O·I·Analytical

Optimization of a Pulsed Flame Photometric Detector for Nontraditional Elements

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Nitrogen
PFPD
Phosphorus
Sulfur
Tin

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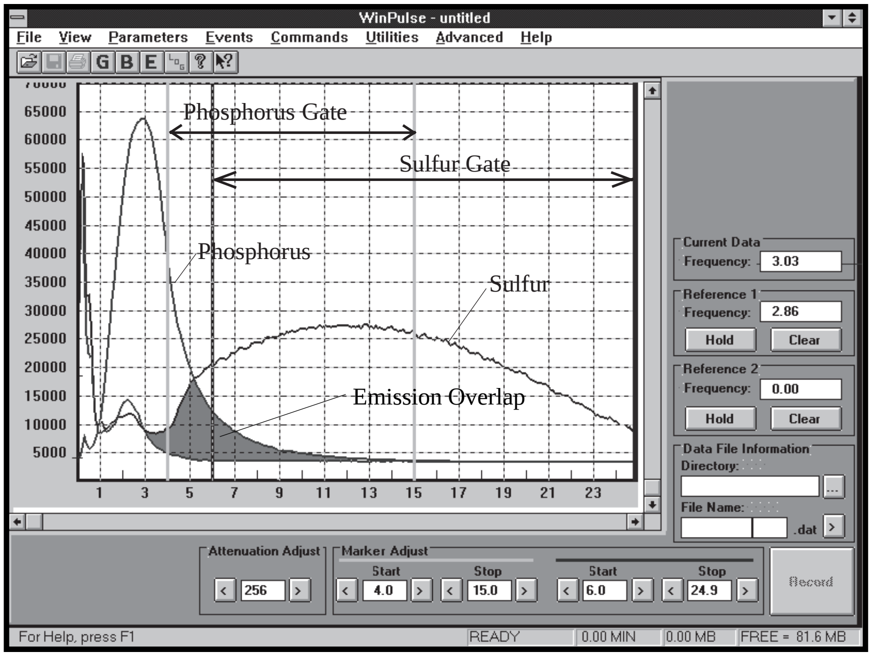
Introduction

The flame photometric detector (FPD) is one of the oldest selective gas chromatography detectors. The FPD is traditionally used for the analysis of compounds containing sulfur and phosphorus. Although it is possible to use the FPD to determine other elements, the interferences present usually significantly reduce the sensitivity of the detector. The pulsed flame photometric detector (PFPD), the newest innovation in flame photometric detectors, reduces the interferences by using emission time domain processing as well as wavelength filtering. This improves both the sensitivity and selectivity of the PFPD for the analysis of elements usually done with other detectors.

Flame photometric detectors combust the effluent from a gas chromatograph (GC) column in a hydrogen-air flame. In the flame, some heteroatoms in compounds eluted from the column form compounds in the excited state. As the compounds relax to the ground state, energy is released in the form of light. The mass of heteroatoms present can be determined by using a photomultiplier tube (PMT) to measure the light emitted. Selectivity for various elements is achieved by adjusting the flame stoichiometry and by changing the optical filter in the PMT to pass selected wavelengths of the emission. In a standard FPD, a narrow bandpass interference filter is commonly used to provide adequate selectivity against other elements and the extensive carbon background emission.

As a result of the pulsing flame in the PFPD, a time dimension is added to the selectivity in addition to the wavelength selectivity in the standard flame photometric detector. Emissions from various elements are characterized by different delays in the emission from the flame. Figure 1 shows the characteristic delays of phosphorus and sulfur emissions in the PFPD using a 2-mm combustor. The phosphorus emission is delayed 1 to 2 milliseconds relative to hydrocarbon emission, with the tail of the emission extending out to at least 15 milliseconds. The sulfur emission is much more delayed, with the emission starting at 4 milliseconds and extending out to at least 25 milliseconds in a clean, optimized system. By setting time gates, interelement interferences can be reduced or eliminated. The ability to use time gating for selectivity allows broad bandpass filters to be used instead of interference filters, increasing the amount of light reaching the PMT, which increases the sensitivity of the detector.



