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Compound Dependence of Response of a Pulsed Flame Photometric Detector Operating in Phosphorus and Sulfur Modes

Application Note 12551098

Keywords
FPD
PFPD
Phosphorus
Sulfur

For many years, the flame photometric detector (FPD) has been used for the analysis of sulfur and phosphorus containing compounds using gas chromatography. Several designs have been developed to improve the performance of the detector. All FPDs function by combusting the column effluent in a hydrogen-air flame and converting the heteroatomic compounds into a molecular species in an excited state that releases some of the energy of reaction by emitting a photon. The emitted light, or chemiluminescence, is then measured using a photomultiplier and the signal is output to a recording device or data system. The detector uses a spectral filter to pass selected wavelengths; the filter determines which element or elements are detected.

There are three main types of flame photometric detectors. In order of development they are the single burner FPD, the dual burner FPD, and the pulsed flame photometric detector (PFPD). Each generation of detectors was developed to enhance the capabilities of the previous generation, providing better selectivity, sensitivity, or uniform response.

The original single burner flame photometric detectors used a hydrogen-air diffusion flame to combust the column effluent. The heteroatomic species emit after passing through the flame, and the emission is measured by the photomultiplier tube. The response of phosphorus is linear with this design, but sulfur has a quadratic response. The response with this design is not equimolar, so the same mass of sulfur in two different compounds may give different signal levels. The response is not equimolar because the sample is burned in a diffusion flame with temperature and flame chemistry gradients. The more stable the compound is, the longer it will take to combust and the flame will be more oxygen-rich in the flame region where the combustion takes place. Since different compounds are combusted at different points in the flame and the flame chemistry varies with position in the flame, the response will be compound dependent.

The dual burner FPD was developed to provide a more equimolar response. In the dual burner design, the initial compound decomposition is separate from the excitation and emission. There are two hydrogen diffusion flames in the dual burner FPD. The initial effluent combustion takes place in the first flame, with the combustion products then fed into the second flame. The excitation and emission take place in the second flame. The response from the dual burner FPD is equimolar because the same molecular species is being excited in the same flame chemistry regardless of the parent compound.

The pulsed flame photometric detector (PFPD) is the latest innovation in flame photometry. The PFPD uses a premixed hydrogen-air mixture flowing through and around a combustor at a rate too low to support continuous combustion. This is shown in Figure 1. The combustor fills with the hydrogen-air mixture until the mixture reaches the ignitor. The mixture is ignited and the flame propagates through the ignitor cap and the combustor until it reaches the combustor support. At this point all the flammable mixture has been burned and the flame is extinguished. The spent gases are swept from the combustor by fresh mixture, and when the fresh mixture reaches the ignitor the cycle is repeated. Repetition rates are usually three to four Hertz.

