

Keywords

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Analysis of Sulfur-Containing Carbamate Pesticides Using a Pulsed Flame Photometric Detector

Introduction

Carbamates are a class of 22 pesticides widely used in agriculture as insecticides, herbicides, and fungicides, as well as some residential applications. They are similar to organophosphates in that they have been shown by the USEPA to pose a human health risk. Many of the carbamate pesticides have also been included in the USDA Pesticide Data Program (PDP). The thiocarbamates contain at least one sulfur atom, making them potential candidates for analysis and quantitation by a sulfur-selective detector. The Pulsed Flame Photometric Detector (PFPD) is regularly used for analysis of the organophosphate pesticides because of its excellent selectivity and extremely low detection limits, but it is also well recognized for sulfur analysis because of its essentially infinite selectivity for sulfur in the presence of complex matrices, exceptional sensitivity, low maintenance requirements, and long-term stability.

Many of the thiocarbamates tend to be thermally labile compounds. Because of this, they have traditionally been analyzed by liquid chromatography (HPLC) rather than by gas chromatography (GC). There are several drawbacks to the HPLC methodology including the need for derivitization, long analysis times, complex instrumentation, and lower sensitivity. A GC with a PFPD is a low-cost alternative for the analysis of some of the less labile or surface reactive thiocarbamates. The analysis time is faster, more sensitive, and subject to fewer matrix interferences. This application note describes the use of the sulfur-selective PFPD for determining two thiocarbamates, pebulate and thiobencarb, in beef tissue extracts.

Experimental

A series of four calibration solutions were prepared containing pebulate and thiobencarb, spanning the range from 5 to 200 ppb. Each calibration solution was analyzed in triplicate on a PFPD that had been configured and optimized for sulfur. An external calibration curve was prepared in the usual manner, plotting detector response (peak area) as a function of thiocarbamate concentration. The resulting calibration curves with associated correlation coefficients are shown in Figure 1. A typical chromatogram of the 10 ppb standard is shown in Figure 2. All of the instrument operating conditions are listed in Table 1.

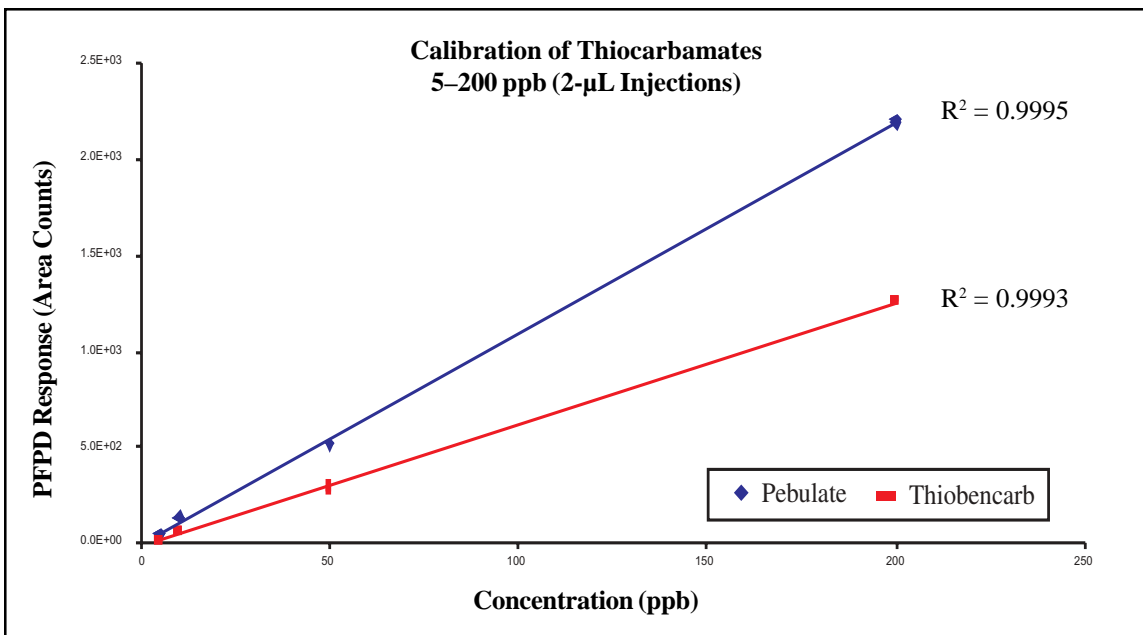


Figure 1. Four-point Calibration Curves for Pebulate and Thiobencarb Spanning the Range from 5–200 ppb

