
6	Ethoprophos	0.05-1.5	89.2K	0.995
7	Naled	0.05-2.5	48.9K	0.998
8	Sulfotep	0.05-1.0	140K	0.990
9	Phorate	0.05-2.0	81.0K	0.996
10	Monocrotophos	0.05-2.5	34.9K	0.991
11	Demeton-s	0.033-1.65	31.9K	0.997
12	Dimethoate	0.05-2.0	90.6K	0.998
13	Diazinon	0.05-2.5	69.9K	0.997
14	Disulfoton	0.05-2.5	75.5K	0.997
15	Methyl parathion	0.05-2.5	79.8K	0.997
16	Fenchlorophos	0.05-2.0	68.6K	0.998
17	Malathion	0.05-2.5	67.1K	0.998
18	Chloropyrifos	0.05-2.5	63.3K	0.998
19	Trichloronate	0.05-2.5	64.8K	0.998
20	Parathion-ethyl	0.05-2.5	77.8K	0.998
21	Fenthion	0.05-2.5	77.9K	0.998
22	Merphos	0.05-2.5	31.1K	0.998
23	Stirophos	0.05-1.5	59.5K	0.996
24	Prothiofos	0.05-1.5	60.1K	0.995
25	Merphos oxone*	0.05-2.5	33.2K	0.998
26	Fensulfothion	0.05-1.5	39.3K	0.990
27	Sulprofos	0.05-1.0	61.4K	0.990
28	Triphenylphosphate(SS)	0.05-1.0	64.2K	0.993
29	EPN	0.05-1.0	62.6K	0.993
30	Azinophos-methyl	0.05-1.5	46.3K	0.995
31	Coumaphos	0.05-2.5	30.9K	0.996

Table 3. IDOC and MDL Data

Analyte	Compound	IDOC %Rsd	IDOC %Recovery	MDL Avg	MDL Std Dev	MDL
1	Dichlorvos (DDVP)	0.83	96.38	0.0172	0.0008	0.0024
2	Mevinphos	1.33	94.12	0.0152	0.0023	0.0066
3	TEPP	1.58	86.20	0.1982	0.0741	0.2090
4	Demeton-o	1.98	91.94	0.0197	0.0042	0.0120
5	Tributylphosphate(SS)	1.92	94.52	0.0214	0.0102	0.0288
6	Ethoprophos	1.64	92.40	0.0169	0.0011	0.0030
7	Naled	2.45	91.10	0.0121	0.0016	0.0046
8	Sulfotep	1.42	94.18	0.0220	0.0010	0.0028
9	Phorate	1.92	94.22	0.0159	0.0009	0.0026
10	Monocrotophos	5.79	84.36	0.1839	0.0286	0.0806
11	Demeton-s	1.55	93.74	0.0158	0.0019	0.0054
12	Dimethoate	1.43	93.84	0.0229	0.0020	0.0057
13	Diazinon	1.61	95.88	0.0162	0.0014	0.0039
14	Disulfoton	1.49	97.12	0.0161	0.0011	0.0030
15	Methyl parathion	1.44	98.16	0.0181	0.0017	0.0048
16	Fenchlorophos	1.66	95.46	0.0173	0.0017	0.0047
17	Malathion	1.19	93.86	0.0222	0.0019	0.0052
18	Chloropyrifos	1.98	95.02	0.0172	0.0025	0.0070
19	Trichloronate	3.54	94.48	0.0166	0.0015	0.0043
20	Parathion-ethyl	1.98	94.04	0.0226	0.0019	0.0053
21	Fenthion	1.43	96.46	0.0180	0.0021	0.0058
22	Merphos	1.33	94.38	0.0176	0.0036	0.0102
23	Stirophos	1.19	95.24	0.0180	0.0009	0.0024
24	Prothiofos	1.18	99.74	0.0173	0.0010	0.0028
25	Merphos oxone	1.90	94.28	0.0188	0.0016	0.0044
26	Fensulfothion	2.37	80.86	0.0187	0.0022	0.0063
27	Sulprofos	0.93	97.44	0.0187	0.0013	0.0037
28	Triphenylphosphate(SS)	1.58	91.52	0.0241	0.0104	0.0294
30	EPN	1.16	95.00	0.0212	0.0019	0.0052
31	Azinophos-methyl	1.20	96.30	0.0166	0.0011	0.0032
32	Coumaphos	1.89	95.28	0.0132	0.0008	0.0024

Several batches of real- world samples including samples from clear to dark brown were run with some requiring dilutions. No carryover or matrix interference was observed. No sample clean-up was performed as per Method 8141B since use of this detector in phosphorus mode minimizes interferences from materials that do not contain phosphorus or sulfur.[4] Please see Figures 4-9. The low-level sample was run after the high-level sample spike duplicate and illustrates there was not a carry-over problem with the analysis.