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Reference 2
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Start: 6.0 Stop: 24.9

For Help, press F1 READY 0.00 MIN 0.00 MB FREE = 81.6 MB

Figure 1. Phosphorus and Sulfur Emissions

The increased selectivity and sensitivity of the PFPD compared to the FPD allows the analysis of elements that are not traditionally determined using flame photometry. Professor Aviv Amirav of Tel Aviv University, the developer of the PFPD, has determined 28 elements using the detector. In many cases, two or more elements can be determined simultaneously with the proper choice of filter and PMT. Some combinations of elements cannot be determined simultaneously. Many of the elements are not commonly determined using gas chromatography, but several important elements that are not commonly analyzed using the FPD can be determined using the PFPD, including nitrogen, arsenic, and tin. The selective analysis of compounds containing these elements is important for some industrial and environmental applications.

Nitrogen

Many pesticides and fungicides contain nitrogen. The common method of determining these compounds is by using a GC with either a nitrogen-phosphorus detector (NPD) or a mass spectrometer (MS). Unlike PFPDs, NPDs can have an unstable baseline, and the response decays as the sensing element (bead) ages. NPDs require frequent recalibration and bead replacement to maintain optimum sensitivity. Mass spectrometers are not as sensitive as selective detectors for the analysis of ultratrace quantities and suffer more from matrix interferences.

A chromatogram of a simple pesticide mixture analyzed using a GC fitted with a PFPD optimized for nitrogen mode detection is shown in Figure 2. The compounds in the mix are present at a level of approximately 50 picograms of nitrogen per component. Note that thimet and chlorpyrifos give a response even though there is no nitrogen in either compound. The PFPD can give good selectivity against interfering elements only if there is little or no time domain or wavelength domain overlap. The phosphorus emission time and wavelength overlap those of nitrogen, so phosphorus will always give a response in nitrogen mode. The determination of nitrogen requires the use of an infrared sensitized PMT, which has an increased noise level compared to the PMTs used for sulfur and phosphorus. The increase in baseline noise decreases signal-to-noise ratios significantly and leads to a much higher detection limit for nitrogen than is obtained for sulfur or phosphorus. Detection limits for various elements are shown in Table 1.

Table 1. Detection Limits for Selected Elements Using the PFPD

Phosphorus	100 fg/sec
Sulfur	1 pg/sec
Nitrogen	30 pg/sec
Arsenic	5 pg/sec
Tin	30 fg/sec

