

Keywords

Mass Spectrometer
NPD
Pesticides
PFPD
Phosphorus
Selectivity
Sensitivity
Sulfur

A New Pulsed Flame Photometric Detector for the Analysis of Pesticides

Introduction

One of the more common analytical problems is the analysis of pesticides or pesticide residues. Pesticides and residues are analyzed in many different sample matrices, usually at very low levels. The sample matrices are often complex, such as food or plant extracts, with many possible interfering compounds. The ideal detector for pesticide analysis is one that is highly selective for the components of interest and very sensitive. Most of the detectors used today are either very selective or very sensitive, but in most cases sensitivity comes at the expense of selectivity. The pulsed flame photometric detector (PFPD) offers increased sensitivity and selectivity for the analysis of sulfur and phosphorus containing pesticides.

Presently, organophosphorus pesticides are widely used. For most applications, they have replaced the older chlorinated pesticides because they are not as persistent in the environment. These pesticides are highly toxic, and many food products are analyzed for their presence. These pesticides may be difficult to detect and quantitate in a complex matrix such as a fruit or vegetable extract using common detectors.

The detectors most commonly used for the analysis of the organophosphorus pesticides are the nitrogen-phosphorus detector (NPD), the flame photometric detector (FPD) and the mass spectrometer (MS). All of these detectors have limitations in the analysis of the complex matrices often encountered in pesticide analysis. The NPD is a very sensitive detector for the organophosphorus pesticides, but there are many naturally occurring organonitrogen compounds in plant tissues that can produce interfering peaks. This makes reliable detection of the organophosphorus pesticides difficult. The NPD also requires frequent recalibration, since response varies as the sensing element ages.

The mass spectrometer is a more selective detector than the NPD when it is operated in scan mode so that the identity of compounds can be confirmed by library matching, but in the full scan mode, most mass spectrometers are not as sensitive as the NPD. The MS is more sensitive in selected ion monitoring mode (SIM), but the ability to confirm the identity of the compounds by library comparison is lost. Setting up a reliable SIM program for the analysis of trace components in a complex matrix requires a skilled operator to select the appropriate primary and confirming ions to monitor in order to reduce the number of false positives. In addition, the sensitivity of the MS is decreased when a major component such as a lipid or wax coelutes with a trace component. The major component reduces the ionization efficiency of the trace component, interfering with the detection at low levels.

*Presented at the 1997 Pittsburgh
Conference on Analytical Chemistry
and Applied Spectroscopy
Atlanta, GA
March 17–20, 1997*



Flame photometric detectors are selective when equipped with a narrow bandpass filter, but the filter will reduce the sensitivity by rejecting a large portion of the emission. The FPD may also have reduced response due to quenching at high concentrations of analyte or with major coeluting lipid or wax peaks. Flameouts may also be a problem when the solvent peak passes through the detector.

The pulsed flame photometric detector reduces many of the problems associated with the other detectors used for the organophosphorus pesticide analysis. The PFPD uses a hydrogen and air mixture at a flow rate that will not support continuous combustion. The combustor is filled with an ignitable gas mixture, the flame is ignited, the flame propagates through the combustor, and the flame burns out when all the fuel is consumed (Figure 1). The cycle is repeated continuously at a rate of 3 to 4 Hertz. The pulsed flame adds a time dimension to the emission analysis in addition to the wavelength selectivity in a conventional FPD. Figure 2 shows the emission profiles of a hydrocarbon, phosphorus, and sulfur. Hydrocarbon emission shows little delay, phosphorus emission shows a slight delay, and sulfur emission occurs over a significantly delayed time period. By analyzing a specific time slice of the emitted radiation, the selectivity of the detector is enhanced. For example, if the time slice from 10 to 24 milliseconds is analyzed, the majority of the emission is from sulfur with only a small contribution from phosphorus and no hydrocarbon contribution.

