O·I·Analytical

Multi-element Analysis of Pesticides Using GC Systems Equipped with Multiple Selective GC Detectors

Application Note 13790799

Keywords
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Pesticides
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Introduction

The two most common classes of pesticides in use today are the organochlorine (OC) and organophosphorus (OP) pesticides. These compounds are commonly analyzed in a variety of sample matrices including food, water, and soil. These pesticide residues are usually present in the sample at very low concentrations, and there can be many potentially interfering compounds extracted from the matrix along with the pesticide, especially in food analysis. For a successful pesticide analysis, a very sensitive and selective detector is required. In the absence of a selective detector, complex sample cleanup procedures are often used to minimize matrix interferences. These procedures obviously take time, add costs, and often cause losses of certain target analytes.

Historically, electron capture detectors (ECD) and electrolytic conductivity detectors (ELCD) have been used for the OC pesticides, with the more selective ELCD used when complex matrices are involved. For the OP pesticides, flame photometric detectors (FPD) and nitrogen-phosphourous detectors (NPD) are most often used. Mass spectrometry (MS) is also widely used now in residue analysis, but additional sample cleanup is often required to minimize the complex matrix background that can make identification difficult if not impossible with many types of samples.

This paper describes the use of two selective detectors for the analysis of OP and OC pesticides. The pulsed flame photometric detector (PFPD) and the halogen specific detector (XSD™) provide the two key factors for successful pesticide residue analysis: high sensitivity and selectivity.

Selective Detectors

The PFPD is not only a very sensitive detector for organophosphorous compounds, but it can simultaneously provide increased sensitivity and selectivity for pesticides containing sulfur. The operating conditions for this detector can be optimized to selectively analyze for phosphorus, sulfur, or nitrogen and to eliminate matrix interference from other heteroatoms. Alternatively, both sulfur and phosphorus pesticides can be analyzed simultaneously with no selectivity preference toward either sulfur or phosphorus through the proper selection of optical filters.

Many OP pesticides also contain sulfur. A standard FPD with a single filter and photomultiplier tube (PMT) can be optimized to detect either phosphorus or sulfur, but typically not both elements simultaneously. The PFPD, as a result of its added time separation of the various heteroatom emissions, is capable of providing phosphorus and sulfur chromatograms concurrently using a single filter and PMT. This capability provides additional confirmational analysis without the need for a second analytical run or the use of a dual filter/PMT configuration commonly used with FPDs. For samples with a high sulfur background, the sulfur interference can be either minimized or completely eliminated by proper selection of PMT, filters, and time-delay gates or by using a dual gate subtraction mode. The ability to collect two element-specific chromatograms concurrently allows the identification of the OP pesticides on the basis of retention time, and additionally, using the presence of both phosphorus and sulfur heteroatoms as confirmation.

The XSD is a very selective and sensitive detector for chlorinated compounds. While the XSD is not quite as sensitive as the ECD, it has virtually no response to matrix interference, resulting in significantly greater selectivity and a reduction in the need for extensive sample preparation. When compared to the ELCD, this detector offers similar sensitivity and selectivity but requires virtually no maintence or upkeep, and it eliminates the use of organic solvents and the associated hardware requirements.

Principal of Operation: PFPD

In the PFPD, the combustor is filled with an ignitable gas mixture of hydrogen and air at a flow rate that will not support continuous combustion. The gas mixture is ignited; the flame propagates through the combustor and extinguishes when all the fuel is consumed. The cycle is repeated continuously at a rate of 3 to 4 Hertz. The advantage of this pulsed flame, compared to the continuous flame in the FPD, is that the pulsing adds a time dimension (delay) to the various heteroatom emission profiles. An electronic time gate is set by the operator to select the particular heteroatom's time-dependent emission of interest, for example HPO* or S_2*. As with an FPD, additional wavelength selectivity is provided by the choice of specific filters and PMTs. In each "flame pulse," combustion of the target analyte yields time-dependent emissions from HPO* and/or S_2* (and a background emission from CH*, C_2*, OH*). The time-dependent behavior results from differences in the kinetics of the various chemical reactions taking place. A typical fluorescence waveform is shown in Figure 1. Note that the