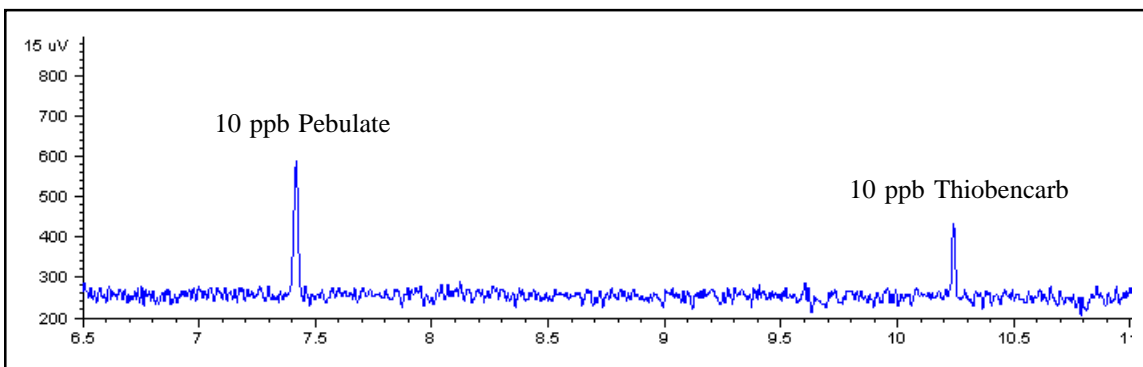


Figure 2. Chromatogram of a Calibration Standard Containing 10 ppb Pebulate and Thiobencarb

Table 1. GC and PFPD Configuration and Operating Conditions for Analysis of Pebulate and Thiobencarb

Inlet	Helium carrier gas 250°C 2-µL injections Pulsed splitless; 50 psi for 0.8 minutes
Column	HP-5 30 m x 0.32 mm I.D. x 0.25-µm film
Oven Program	60°C for 1 minute 20°C/minute to 300°C Hold for 1 minute
Detector	PFPD 2-mm combustor; BG-12 filter 220°C Gases tuned for sulfur Linear mode

Approximately one week after developing the calibration curves, three different beef tissue extracts were spiked with the two analytes of interest at 10 ppb and 100 ppb. Aliquots of the spiked and unspiked beef extracts were analyzed using the conditions described earlier. Ten replicate aliquots of the 10 ppb and 100 ppb standards were also analyzed as part of the same sequence to demonstrate detector stability.

Results and Discussion

Calibration

Both pebulate and thiobencarb produced excellent calibration curves with linear correlation coefficients of 0.9995 and 0.9993, respectively. One thing to note, however, is that the slopes for the two calibration curves are quite different. The PFPD is an inherently equimolar response detector for sulfur. In other words, the sulfur's chemiluminescence response is independent of a compound's molecular structure, and a fixed concentration of sulfur will give the same PFPD response regardless of the parent compound. Since pebulate and thiobencarb both have only one sulfur and their molar masses are quite similar (see Figure 3), the equimolar response feature of the PFPD would be expected to result in calibration curves with nearly identical slopes. The fact that the slopes for these two lines are so different indicates that at least the thiobencarb, and possibly the pebulate as well, are subject to some degree of breakdown during sample/standard preparation and/or the GC analysis. This suspicion is confirmed by a close examination of the baseline from one of the high-concentration standards. Figure 4 shows that there are a number of small, unexpected sulfur peaks in the baseline that support the suggestion of potential breakdown of one or both of these thiocarbamates. In spite of the potential for breakdown, repeatability from run to run remained quite good. Relative standard deviations (%RSD) for the triplicate injections made during the calibration varied from 4.8% at 5 ppb to 0.5% at 200 ppb.

