O·I·Analytical

Analysis of Sulfur-Containing Flavor Compounds By GC/MS With A PFPD

Application Note 19060203

Keywords
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PFPD
Sulfur Compounds

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Abstract
Sulfur compounds are an important component of flavor analysis because of their unique contribution to the overall taste and aroma in complex mixtures. The sulfur compounds in many types of samples are responsible for specific and distinctive flavors, but can be difficult to analyze and identify because they are often present at such minimal concentrations. Gas chromatography with a mass selective detector is frequently used to identify the major components in flavors, but is not sensitive enough to differentiate the sulfur compounds at trace levels. This application note presents a unique method, coupling an OI Analytical Pulsed Flame Photometric Detector (PFPD) to a GC/MS and an FID for identification and quantitation of sulfur compounds in coffee and other flavor and fragrance samples.

Introduction
The presence or absence of selected sulfur compounds in coffee can have a significant impact on the quality of the final product. Trace levels of specific sulfur-containing compounds often are responsible for imparting the characteristic pleasant taste and aroma of coffee, while increased concentrations or absence of selected compounds may be responsible for variations in flavor among different blends. Many of the individual sulfur compounds that are responsible for the distinctive flavors in coffee can be difficult to detect by conventional GC or GC/MS techniques because they are present at extremely low concentrations, and they are often lost in the complex MS or FID chromatogram. It can be difficult or even impossible to identify the low-level sulfur compounds in an MS or FID chromatogram without some way to identify where they are by retention time.

To solve this problem, a sulfur selective detector is often used in parallel with the MS to assist with the location and identification of sulfur containing species in difficult matrices. The OI Analytical Pulsed Flame Photometric Detector (PFPD) shown in Figure 1 is ideally suited to this type of application because of its extreme selectivity and sensitivity for sulfur, and its ability to detect sulfur compounds in an otherwise interfering matrix. Individual sulfur peaks can be easily picked out of a forest of other compounds for possible identification. For this application note, analyses of the headspace from several coffee samples are used to demonstrate this technique.

Figure 1. Model 5380 PFPD

Experimental

Instrumentation

An Agilent 6890N gas chromatograph (GC) was configured with three detectors, an MS, an FID, and an OI Analytical PFPD, as shown in Figure 2. The three detectors were arranged to run in parallel by splitting the carrier gas at the end of the analytical column. The split was prepared using a Valco low dead volume connector and a 3-hole ferrule, and resulted in relative carrier gas flows to the MS:FID:PFPD of 1:10:10, with a total carrier gas flow of approximately 2.9 mL/min. Figure 3 is a photograph illustrating the column connection.

Figure 2. Photograph of the analytical instrumentation.The photograph on the right shows a close up of the Agilent FID in the front detector position (used for compound quantitation) and the OI Analytical PFPD in the back detector position (used for sulfur compound identification).

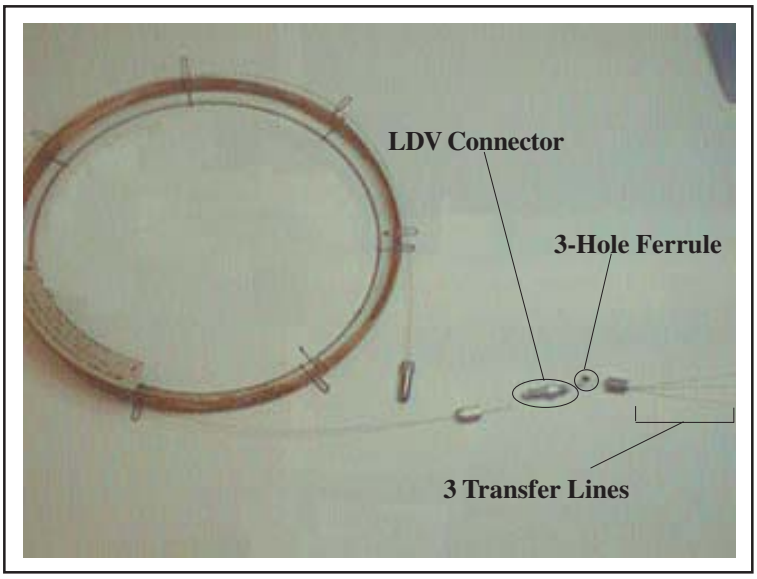

Figure 3. Photograph illustrating how the analytical column was connected to three parallel detectors using a Valco low dead volume connector, a 3-hole ferrule, and three lengths of column as transfer lines.