It was found that Naled and Monocrotophos in particular tended to recover low in the daily calibration check after running samples the day before. Replacing the inlet liner brought the recovery back up.

Figure 4. 1 ppm Standard

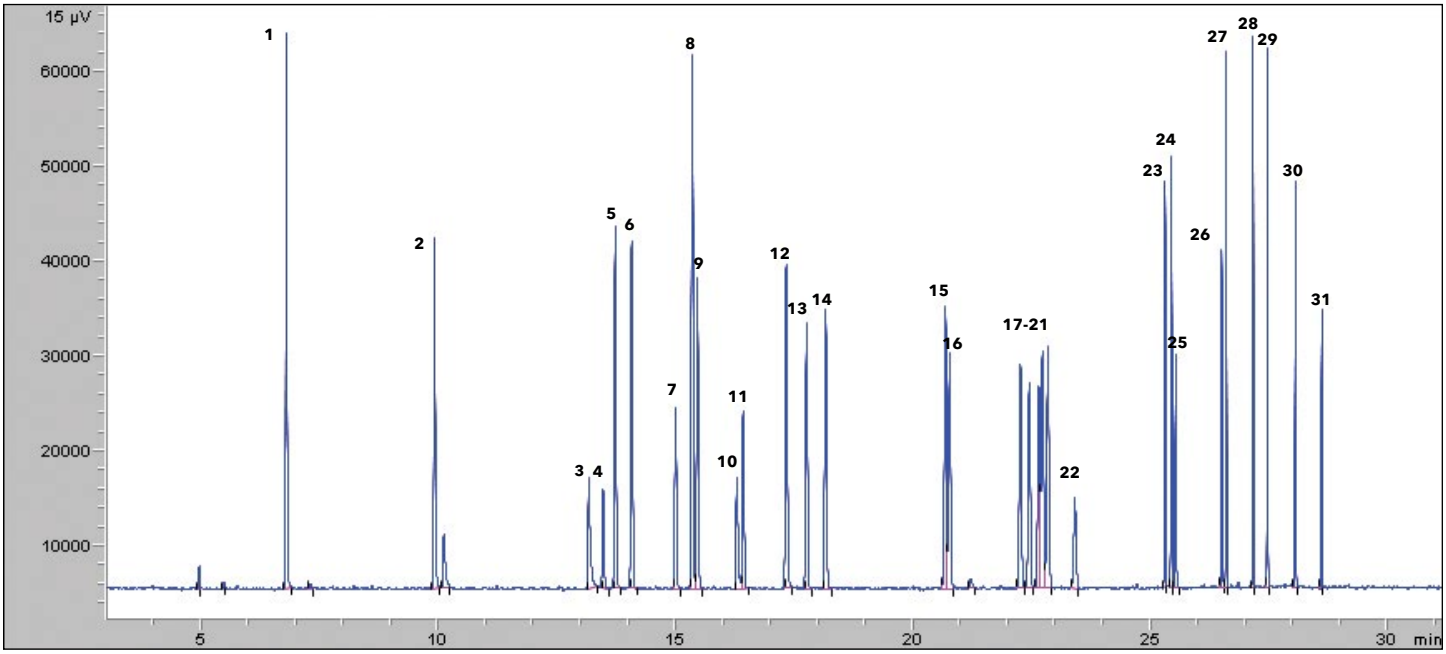


Figure 5. Extraction Blank

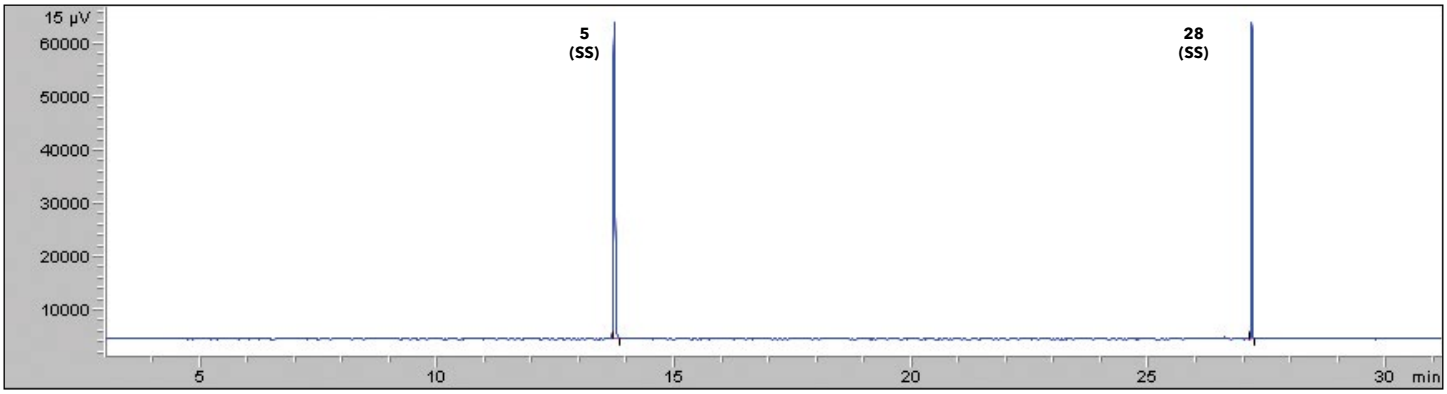


Figure 6. High Level Sample

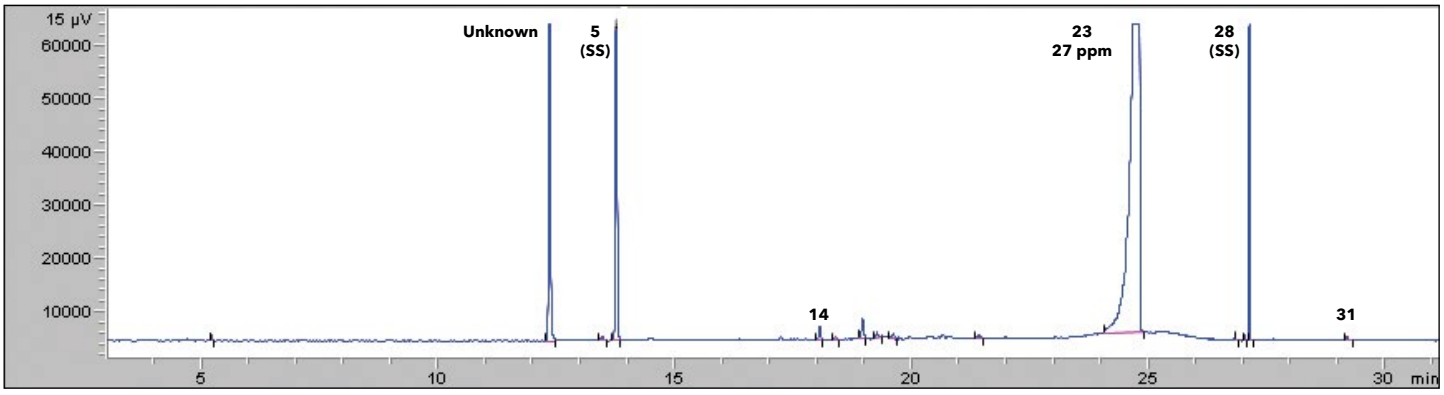


Figure 7. High-Level Sample Spike

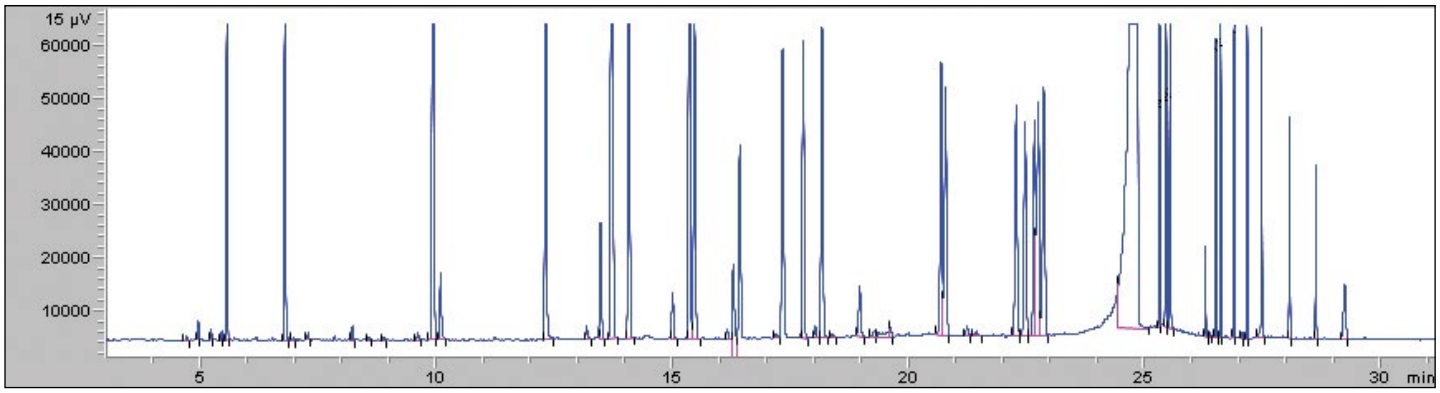


Figure 8. High-Level Sample Spike Duplicate

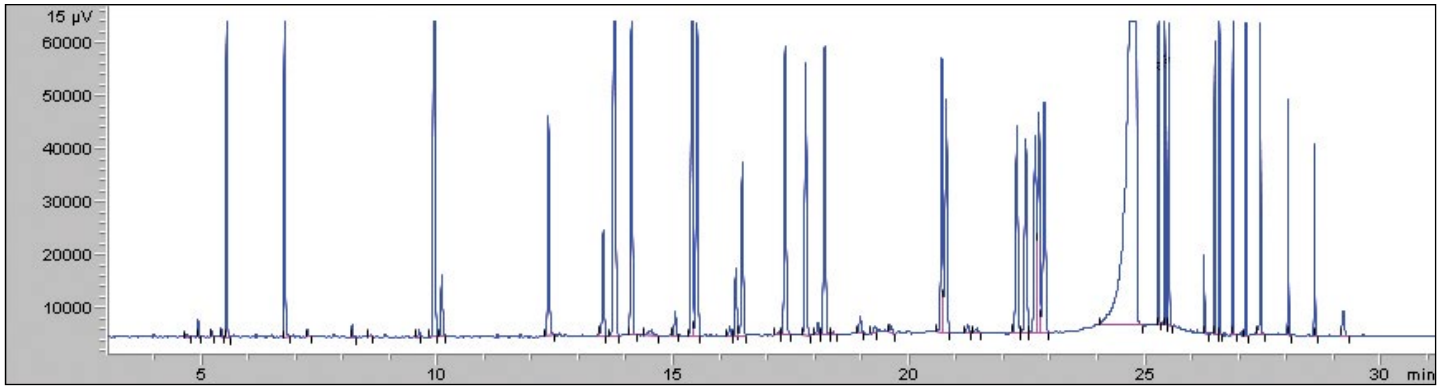
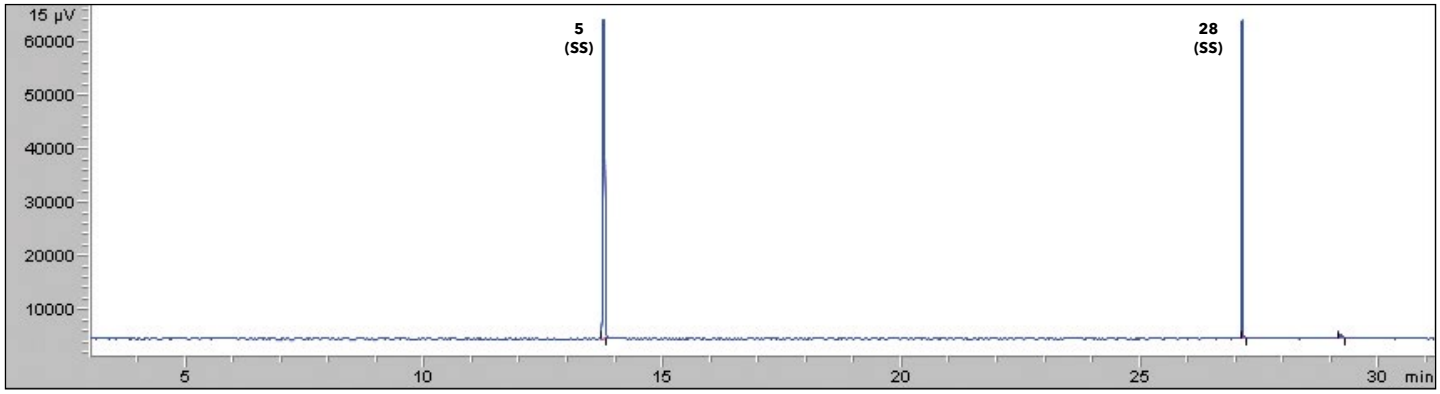


Figure 9. Low-Level Sample



Conclusions

The PFPD is an excellent detector for the analysis of organophosphorus pesticides. The detector is both sensitive and selective. In general, many labs run this analysis using splitless injection so it can be advantageous to be able to run the analysis using a higher split. The PFPD is an easy-to-maintain detector. Since the flame temperature is 2200 °C, the detector is self-cleaning so there is no coking or soot formation. For these reasons, the PFPD offers an ideal alternative to FPD and NPD detectors.

References

1. USEPA. Acts through Organophosphate Insecticides, Chapter 5. 6th Edition.

2. OI Analytical. A New Pulsed Flame Photometric Detector for the Analysis of Pesticides. 1997.

3. OI Analytical. Using the Pulsed Flame Photometric Detector (PFPD) for Low-Level Analysis of Organophosphorus Pesticides. 2006.

4. USEPA. Method 8141B Organophosphorus Compounds by Gas Chromatography. Revision 2, 2007.

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OI Analytical, a Xylem brand
PO Box 9010
College Station, TX 77842-9010

+1.979.690.1711
oi-info@xyleminc.com
oico.com

oico.com/Environmental

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