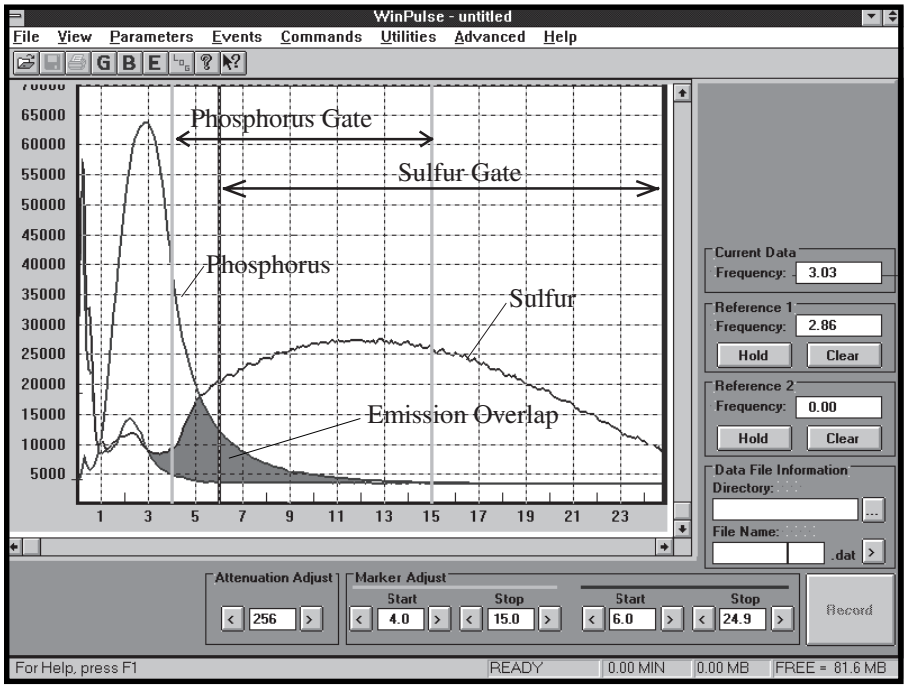


Figure 1. PFPD Fluorescence Waveform, Using OI Analytical's WinPulse Software

phosphorus emission occurs in the earlier time domain of the pulse and runs from about 1 to 15 msec after the intial flame pulse. On the other hand, the sulfur emission begins at approximately 4 msec and runs out to 25 msec. Electronic gates are set using the software to optimize the selectivity between these two emissions as needed. Although some overlap of the emissions is observed (as shown in the shaded area), this can be minimized by selecting the proper gates or taking advantage of the dual gate subtraction technique.

Principal of Operation: XSD

The XSD operates by combusting the GC column effluent in a stream of air. The combustion products of the halogenated compounds then react with alkali metal atoms on the surface of an electrically charged (pure) platinum bead. This reaction causes an increase in the emission of electrons from the surface. This increase in electron emission (current) is measured and provides the detector signal (see OI Analytical Application Note 07670797, "A New Halogen Specific Detector: The Model 5360 XSD™"). A diagram of the XSD is shown in Figure 2.