Sample Preparation

The headspace sample was prepared for introduction into the GC by placing approximately 20 grams of commercially blended and ground coffee from the supermarket into a tightly sealed half-pint Mason jar. The lid of the jar was adapted to attach a standard GC inlet liner that had been packed with 100 mg Tenax® TA (20/35 mesh, preconditioned and baked before use). (See Figure 4.) The sample was purged with helium for 30 minutes at 50 mL/min, and the headspace gases were trapped onto the sorbent. After purging, the inlet liner was quickly transferred to the hot split/splitless inlet of the 6890N, sealed in place, and immediately thermally desorbed onto the GC column. The experimental conditions for the GC are shown in Table 1.

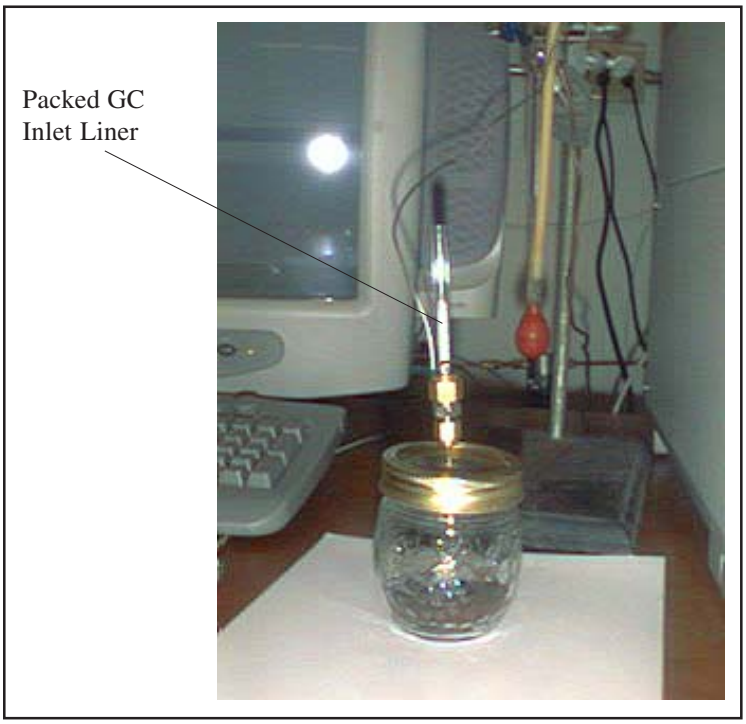

Figure 4. Photograph of the Mason jar apparatus used to prepare the headspace samples.

Table 1. Instrument configuration and operating conditions

Component	Setting
GC	Agilent 6890N
Inlet Conditions	260°C, split injection mode; 15:1 split ratio
GC Analytical Column	HP-5, 60 m x 0.32 mm ID x 0.25 µm film, He carrier gas, ~2.9 mL/min column flow Connected to 3 parallel detectors with a low dead volume connector and a 3-hole ferrule
Oven Program	30°C for 2 minutes, 2°C/minute to 260°C, hold for 20.5 minutes, total run time 145 minutes
MS	Agilent 5973N operated in scan mode, scan range from m/z 25 to m/z 350 with 2.3 scans per second
FID	Agilent FID, 250°C
PFPD	OI Analytical PFPD, configured for sulfur 2 mm combustor, BG-12 filter, H_2/air tuned for sulfur

Results and Discussion

The three simultaneous chromatograms from analysis of coffee "A" are shown Figure 5. The top chromatogram is the MS trace in full scan mode, which was used to confirm (by mass spectrum) the identity of selected peaks of interest. The middle chromatogram, which is very similar, is from the FID and was used for quantifying the relative abundances of each compound identified in the MS chromatogram. The third, bottom chromatogram is from the PFPD and was used to accurately pinpoint the location of specific, individual sulfur peaks in the MS chromatogram. The PFPD trace clearly shows the very large number of sulfur compounds present in the coffee, many of which might otherwise be overlooked or not identified from the MS or FID alone. When this system was configured using an FPD in place of the PFPD, only 10-20 sulfur peaks were detected.