A diagram of the PFPD is shown in Figure 3. The combustion of the gas mixture begins when it reaches the ignitor. The flame then propagates through the combustor, the heteroatoms are excited and emit light, the emitted light passes through the light pipe and filter, then is amplified by the photomultiplier tube. The signal from the photomultiplier tube is then passed into the detector controller electronics where it is processed and a 0 to 1 volt analog signal is then output to the gas chromatograph data system. Changing the filter and photomultiplier tube changes the selectivity for various heteroatoms.

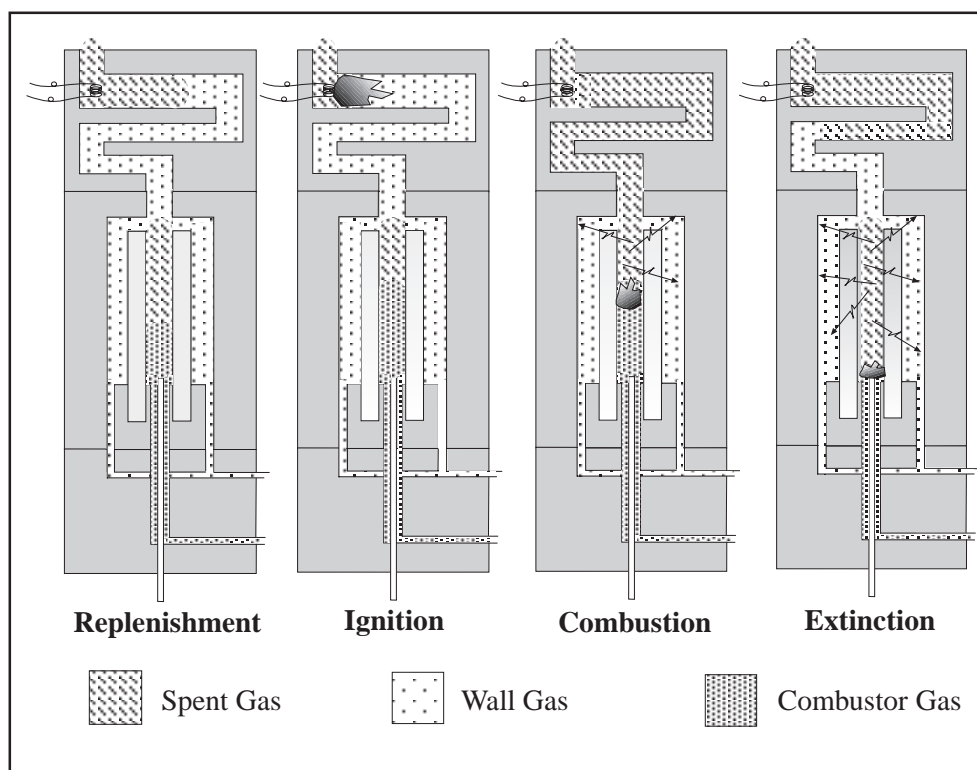


Figure 1. Four Phase Cycle of Propagating Flame

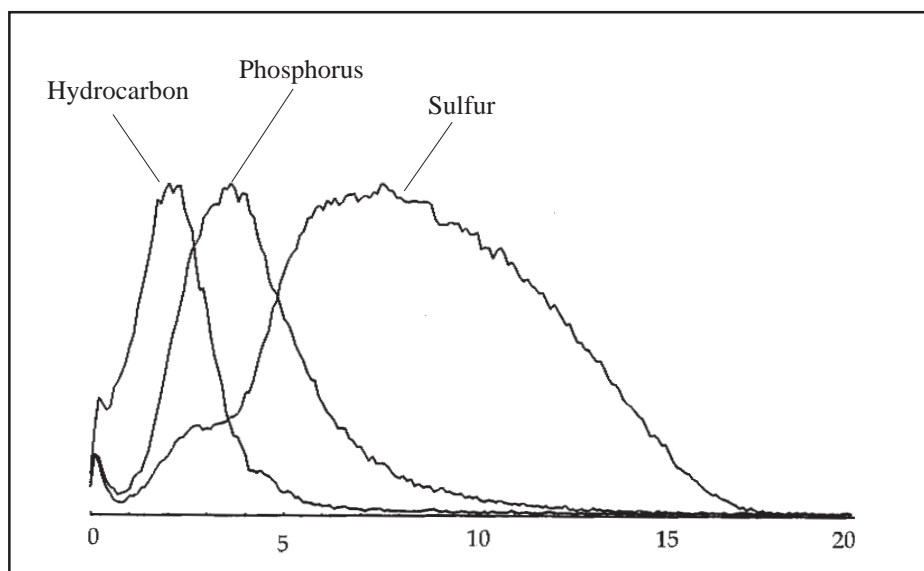


Figure 2. Emission in the PFPD

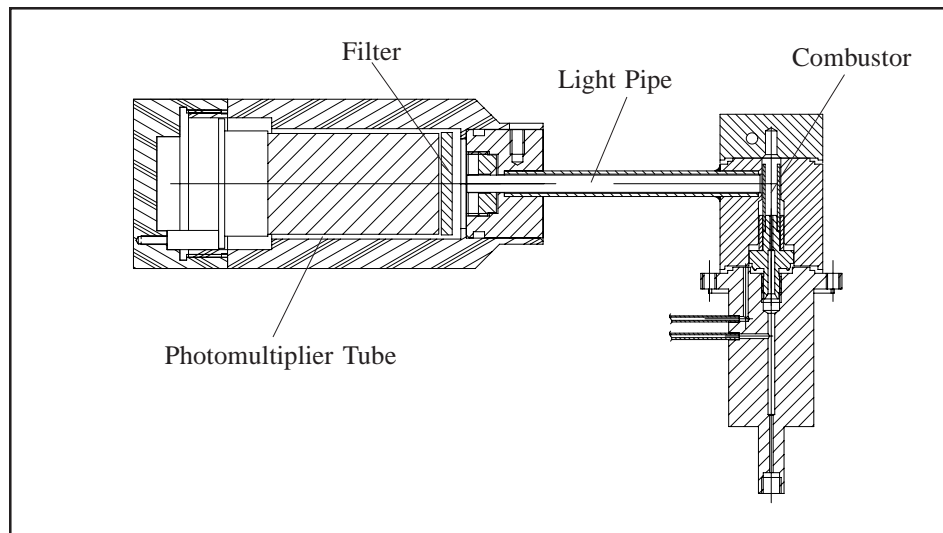


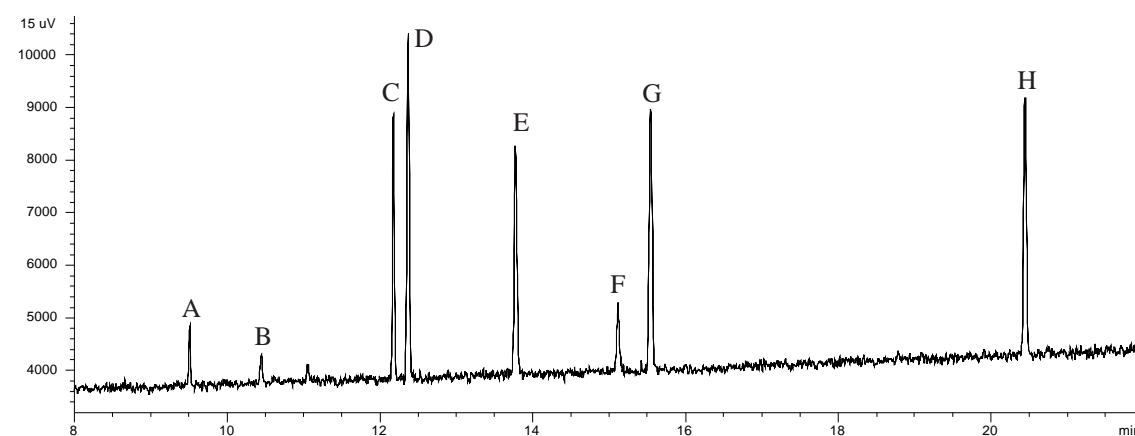
Figure 3. Diagram of the OI Analytical Pulsed Flame Photometric Detector

An OI Analytical Model 5380 PFPD was installed onto a Hewlett-Packard Model 6890 gas chromatograph fitted with a split/splitless injection port. Data was collected using Hewlett-Packard ChemStation GC Software. The samples were injected in splitless mode using an OI Analytical Model 4105 Liquid Autosampler.