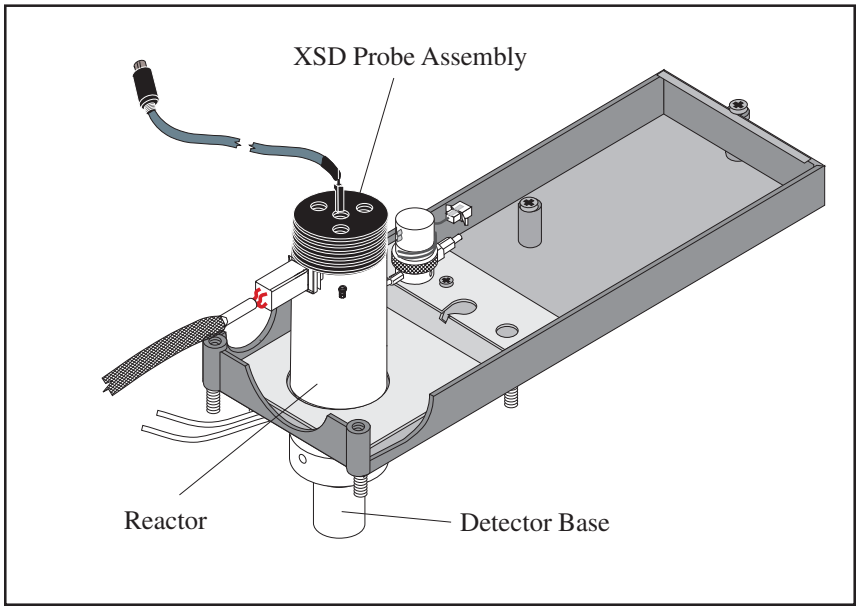


Figure 2. Halogen Specific Detector (XSD) - HP 6890 Configuration

Pesticide Analysis

One of the most common analytical problems is the analysis of pesticide and pesticide residues. The sample matrices are often complex, such as those encountered with many food or plant extracts, with many possible interfering compounds. The ideal detector is one that is both highly selective for the components of interest and sensitive enough to detect the target analytes at low (ppb) concentrations commonly found in these matrices. Many detectors in use today are either very selective or very sensitive, but in most cases selectivity comes at the expense of sensitivity. The PFPD and the XSD are both highly sensitive detectors with detection capability in the picogram-per-injection range, making them ideal for multiresidue pesticide analysis. Using the two together takes full advantage of the selectivity of each without significantly sacrificing any of their individual sensitivity.

To demonstrate the use of these detectors for low-level pesticide analyses, samples where run under identical chromatographic conditions using both detectors, with the PFPD optimized separately for phosphorus, sulfur, and then nitrogen detection. Note that the chromatograms shown here are with the PFPD optimized in each case for the particular heteroatom selectivity. Slightly different results would be obtained using a configuration with less

selective optical filters (e.g., using filter UV-34-clear). Each pesticide in the mix contains at least two different heteroatoms that can used to identify and confirm the identity of individual components in the mix. Comparison of the responses in the different modes provides identification and confirmation information from the expected response (or lack of response) from each heteroatom present.

Experimental

The chromatograms shown here were obtained using the PFPD and XSD installed on an HP 6890 GC equipped with an EPC split/splitless injector. The injector was operated at 270°C in the pulsed splitless mode with a 1 minute purge time, and all injections were 1 mL. Pesticide standards at two different concentration levels were used to demonstrate the relative sensitivity of the PFPD in the S, P, and N modes. The column was an HP-5MS, 30 meters long with a 0.25 mm ID and a 0.25 mm film thickness. Helium was used as the carrier gas, with a constant column flow rate of 1 mL/minute. The GC temperature program was 60°C for 1 minute, 25°C/minute to 140°C, 6°C/minute to 240°C, 20°C/minute to 280°C, hold for 2 minutes. The PFPD operating conditions are listed in Table 1.

Table 1. PFPD Operating Conditions

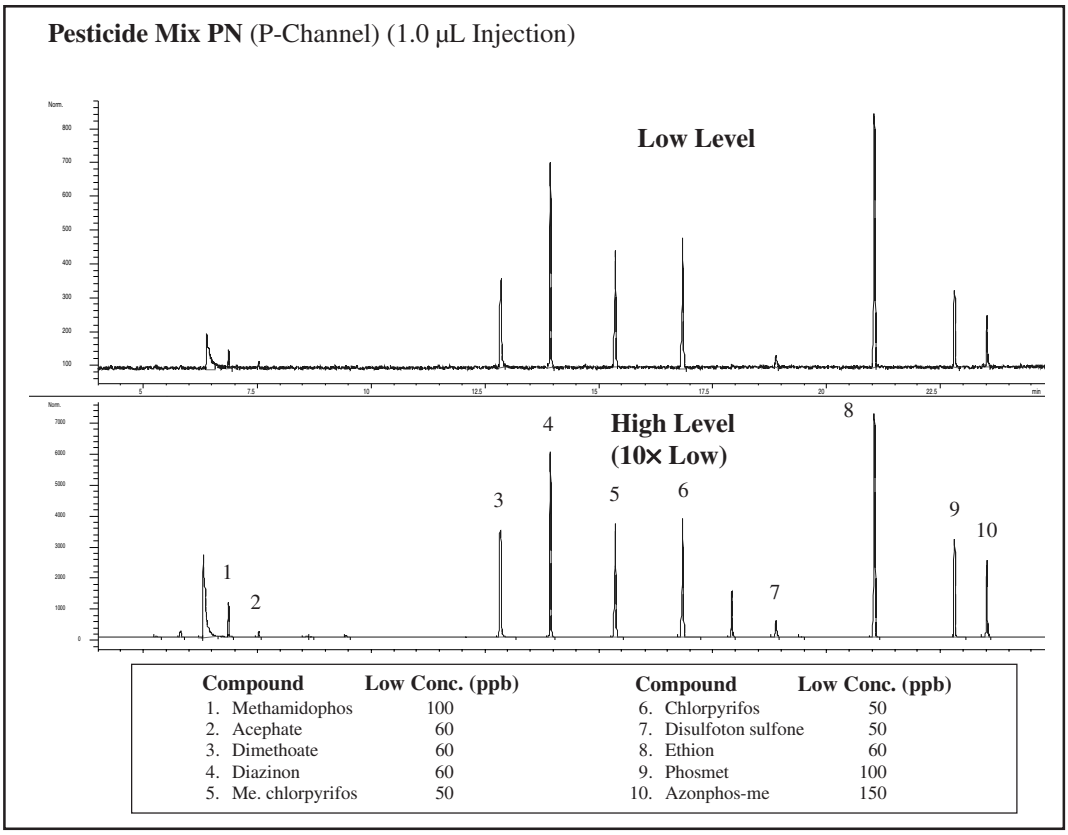
Mode	Detector Temp.	Gas Mix	Optical Filter	PMT
Phosphourous	300°C	H_2/Air Ratio 0.85–0.95	WG-345	R-1924
Sulfur	250°C	H_2/Air Ratio 1.1–1.2	BG-12	R-1924
Nitrogen	250°C	H_2 rich	RG-695	R-1925