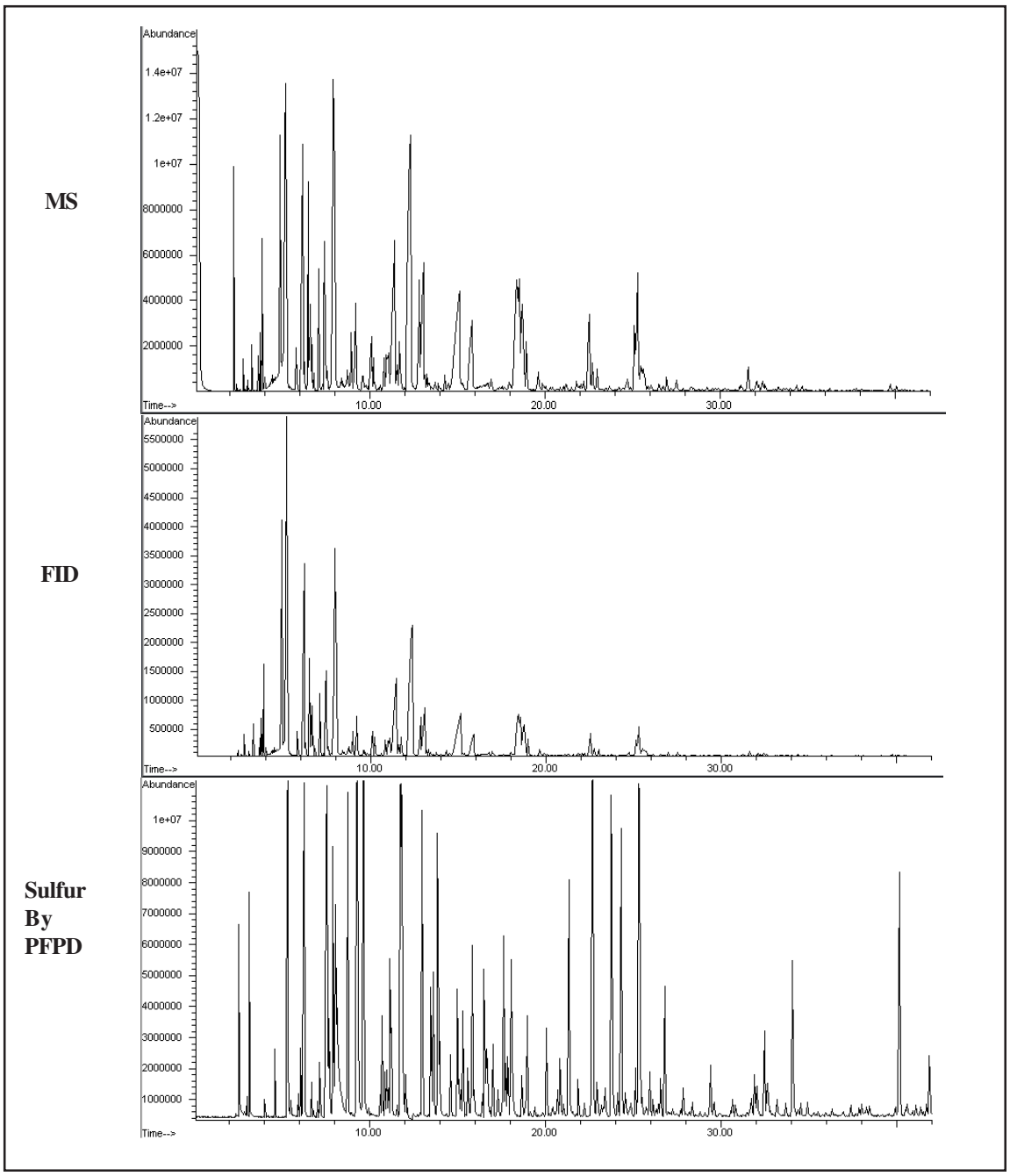

Figure 5. Simultaneous MS, FID, and PFPD chromatograms from analysis of headspace gases from coffee A.

To illustrate how the sulfur selective PFPD chromatogram can be used to identify the low concentration sulfur compounds, an expanded portion of the MS and PFPD chromatograms is shown in Figure 6. There are two strong peaks in the PFPD chromatogram at 23.75 and 24.29 minutes, which correspond to sulfur compounds in the MS chromatogram at 23.67 and 24.23 minutes, respectively. The small and reproducible "offset" in retention times between the MS and the PFPD chromatograms is due to the MS transfer line being under high vacuum, while the other two transfer lines are under slight positive pressure. Figures 6A and 6B are the library search results for these two sulfur compounds, which might otherwise have been overlooked in the MS or FID chromatogram alone. Using the PFPD in parallel with the MS, it was possible to locate between 200 and 300 individual sulfur species in the complex MS chromatogram.