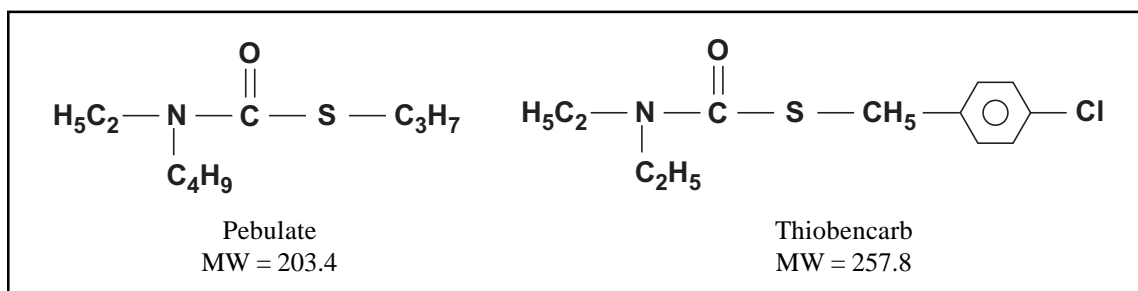


Figure 3. Chemical Structure and Molecular Weight of Pebulate and Thiobencarb

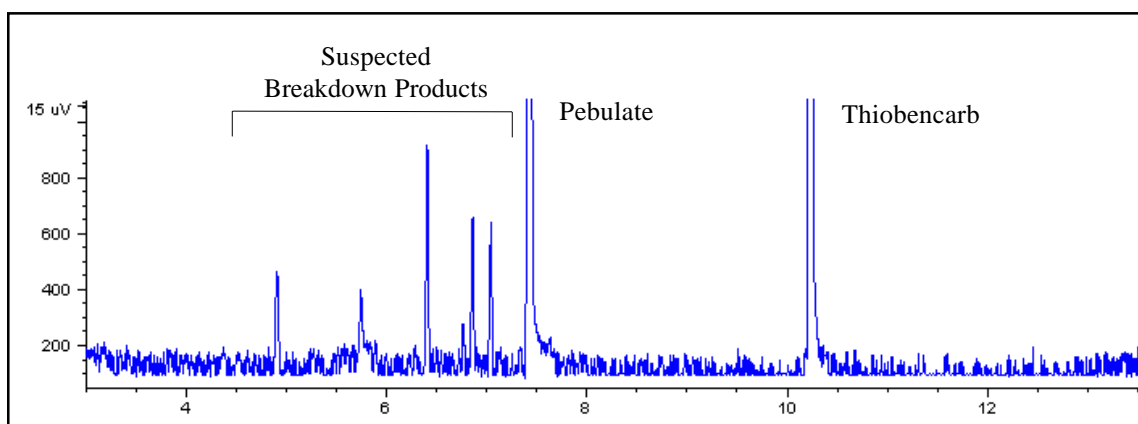


Figure 4. Expanded Baseline View of a High Concentration Thiocarbamate Pesticide Standard Showing the Suspected Breakdown Products

Repeatability

Ten replicate analyses were made of the 10 ppb and 100 ppb standards to determine run-to-run repeatability at both ends of the calibration range. The overlaid chromatograms and tabulated results are shown in Figures 5 and 6. As expected, the 10 ppb thiobencarb had the smallest peak areas and thus the highest relative standard deviation. All three of the other RSDs were less than 5%, with the largest peaks, 100 ppb pebulate, responsible for the best precision and an RSD of 1.3%. A third thiocarbamate pesticide, thia-bendazole, was included in the 100 ppb mix to determine if it was also a potential candidate for GC analyses. As can be seen from Figure 7, the peak areas for this compound varied considerably over the ten replicate analyses, suggesting significant reactivity and breakdown of the thiabenzazole using these conditions. Switching to a Restek Siltek™ Uniliner® reduced residence time in the inlet and minimized interactions with metal surfaces, improving repeatability as shown in Figure 8.