Results

Figure 3 shows PFPD chromatograms of a pesticide standard at both the high and low concentrations. The detector used to acquire these data was configured with a WG-345 optical filter, which permits transmission of sulfur and phosphorus emissions, and was optimized to provide detection of both heteroatoms. These chromatograms are from the phosphorus gated output (from 5–14 msec).

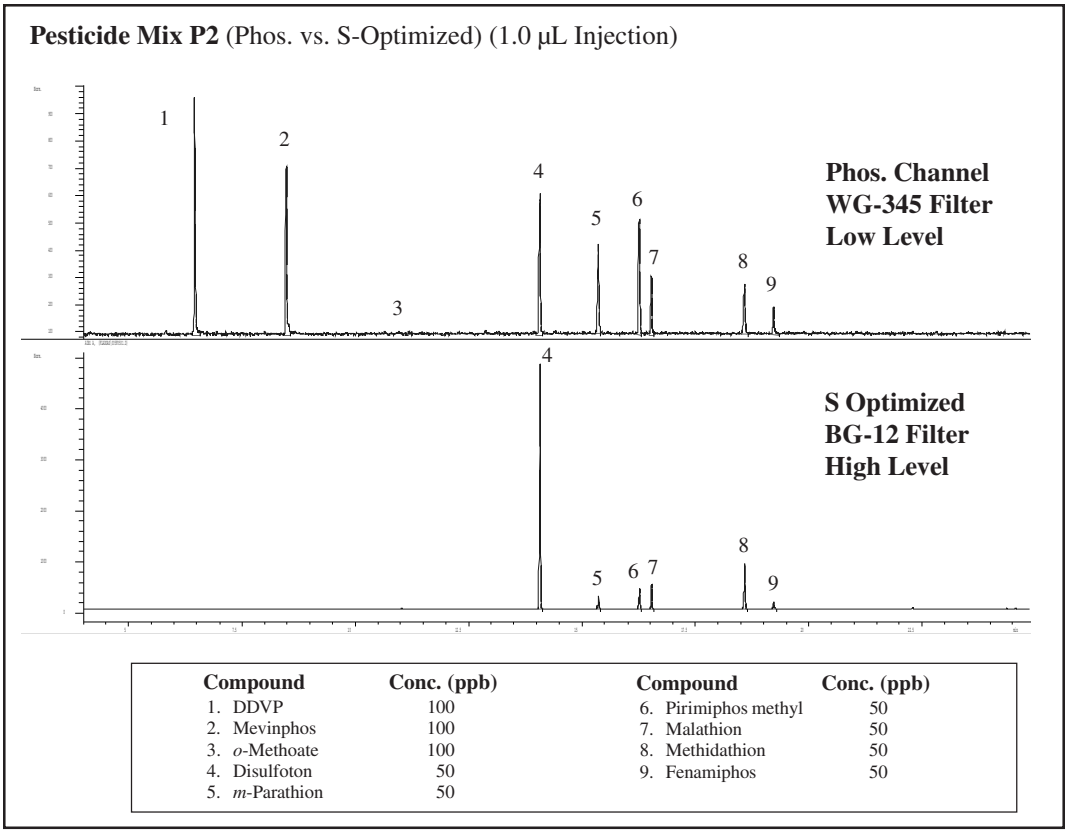
Figure 4 shows PFPD chromatograms from a second standard mix. The top trace was acquired with the detector optimized for phosphorus, while the bottom trace was acquired under identical GC conditions but with the PFPD optimized for sulfur. Note that the two compounds containing phosphorus (DDVP and mevinphos) show no response on the sulfur channel due to the use of the selective BG-12 optical filter. It should be noted that for compounds that respond on both channnels (i.e., compounds containing both sulfur and phosphorus), the relative response between channels can be used as further confirmation of the identity of the compound.