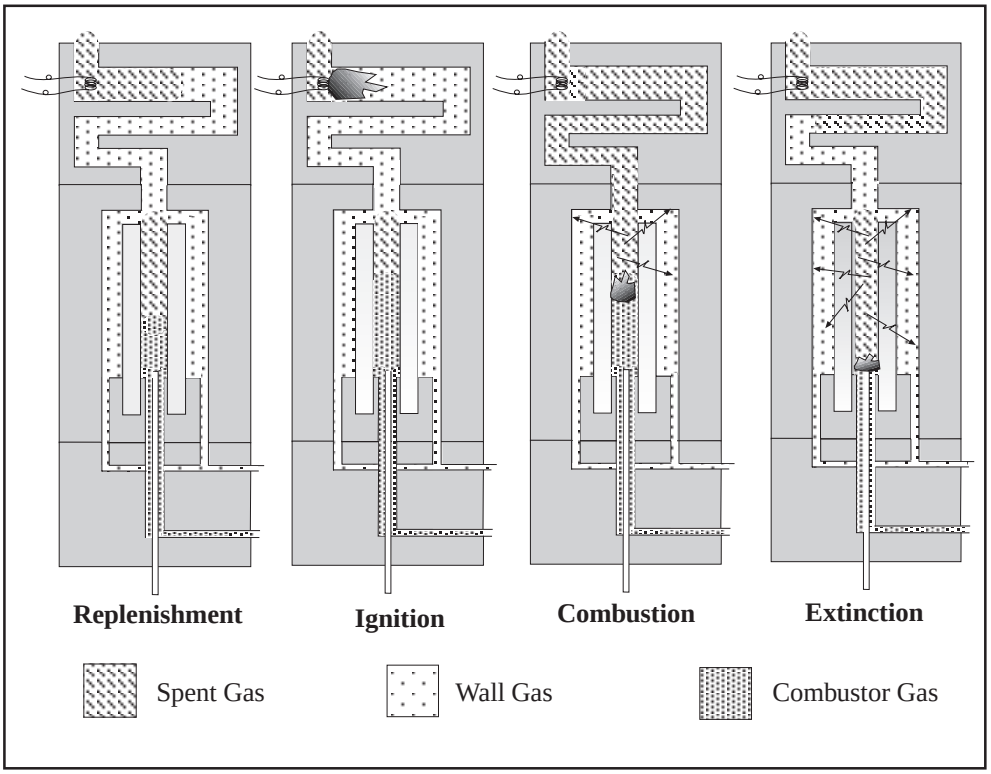

Figure 1. Four Phase Cycle of Propagating Flame

The hydrogen and air are premixed, so there are no gas composition and temperature gradients in the flame. The constant gas mixture and temperature ensure uniform flame conditions for all compounds, so the response in the PFPD is equimolar. The PFPD has the equimolar response of the dual burner FPD without the complexity required by the dual burner design. The equimolar response can be observed by examination of the emission profiles in the WinPulse™ software (OI Analytical) or in the optional PulseView data collection and reanalysis software. The emission profile is characteristic of the flame conditions when the element is excited. The emission profiles for a heteroatom in different compounds are the same, so the flame chemistry during excitation is the same. If the flame chemistry is the same, the molar response will be the same. Differences in the emission profile indicate changes in the flame chemistry, and thus deviations from equimolar response.

In addition to the equimolar response, the PFPD also has increased selectivity compared to the FPD. The selectivity of the FPD is dependent only on the filter used between the flame and the photomultiplier tube. The PFPD adds the time dimension to selectivity. This is shown in Figure 2 where the emission profiles of hydrocarbon, phosphorus, and sulfur are shown. Hydrocarbon is not delayed significantly, phosphorus emission is slightly delayed, and the sulfur emission is delayed more than the other species. By selecting an appropriate time slice of the emission to integrate, the selectivity of the PFPD is enhanced. The additional selectivity also aids in achieving equimolar response, as contributions to the emission from interfering species are reduced.

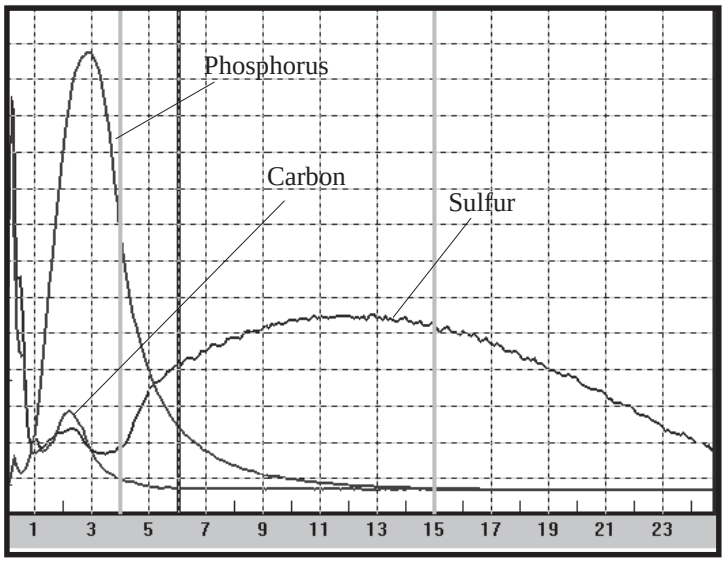

Figure 2. Carbon, Phosphorus, and Sulfur Emission Lifetimes

To determine if the response was equimolar, a series of sulfur and phosphorus standards were run. The response factors for the compounds were calculated and compared to determine if the response is truly equimolar. An appropriate filter and gates optimized for the element of interest were used for these determinations.