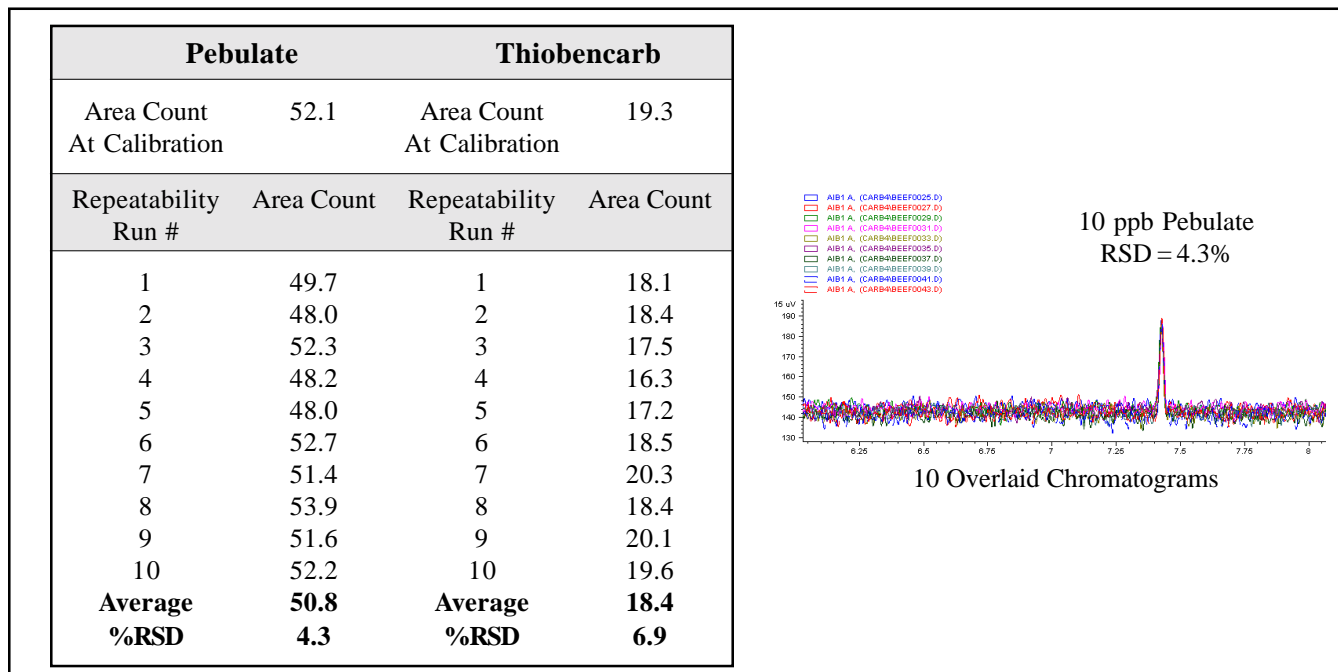


Figure 5. Repeatability of Pebulate and Thiobencarb Analyses at 10 ppb

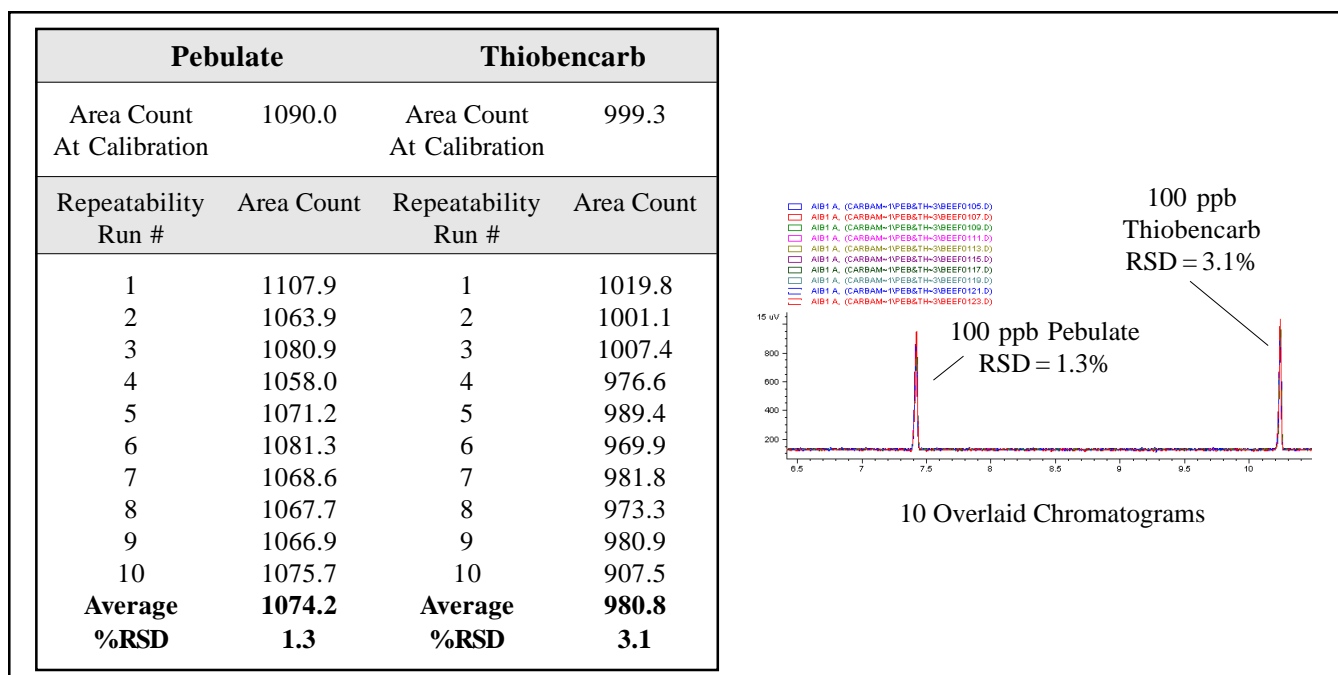


Figure 6. Repeatability of Pebulate and Thiobencarb Analyses at 100 ppb

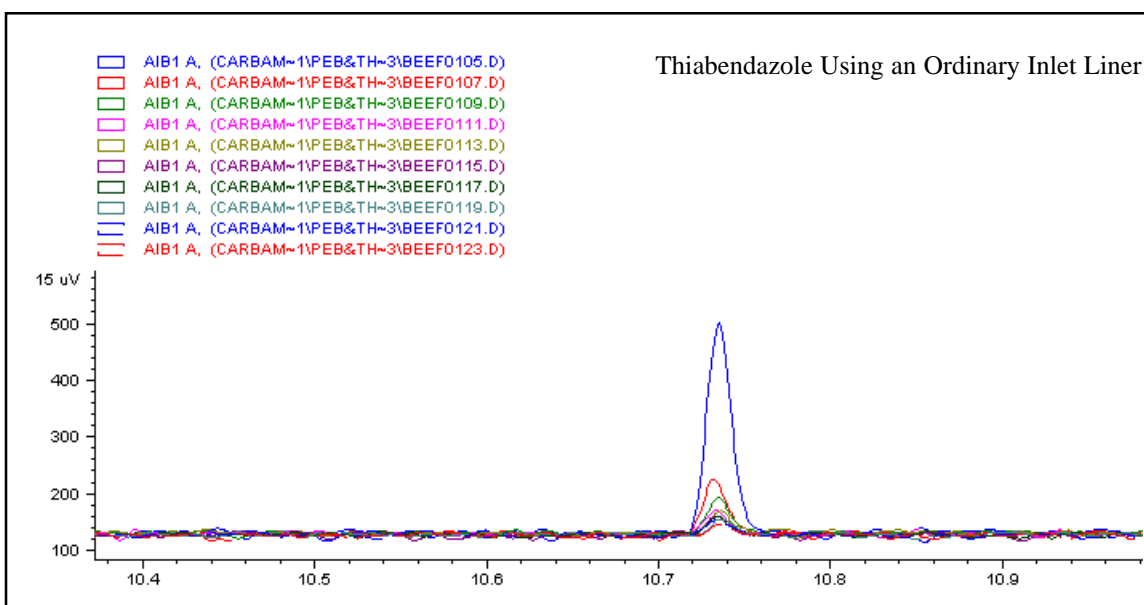


Figure 7. Overlaid PFPD Sulfur Chromatograms of Ten Replicate Analyses of Thiabendazole. The Inconsistent Results for Thiabendazole Using these Conditions Indicate Significant Thermal or Surface Reactivity.

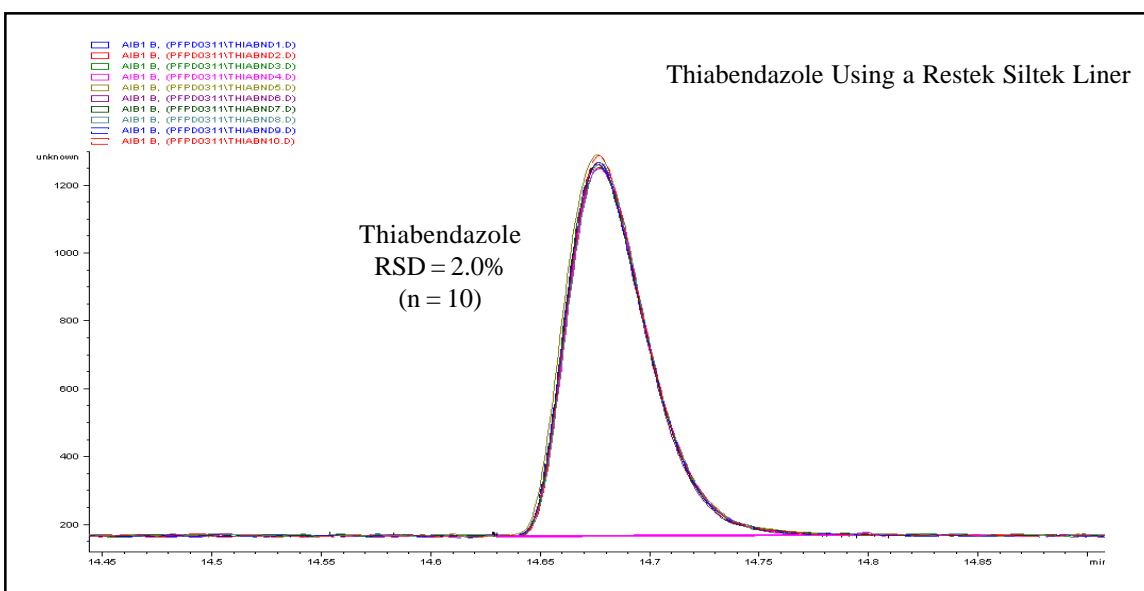


Figure 8. Overlaid PFPD Sulfur Chromatograms of Ten Replicate Analyses of Thiabendazole Using the Restek Siltek Uniliner to Reduce Breakdown. RSD Over the Ten Analyses was 2.0% (Figure is Courtesy of the USDA in Gastonia, NC).

Beef Tissue Extracts

Extracts of beef fat, beef muscle, and beef liver were spiked with the two compounds of interest at 10 ppb and at 100 ppb and analyzed along with unspiked aliquots using the GC and PFPD conditions described earlier. The resulting PFPD sulfur chromatograms are shown in Figures 9, 10, and 11. Figure 9 represents the original beef fat extract, plus the same extract spiked at 10 ppb and 100 ppb. Evident from the unspiked chromatogram is the fact that the beef fat extract did not contain either pebulate or thiobencarb, but did show evidence of several other sulfur compounds at approximately the 5 to 10 ppb range. The beef muscle extract (Figure 10) and the beef liver extract (Figure 11) showed similar results. Neither of the target compounds were present in the original muscle or liver extracts, but were easily identified and quantified in the spikes. As expected, the liver extract contained the most number of additional sulfur peaks, all at estimated concentrations in the 5 to 10 ppb range. In all cases, areas for the pebulate and thiobencarb spikes were consistent with the repeatability runs shown above.