Figure 5 demonstrates the usefulness of operating the PFPD and XSD together as a screening tool for the organophosphorus and organochlorine pesticides. About 20% of the compounds on the USEPA's pesticide list contain sulfur and nitrogen, but no phosphorus. Generally, these pesticides are analyzed with an NPD, which responds to the nitrogen atoms. However, for sample matrices with a large number of naturally occurring nitrogen-containing compounds, the chromatogram on a NPD can be quite complex. The PFPD with its increased sulfur sensitivity relative to the FPD (approximately 10 fold), permits detection of sulfur pesticides approaching the low levels required of residue analyses without the additional interference from nitrogen containing compounds. In this chromatogram note the peak for thiabendazole, which contains sulfur only, on the sulfur



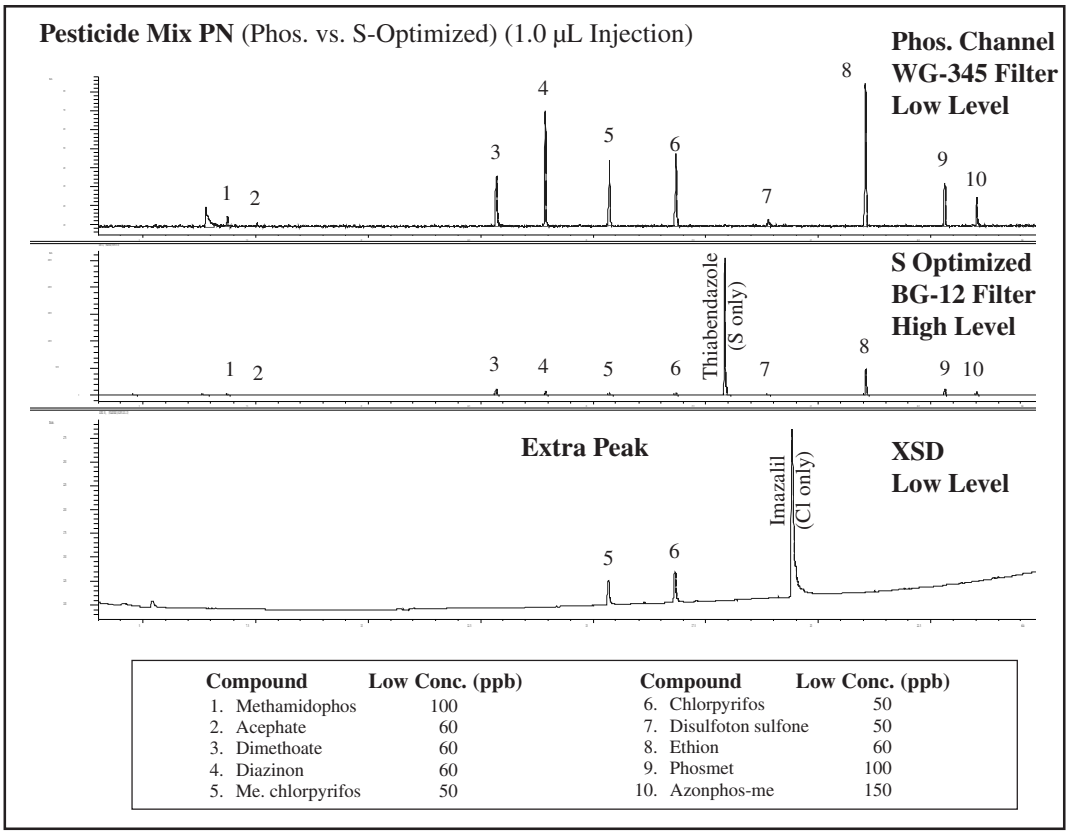
Compound	Low Conc. (ppb)	Compound	Low Conc. (ppb)
1. Methamidophos	100	6. Chlorpyrifos	50
2. Acephate	60	7. Disulfoton sulfone	50
3. Dimethoate	60	8. Ethion	60
4. Diazinon	60	9. Phosmet	100
5. Me. chlorpyrifos	50	10. Azonphos-me	150