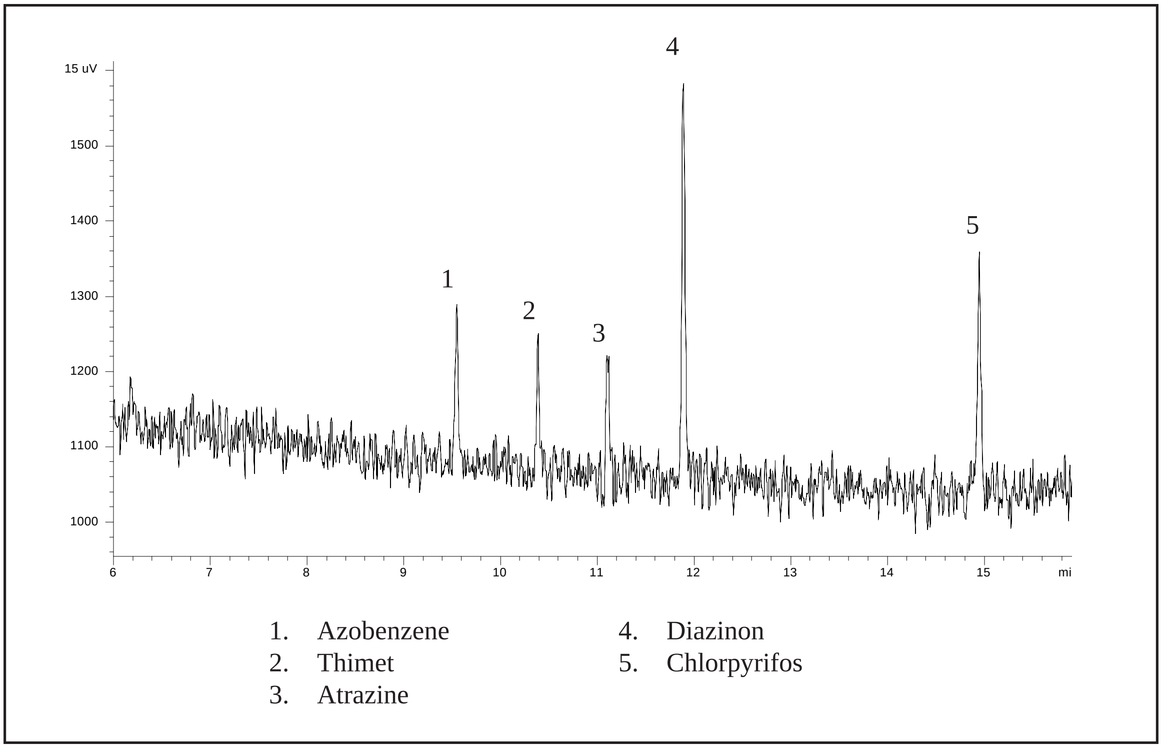


Figure 2. Chromatogram of Pesticide Mixture Using the PFPD in Nitrogen Mode

Arsenic

Arsenic is an element that is a significant impurity in some industrial processes. The level of arsenic is low in many feedstocks; however, arsenic is a very aggressive catalyst poison. In many processes, it is important to verify that the arsenic is removed before the feedstock is sent to the reactor. Arsenic has a very long emission delay in the PFPD, and it is not subject to significant interelement interferences other than sulfur. Sulfur and arsenic compounds can be resolved chromatographically, so arsenic can be determined very selectively at a very low level. Figure 3 is a chromatogram of 16 picograms of arsenic on column. Analysis of arsenic compounds down to the low parts per billion level is possible with the PFPD.

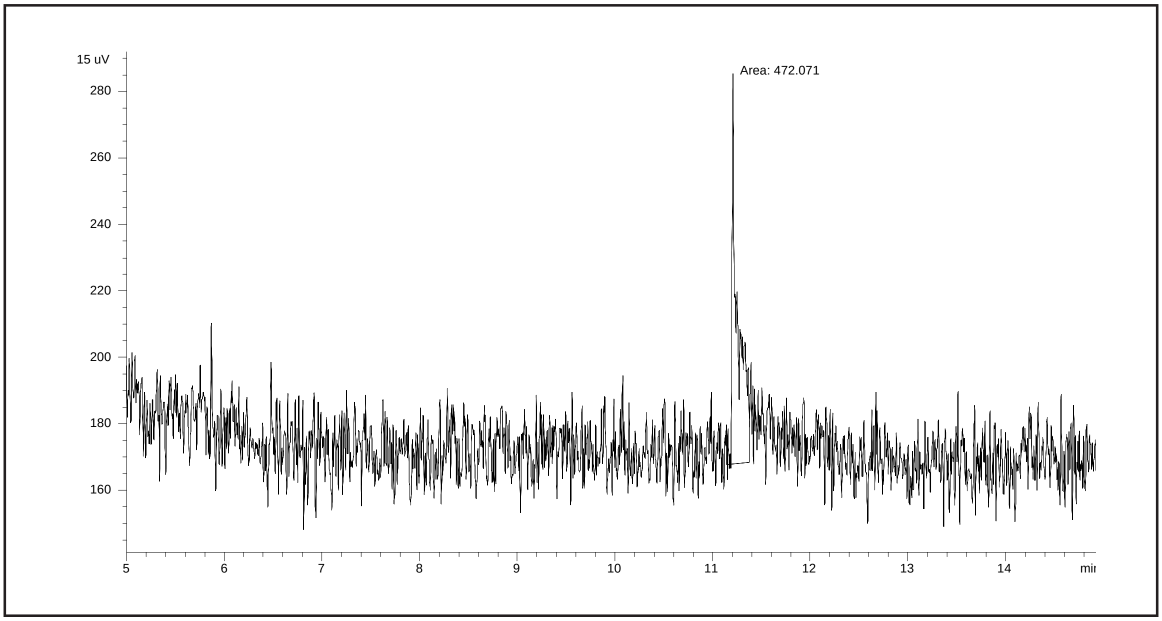
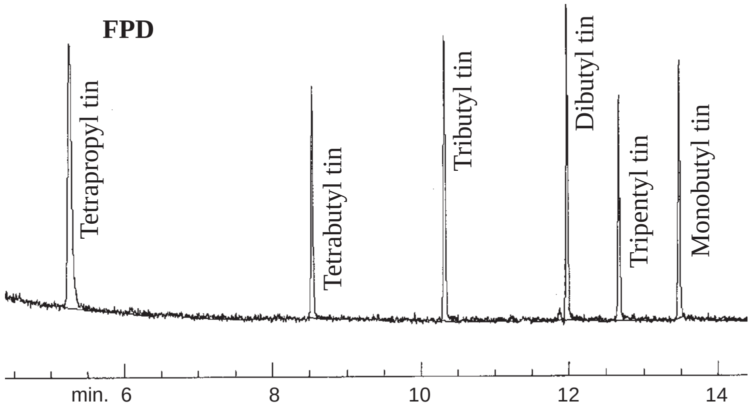