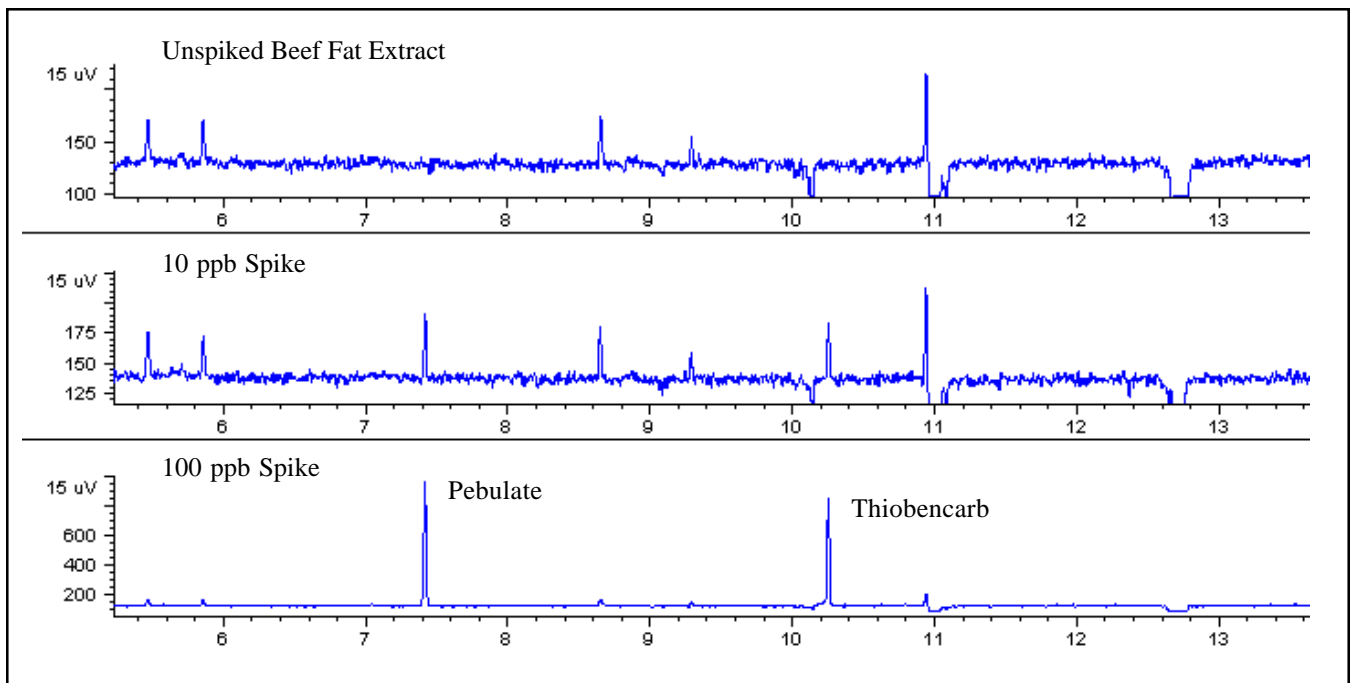


Figure 9. PFPD Sulfur Chromatograms of a Beef Fat Extract. The Top Trace is an Unspiked Aliquot Showing that there was No Pebulate or Thiobencarb in the Original Sample. The Middle and Bottom Traces are the 10 ppb and 100 ppb Spikes, Respectively.