Figure 3. Chromatograms of the Pesticides Standard



Compound	Conc. (ppb)	Compound	Conc. (ppb)
1. DDVP	100	6. Pirimiphos methyl	50
2. Mevinphos	100	7. Malathion	50
3. *o*-Methoate	100	8. Methidathion	50
4. Disulfoton	50	9. Fenamiphos	50
5. *m*-Parathion	50		

Figure 4. Chromatograms of the P2 Standard Mix



Compound	Low Conc. (ppb)	Compound	Low Conc. (ppb)
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2. Acephate	60	7. Disulfoton sulfone	50
3. Dimethoate	60	8. Ethion	60
4. Diazinon	60	9. Phosmet	100
5. Me. chlorpyrifos	50	10. Azonphos-me	150

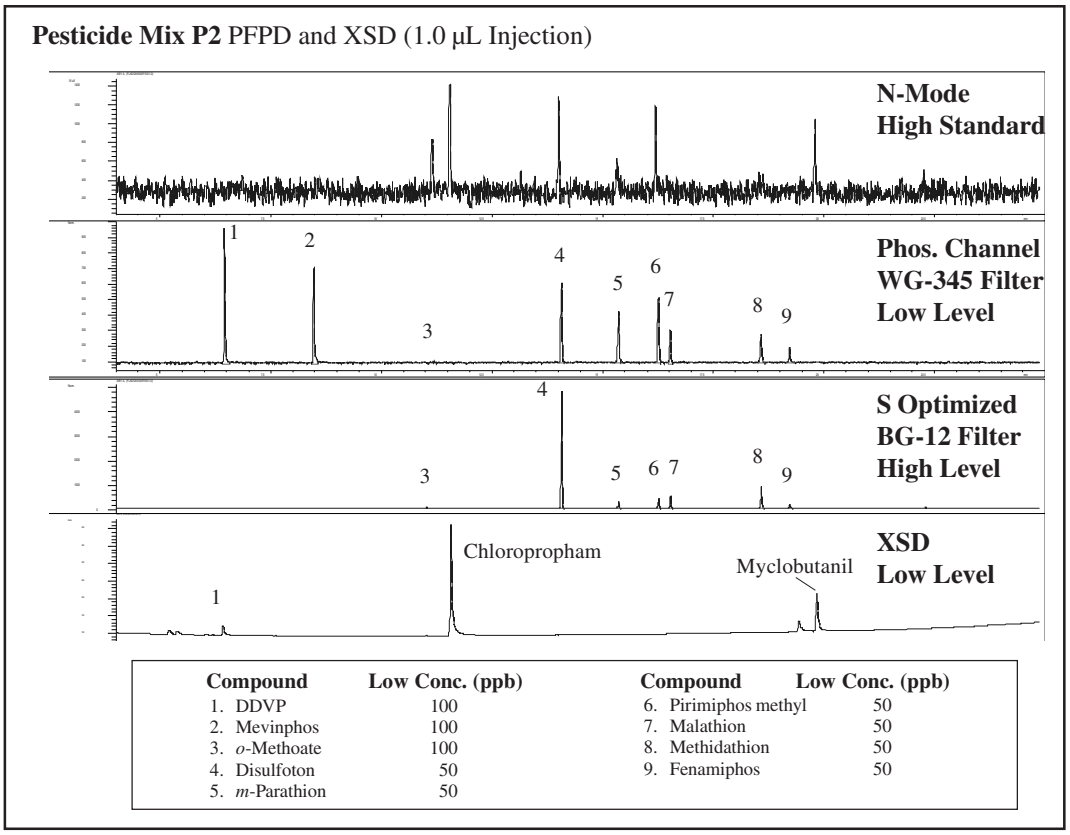
Figure 5. Operation of the Tandem PFPD and XSD

channel, with no corresponding response when the PFPD is optimized for phosphorus. Furthermore, note that the XSD chromatogram only shows peaks for pesticides containing chlorine. For example, the only heteroatom in imazalil is chlorine, resulting in a peak in the XSD trace, but with no corresponding response in either of the two PFPD traces, sulfur and phosphorus.