Figure 4 is a chromatogram of a 30 picogram per component organophosphorus pesticide mix. This figure demonstrates the sensitivity of the PFPD for phosphorus containing compounds. The pesticides in this standard mixture contain approximately 10% phosphorus, so the chromatogram shows compounds with about 3 picograms phosphorus in each pesticide. Subpicogram levels of phosphorus are easily detected, with a detection limit for the pesticides of approximately 2 picograms of compound.

The graphs of response versus concentration for disulfoton and methyl parathion (Figures 5 and 6) show the linearity of response of the PFPD for low-level standards. The amount of pesticide injected ranges from 10 to 100 picograms of compound or approximately 1 to 10 picograms of phosphorus. The other pesticides in the mixture also had excellent linearity of response.

Detector: OI Analytical Model 5380 PFPD
 Detector Temp: 250°C
 GC: HP 6890
 Injector: Split/splitless
 Injection Mode: Splitless
 Injector Temp: 270°C
 Column: HP-5M5 30 m x 0.25 mm, 0.25 μ phase
 Column Flow: 1 mL/min, constant flow mode
 Oven: 60°C for 1 min to 170°C @ 25°C/min, to 210°C @ 4°C/min, to 250°C @ 6°C/min, to 310°C @ 25°C/min, hold for 2 min.



- | | |
|---------------|---------------------|
| A. Demeton O | E. Methyl Parathion |
| B. Demeton S | F. Malathion |
| C. Diazinon | G. Parathion Ethyl |
| D. Disulfoton | H. Ethion |