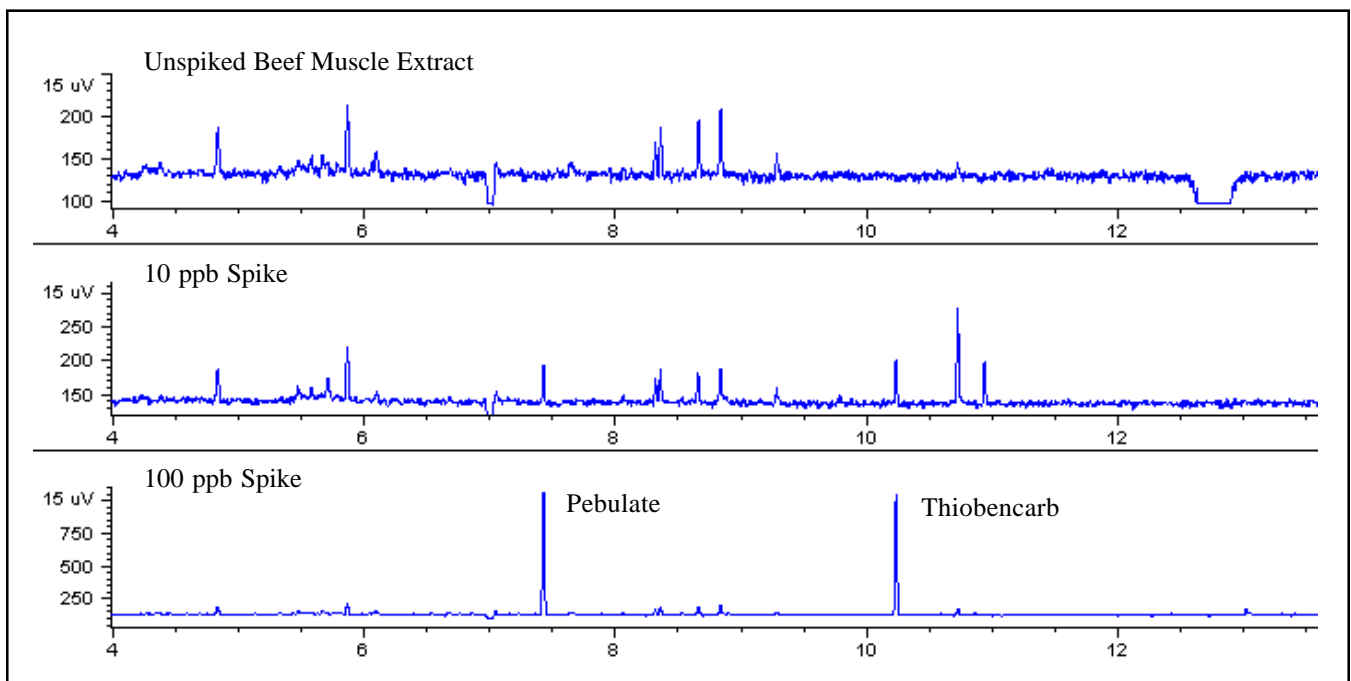


Figure 10. PFPD Sulfur Chromatograms of a Beef Muscle Extract. The Top Trace is an Unspiked Aliquot Showing that there was No Pebulate or Thiobencarb in the Original Sample. The Middle and Bottom Traces are the 10 ppb and 100 ppb Spikes, Respectively.

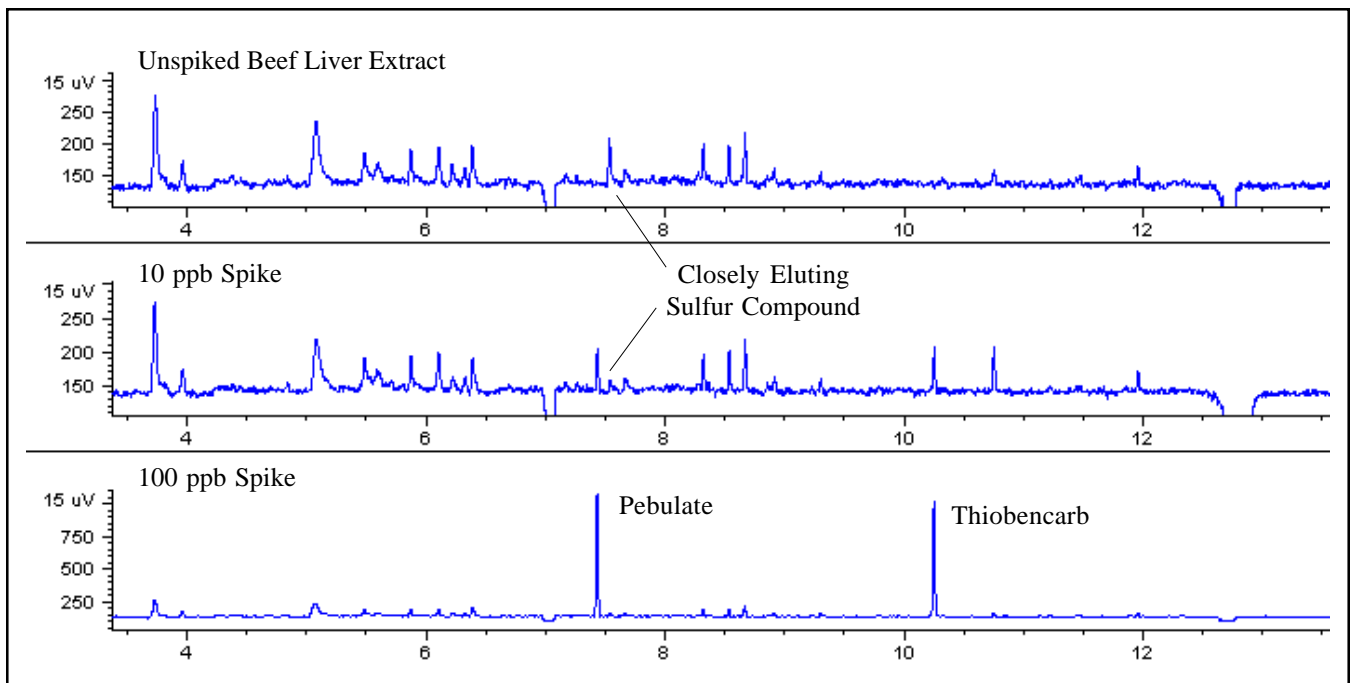


Figure 11. PFPD Sulfur Chromatograms of a Beef Liver Extract. Note that Although All Three Beef Tissue Extracts Contained Sulfur Peaks in the Range of Approximately 5 to 10 ppb, the Liver Extract Contained Many More Sulfur Compounds than Either of the Other Two, As Expected.