Figures 6 and 7 demonstrate the added dimension of PFPD sensitivity when it is optimized for nitrogen detection. Although detection limits are limited in nitrogen mode, when compared to an NPD, analysis of the higher concentrations is very feasible and provides an alternative to NPD detection (with improved peak shape versus NPD). As shown in Figure 6, the two peaks that respond in both phosphorus and nitrogen channels, disulfoton and pirimiphos methyl, exhibit no peak tailing at all, as would usually be seen when using the NPD. The emission times and wavelengths of phosphorus and nitrogen overlap in a manner such that it is possible to choose a filter and PMT combination to generate a phosphorus chromatogram without nitrogen compounds being detected. However, there is not a filter and PMT combination that will eliminate phosphorus emission. Chromatograms run in nitrogen mode will show response from phosphorus containing compounds in the sample.

Conclusion

The combination of the PFPD and the XSD operated in parallel allows the simultaneous analysis of organophosphorus, organosulfur, and organochlorine pesticides. A single injection, dual column analysis to screen for both the OP and OC pesticides is now possible with the added benefit of an additional (confirmational) channel providing chromatograms for the S-containing pesticides. The freedom from interferences of these detectors allows samples to be run after extraction with little or no sample cleanup. The high selectivity and increased sensitivity provided by these detectors make them ideal for multiresidue pesticide analysis. The additional flexibility of multiple operationional modes provided by the PFPD provides a powerful tool to optimize the selectivity needed to match challenging sample matices. Interference from complex matrices can be easily eliminated by changing the basic operational parameters of the PFPD detector.



Compound	Low Conc. (ppb)	Compound	Low Conc. (ppb)
1. DDVP	100	6. Pirimiphos methyl	50
2. Mevinphos	100	7. Malathion	50
3. *o*-Methoate	100	8. Methidathion	50
4. Disulfoton	50	9. Fenamiphos	50
5. *m*-Parathion	50		

Figure 6. Pesticide Analysis by PFPD (S, P, N optimized) and XSD

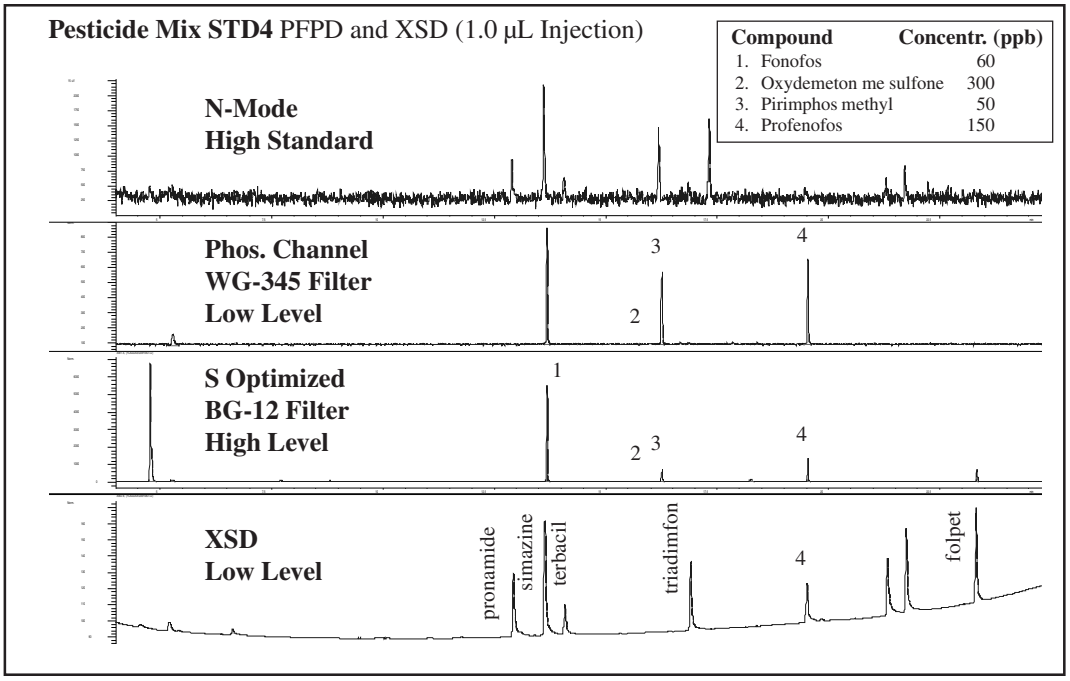


Figure 7. Pesticide Analysis by PFPD (S, P, N optimized) and XSD

Table 2. Composition of Low-Level Pesticide Mix PN, Pesticide Mix P2, and Pesticide Mix STD4