Three different mixtures of sulfur compounds were analyzed. The chromatograms of these mixes are shown in Figures 3, 4, and 5. The sulfur species used were all volatile, so the same compounds were used in more than one mixture to control the effects of loss of compounds during standard preparation. The response factors for the sulfur compounds are given in Table 1. The response factors for the various compounds are all very similar. The relative standard deviation (RSD) of the response factors is less than 4%. The response factors that are significantly lower than the average are for the most volatile compounds, which are the ones most likely to evaporate during sample preparation.

The same procedure was used for the phosphorus compounds, but since the phosphorus compounds were not volatile only one standard mixture was used. The chromatogram of the phosphorus standard is shown in Figure 6. The response factors calculated for the phosphorus compounds are given in Table 2. The response factors for the compounds are similar in most cases, with the response factor for azinphos methyl being significantly lower than the others. The RSD of the response factors for this sample set was 9.7%. Azinphos methyl is one of the more difficult organophosphorus pesticides to get good recovery of, regardless of the detector. If the response of azinphos methyl is excluded from the calculation, the RSD of the response factors is 4.5%. Many of the compounds in this mixture are labile and easily decomposed in a gas chromatograph inlet liner or column if any active sites are present. There are some small peaks in the chromatogram, which are probably decomposition products of the compounds in the standard mixture.

The response of the PFPD is inherently equimolar. For the sulfur compounds in this study the deviations from equimolar response are due to loss of the most volatile components during sample preparation. The deviations from equimolar response in the phosphorus compounds are due to decomposition of the labile compounds in the inlet liner or column.