Figure 3. Chromatogram of 16 pg Arsenic Using the PFPD

Tin

Tin is now determined in water in coastal areas where there has been significant shipbuilding or maintenance activity. Large quantities of tin-based antifouling paints were used in those industries, and tin from these sources may adversely affect shellfish hatcheries. The USEPA has mandated a tin monitoring program, and conventional FPDs have been used for some of this work. Although useful for this application, the FPD is not sensitive enough to detect the levels of tin the USEPA prefers to analyze. Chromatograms of organotin compounds are shown in Figure 4. The sensitivity of the determination of tin using the PFPD is approximately 100 times greater than the sensitivity of the standard FPD. There is more tailing of the tin compounds in the PFPD than there is in the FPD. This is due to surface adsorption of tin onto the quartz combustor of the PFPD. Some FPDs may be fitted with an optional quartz chimney to enhance the detection of tin. When the quartz chimney is fitted, the FPD shows the same type of tailing seen in the PFPD.

Oven: 100°C for 1 min, to 285°C at 10°C/min; 15 psi constant pressure; 500 pg on column
Column Rtx-5



Oven: 100°C for 1 min, to 285°C at 10°C/min; 15 psi constant pressure; 5.0 pg on column
Column: Rtx-35

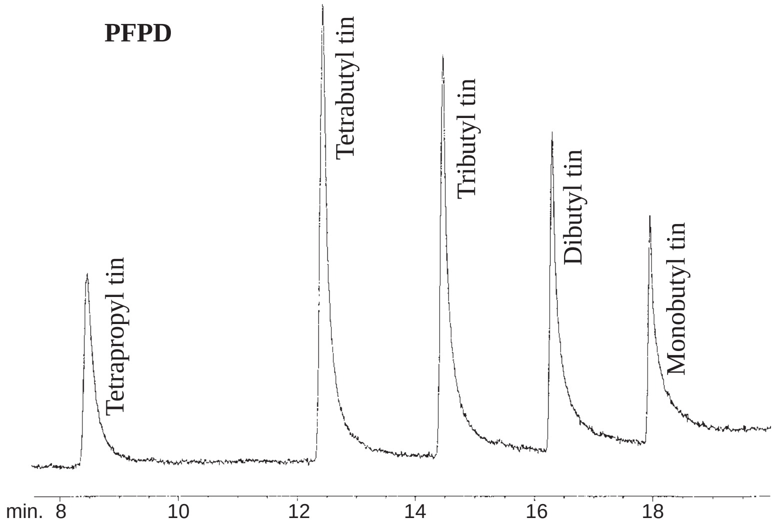


Figure 4. Organotin Compounds (500 pg) by GC/FPD and GC/PFPD (compliments of Restek Corp.)

Conclusion

The PFPD offers improved sensitivity and selectivity for many elements compared to other detectors. In cases like nitrogen where the sensitivity and selectivity are not enhanced, the PFPD may be more stable than other detectors used in the analysis. Table 2 lists some of the elements that may be determined on the PFPD, with the appropriate optical filter and photomultiplier tube.

Table 2. Filter and Photomultiplier Tubes for the Determination of Various Elements Using the PFPD

Element	PMT	Filter
Sulfur	R1924	BG-12
Phosphorus	R1924	GG-495
Sulfur and Phosphorus	R1924	UV-34
Nitrogen	R1925	RG-695
Arsenic	R1924	GG-495
Tin	R1924	BG-12

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