Figure 4. 30 pg/Component Organophosphorus Pesticide Mix

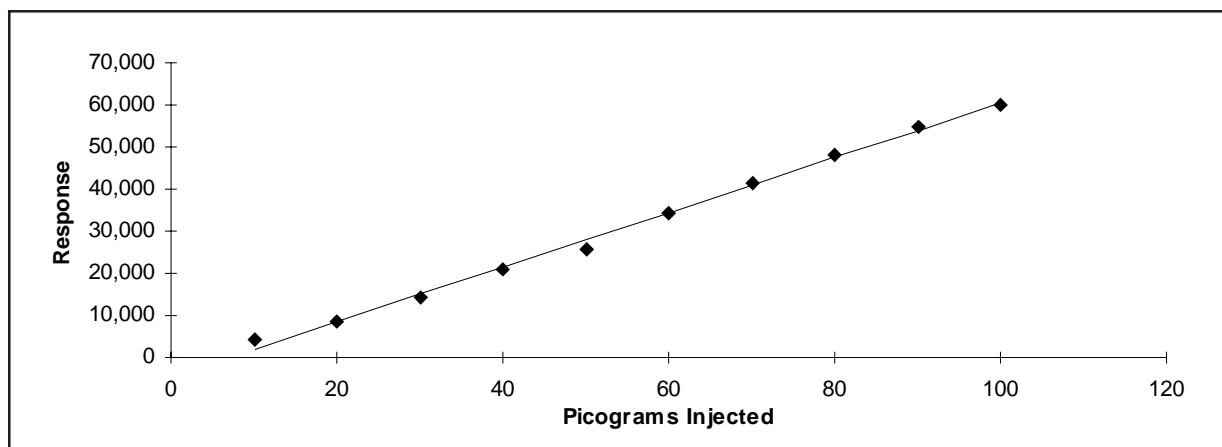


Figure 5. Response Curve for Disulfoton

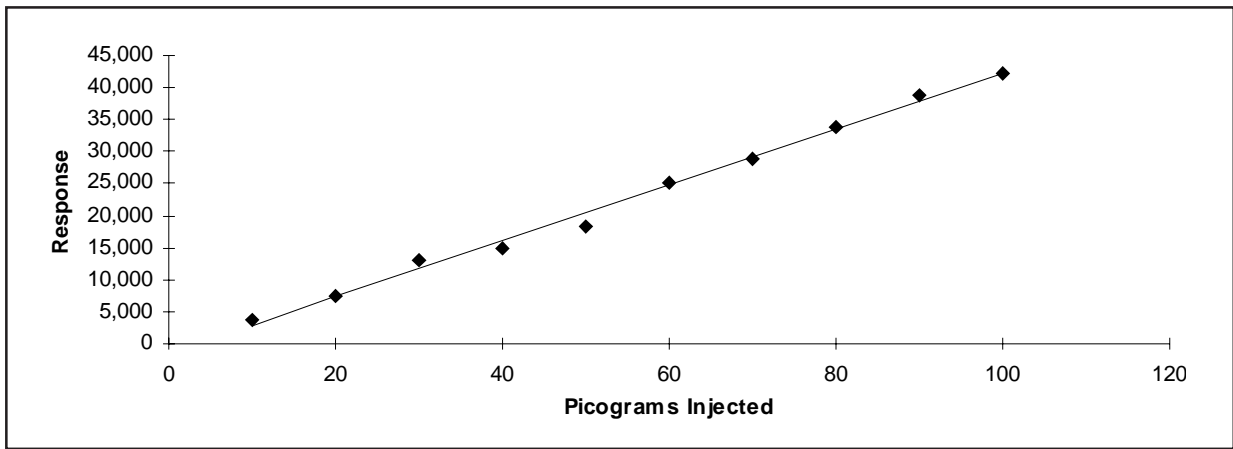


Figure 6. Response Curve for Methyl Parathion

Figures 7 and 8 are response curves of demeton O and methyl parathion at higher concentration levels. The standards for these curves ranged from 100 to 1500 picograms per component or approximately 10 to 150 pg phosphorus per compound. Linearity is also excellent for the pesticides at the higher concentration range.