Compound Number	Compound Name	Chemical Formula	Conc (ppb)	No. of Each Heteroatom			
				N	S	P	Cl
Low-Level Pesticide Mix PN							
1	Methamidophos	$C_2H_8NO_2PS$	100	1	1	1	0
2	Acephate (Orthene)	$C_4H_{10}NO_3PS$	60	1	1	1	0
3	Diazinon (Dimpylate)	$C_{12}H_{21}N_2O_3PS$	60	2	1	1	0
4	Dimethoate	$C_5H_{12}NO_3PS_2$	60	1	2	1	0
5	Methyl chlorpyrofos	$C_7H_7Cl_3NO_3P_5$	50	1	1	1	3
6	Chlorpyrofos	$C_9H_{11}C_{l3}NO_3PS$	50	1	1	1	0
7	Thiabendazole	$C_{10}H_7N_3S$	500	3	1	0	0
8	Imazalil	$C_{14}H_{14}Cl_2N_2O$	1000	2	0	0	2
9	Disulfoton Sulfone	$C_8H_{19}O_4PS_3$	50	0	3	1	0
10	Ethion	$C_9H_{22}O_4P_2S_4$	60	0	4	2	0
11	Phosmet	$C_{11}H_{12}NO_4PS_2$	100	1	2	1	0
12	Azinphos methyl	$C_{10}H_{12}N_3O_3PS_2$	150	3	2	1	0
Pesticide Mix P2							
1	Dichlovos	$C_4H_7C_{l2}O_4P$	100	0	0	1	0
2	Mevinphos	$C_7H_{13}O_6P$	100	0	0	1	0
3	Omethoate	$C_5H_{12}NO_4PS$	100	1	1	1	0
4	Diphenylamine	$C_{12}H_{11}N$	1000	1	0	0	0
5	Chlorpropham	$C_{10}H_{12}ClNO$	1000	1	0	0	1
6	Disulfoton	$C_8H_{19}O_2PS_3$	50	0	3	1	0
7	Methyl parathion	$C_8H_{10}NO_5PS$	50	1	1	1	0
8	Pirimiphos methyl	$C_8H_{22}NO_3PS$	50	1	1	1	0
9	Malathion	$C_{10}H_{19}O_6PS_2$	50	0	2	1	0
10	Methidathion	$C_6H_{11}N_2O_4PS_3$	50	2	3	1	0
11	Fenamiphos	$C_{13}H_{22}NO_3PS$	50	1	1	1	0
12	Myclobutanil	$C_{15}H_{17}ClN_4$	500	4	0	0	4
Pesticide Mix STD4							
1	Simizine	$C_7H_{12}ClN_5$	150	3	0	0	1
2	Pronamide	$C_{12}H_{11}Cl_2NO$	100	1	0	0	2
3	Fonofos	$C_{10}H_{15}OPS_2$	60	0	2	1	0
4	Terbacil	$C_9H_{13}ClN_2O_2$	200	2	0	0	1
5	Pirimiphos methyl	$C_8H_{22}NO_3PS$	50	–	–	–	–
6	Triadimefon	$C_{14}H_{16}ClN_3O_2$	150	3	0	0	1
7	Olxydemeton methyl sulfone	$C_6H_{15}O_5PS_2$	300	–	2	1	–
8	Diphenamid	$C_{16}H_{17}NO$	1000	1	0	0	0
9	Profenofos		150	–	–	–	–
10	Folpet	$C_9H_4Cl_3NO_2S$	200	1	1	0	3
11	Norflurazon	$C_{12}H_9ClF_3N_3O$	250	3	0	0	1
12	Norflurazon metabolite		250	–	–	–	–
13	Tetradifon	$C_{12}H_6Cl_4O_2S$	50	0	1	0	4

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