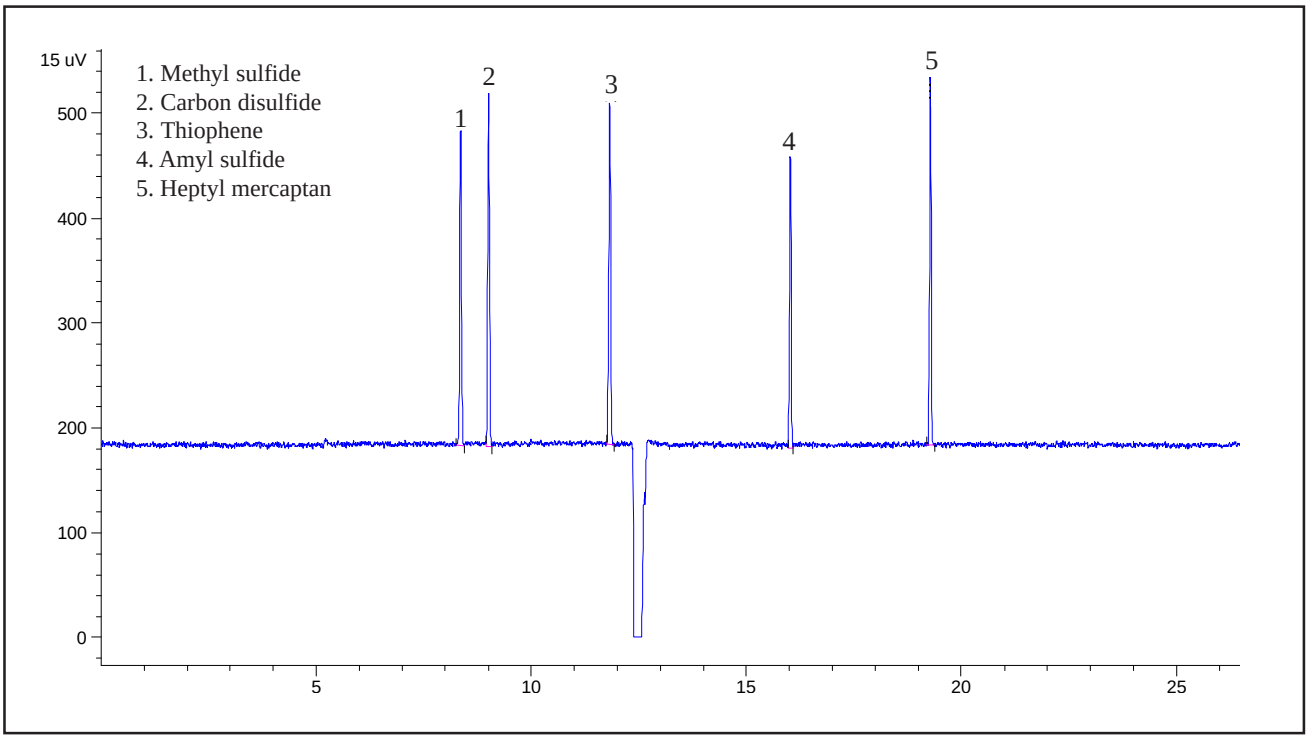

Figure 3. Sulfur Standard 1

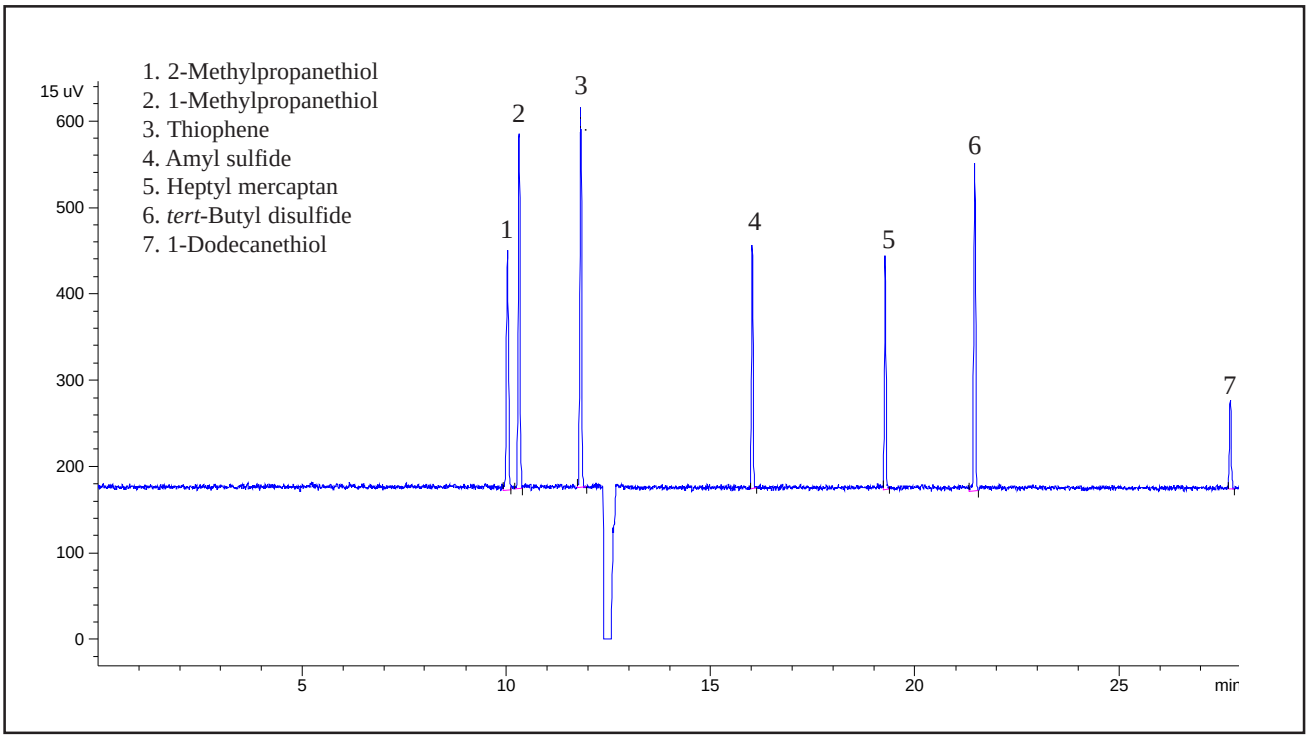

Figure 4. Sulfur Standard 2

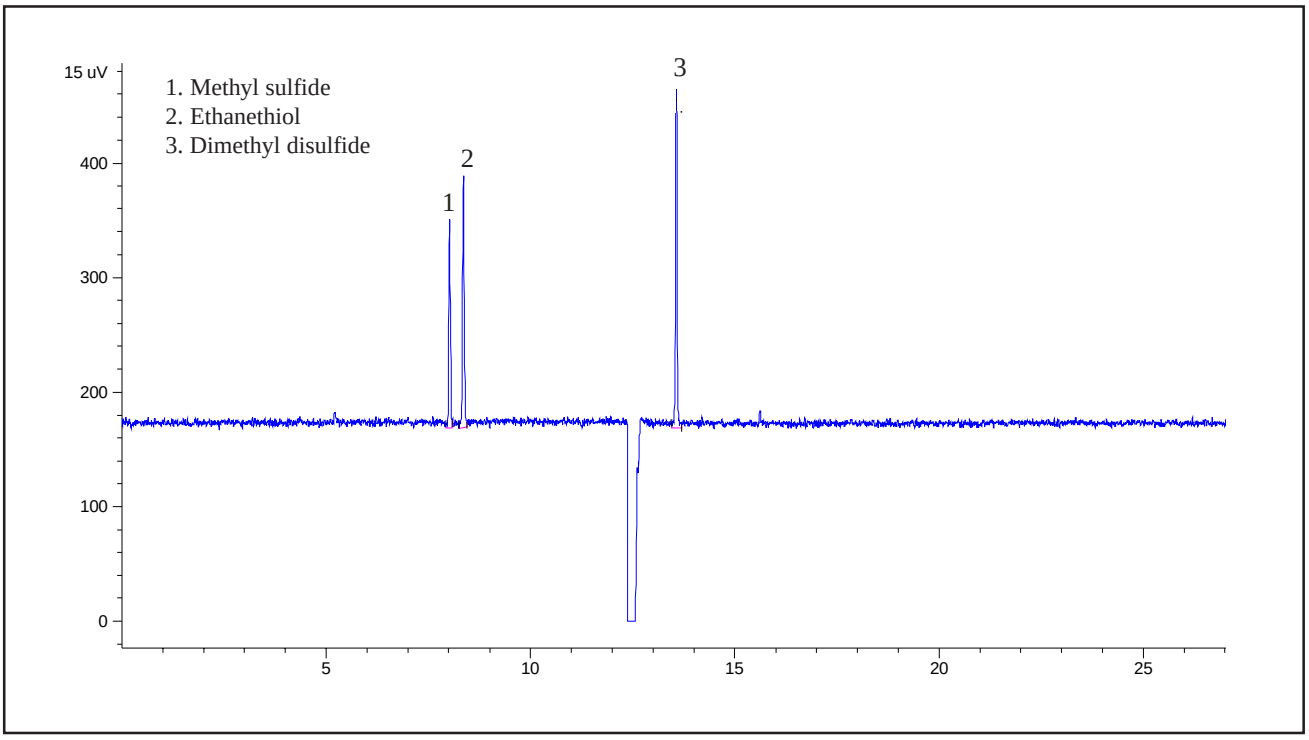

Figure 5. Sulfur Standard 3

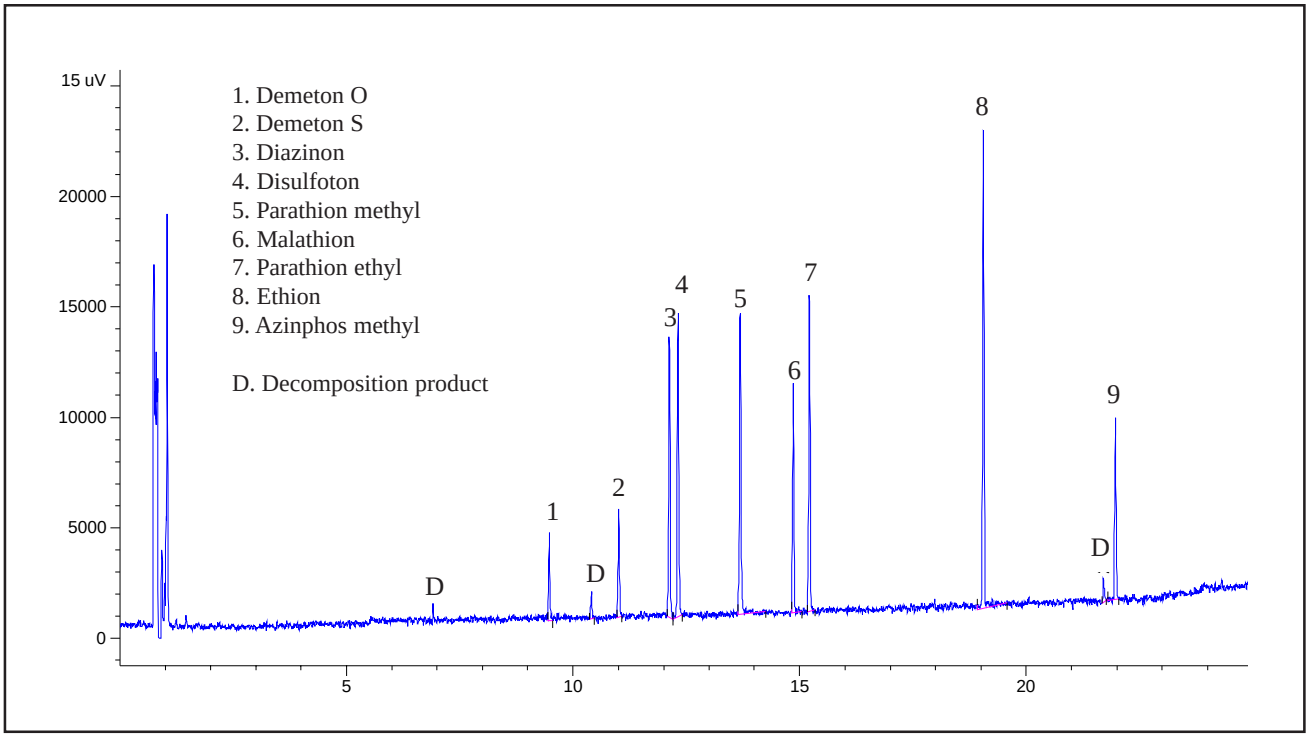

Figure 6. Chromatogram of Phosphorus Standard

Table 1. Compound Dependence of Sulfur Response

Compound	Picograms	Response	RF
Methyl sulfide	518	897	1.73
Carbon disulfide	559	1007	1.80
Thiophene	517	965	1.87
Amyl sulfide	410	775	1.89
Heptyl mercaptan	481	948	1.97
2-Methylpropanethiol	526	1004	1.91
1-Methylpropanethiol	673	1281	1.90
Thiophene	681	1351	1.98
Amyl sulfide	429	782	1.83
Heptyl mercaptan	375	738	1.97
tert-Butyl disulfide	634	1177	1.86
1-Dodecanethiol	169	321	1.89
Methyl sulfide	300	540	1.80
Ethanethiol	375	672	1.79
Dimethyl disulfide	483	881	1.83
Mean			1.87
SD			0.07
RSD			3.94

Table 2. Compound Dependence of Phosphorus Response

Compound	Picograms	Response	RF
Demeton O	3.25	8541	2629
Demeton S	4.37	11459	2622
Diazinon	10.18	28038	2754
Disulfoton	11.29	32883	2913
Parathion methyl	10.64	30746	2890
Malathion	8.38	22046	2631
Parathion ethyl	11.77	31878	2708
Ethion	16.11	46299	2874
Azinphos methyl	9.76	20078	2057
Mean			2675
SD			259
RSD			9.69

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