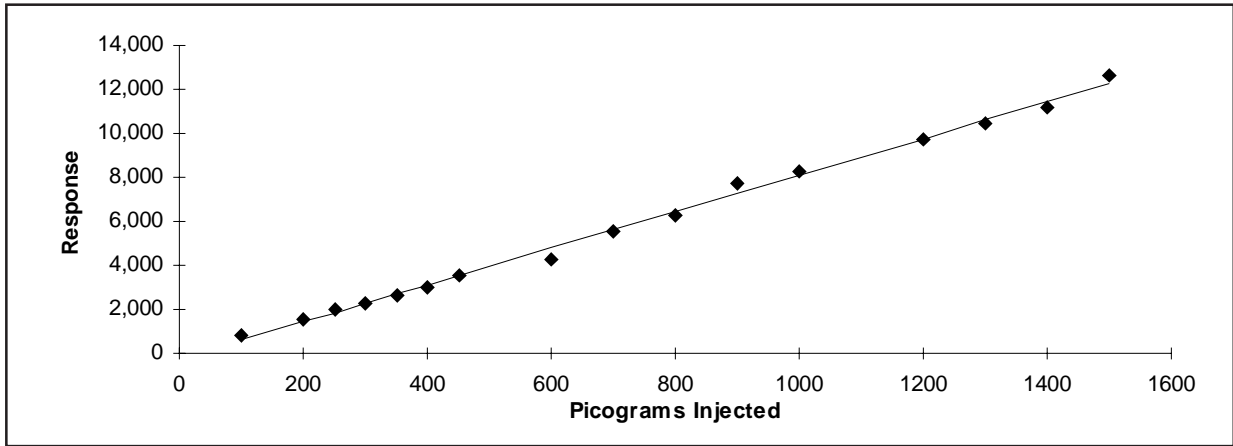


Figure 7. Response Curve for Demeton O

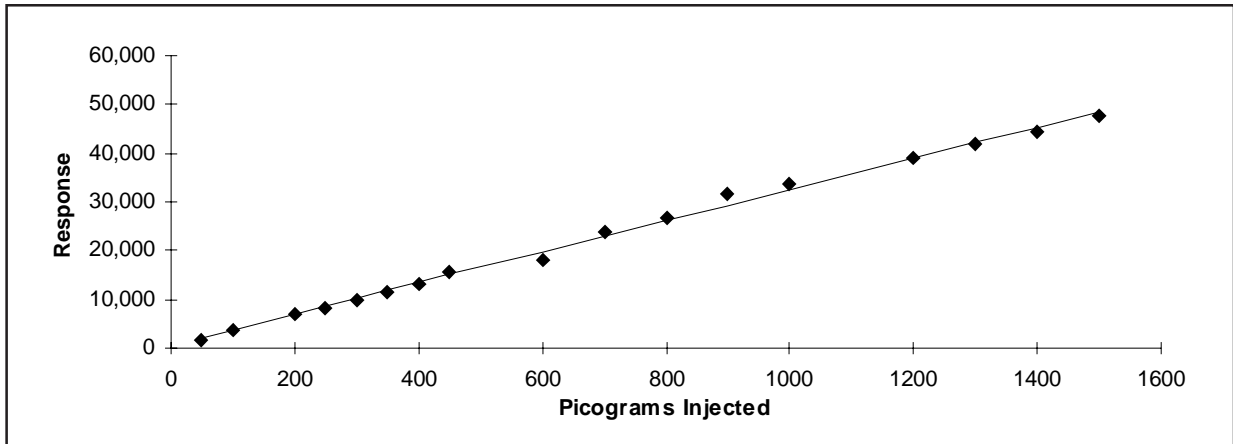


Figure 8. Response Curve for Methyl Parathion

Finally, the time resolution of the emission may be used to perform simultaneous dual element analysis using the PFPD. Many organophosphorus pesticides also contain sulfur. The detector controller of the OI Analytical Model 5380 PFPD can output data from two time slices of the emission simultaneously; this ability can be used to collect independent sulfur and phosphorus chromatograms. Figure 9 is a chromatogram of the 30 picogram organophosphorus pesticides collected in sulfur mode. (The GC conditions and identification key are the same as Figure 4.) The sensitivity in sulfur mode is lower than in phosphorus mode, but at concentrations higher than 30 picograms per component, the dual gate design of the controller allows a confirmatory sulfur mode chromatogram to be collected simultaneously with the phosphorus mode chromatogram.