The PFPD is capable of outputting two simultaneous signals or chromatograms. For these samples, the first signal was used to quantify the sulfur compounds detected in the extracts, as shown above. The second signal was used to monitor the presence of potential interferences from a hydrocarbon background. This capability is illustrated in Figure 12. The top trace is the sulfur chromatogram from the beef liver extract spiked at 10 ppb, indicating the positions of pebulate at approximately 7.4 minutes and thiobencarb at about 10.2 minutes. The bottom trace is the hydrocarbon chromatogram illustrating two very large hydrocarbon contaminant peaks at 7 minutes and 12.5 minutes, as well as several smaller hydrocarbon compounds. Without the second-signal capability of the PFPD, it would be difficult to determine whether there were any closely eluting contaminants that could potentially cause interference with the analytes of interest. Although not part of this study, the PFPD can measure sulfur and phosphorus simultaneously and could be used to analyze phosphorus pesticides along with the carbamate analysis.

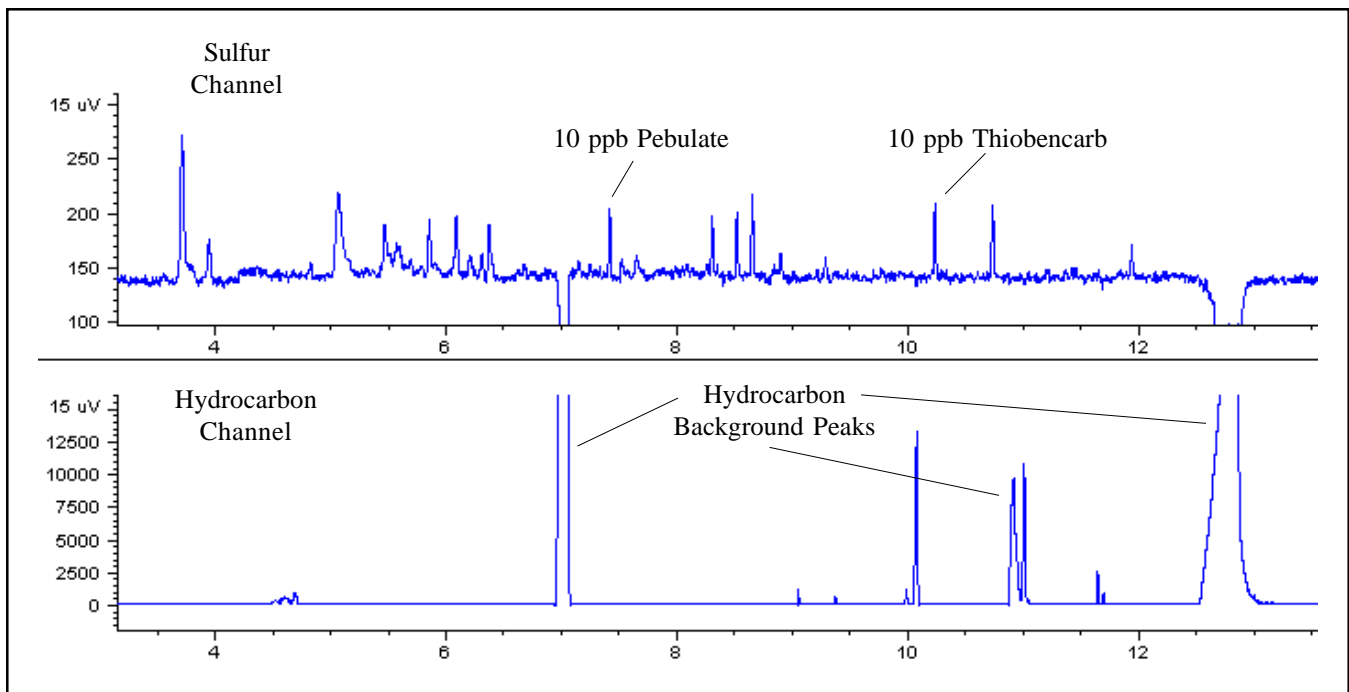


Figure 12. PFPD Sulfur and Hydrocarbon Chromatograms of the Beef Liver Extract Spiked with 10 ppb Pebulate and Thiobencarb. Note the Presence of Two Large Hydrocarbon Peaks at 7 and 12.5 Minutes, as well as Several Smaller Peaks, Which Might Not Otherwise be Detected as Potential Interferences.

Conclusions

In general, thiocarbamate pesticides tend to be thermally labile compounds that are not easily analyzed using traditional GC methodology. However, there are a few select thiocarbamates that do remain stable and can be analyzed using a GC-based, sulfur-selective PFPD. The traditional GC techniques are faster, simpler, and more sensitive than the HPLC methods that are usually applied to this class of compounds. The dual channel capability of the PFPD allows for monitoring of an additional hydrocarbon channel that may contain potential interferences. Detection and quantitation of pebulate and thiobencarb are possible into the single-digit ppb range.

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