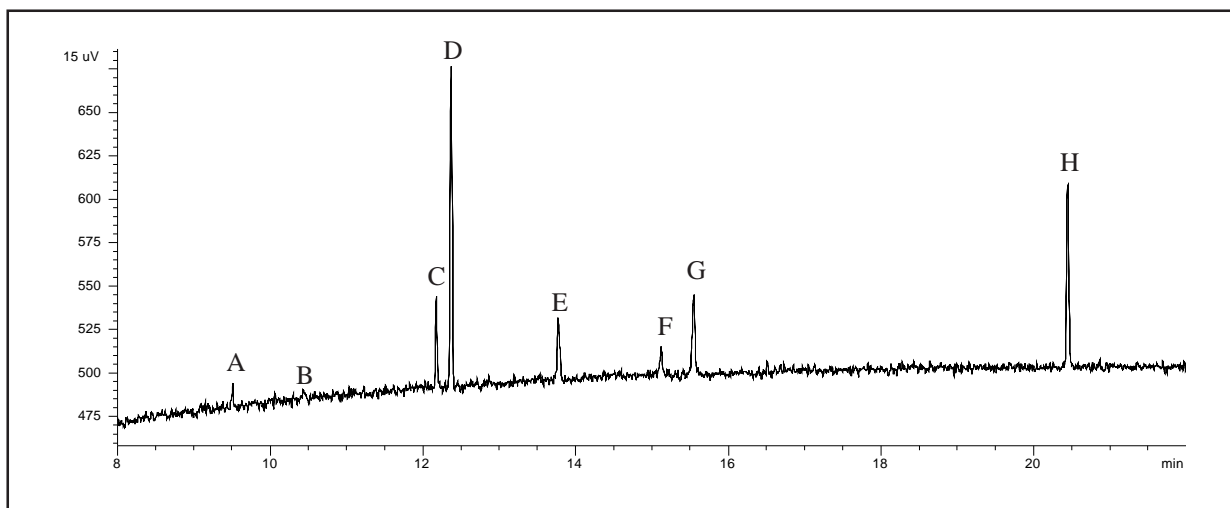
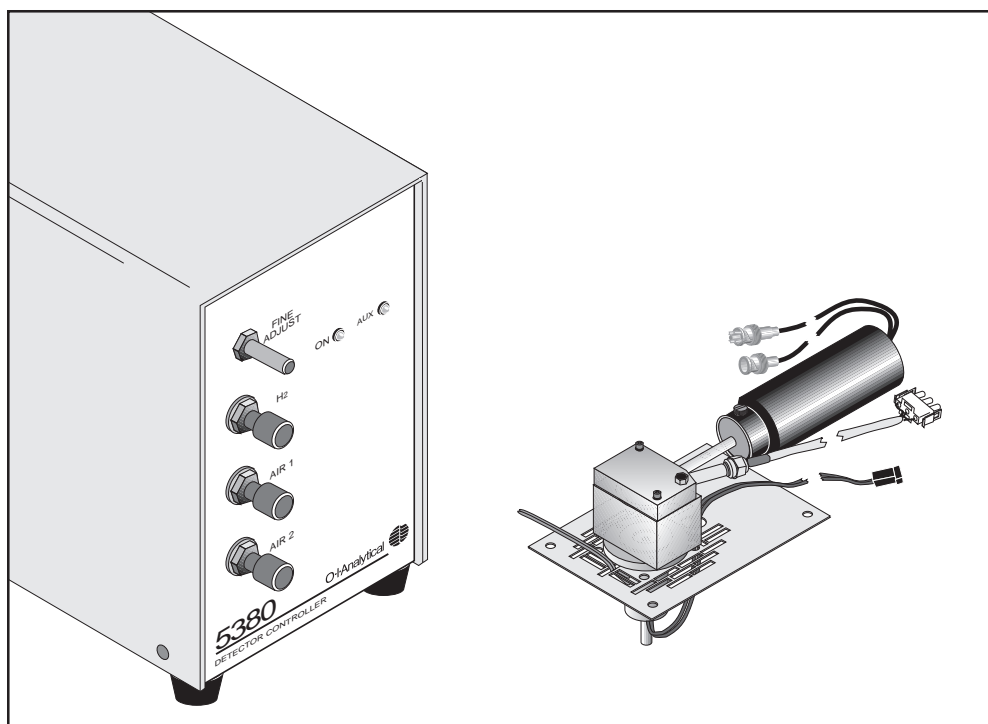


Figure 9. 30 pg Organophosphorus Pesticides Collected in Sulfur Mode

Conclusion

The Model 5380 PFPD is an excellent detector for the analysis of organophosphorus pesticides. The detector is both sensitive and selective. The linearity of response is excellent for the organophosphorus pesticides. The majority of organophosphorus pesticides also contain sulfur. The dual output channel design of the OI Analytical Model 5380 PFPD allows the collection of phosphorus chromatograms to identify and quantify the pesticides, while simultaneous collection of sulfur chromatograms allows confirmation of the pesticides.



OI Analytical Model 5380 Pulsed Flame Photometric Detector (PFPD) and Controller



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