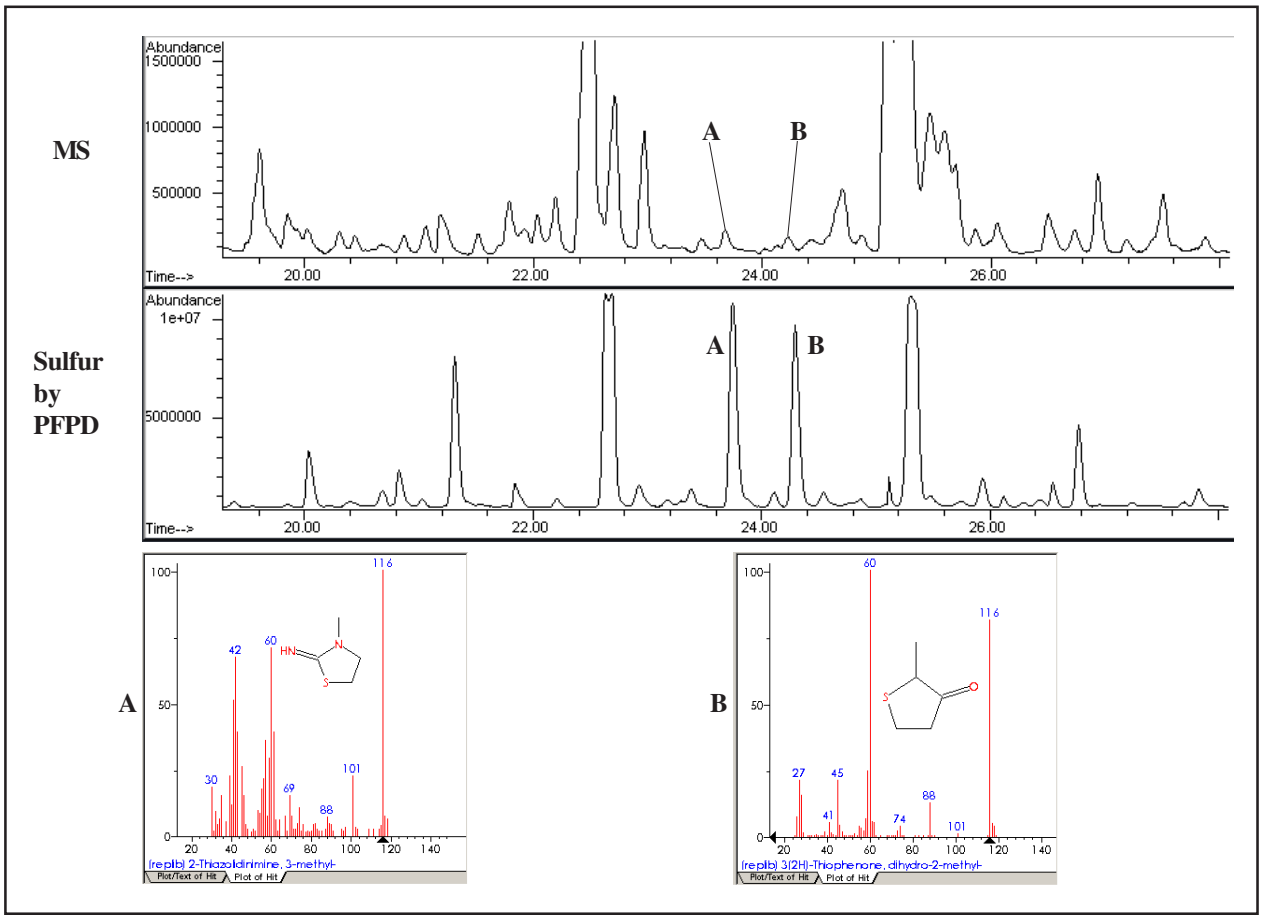

Figure 6. Expanded portion of the MS and PFPD chromatograms from 19 to 28 minutes. Retention times for two of the sulfur peaks in the PFPD chromatogram have been used to identify corresponding sulfur compounds in the MS trace. The NIST library search results for these two peaks are shown in 6A and 6B.

The PFPD sulfur chromatograms for three different coffee blends are shown in Figure 7. These chromatograms illustrate the variation in the sulfur profiles from three distinctive commercial coffee blends, and demonstrate the potential for detailed, competitive or QA/QC flavor analysis based on the sulfur profile.

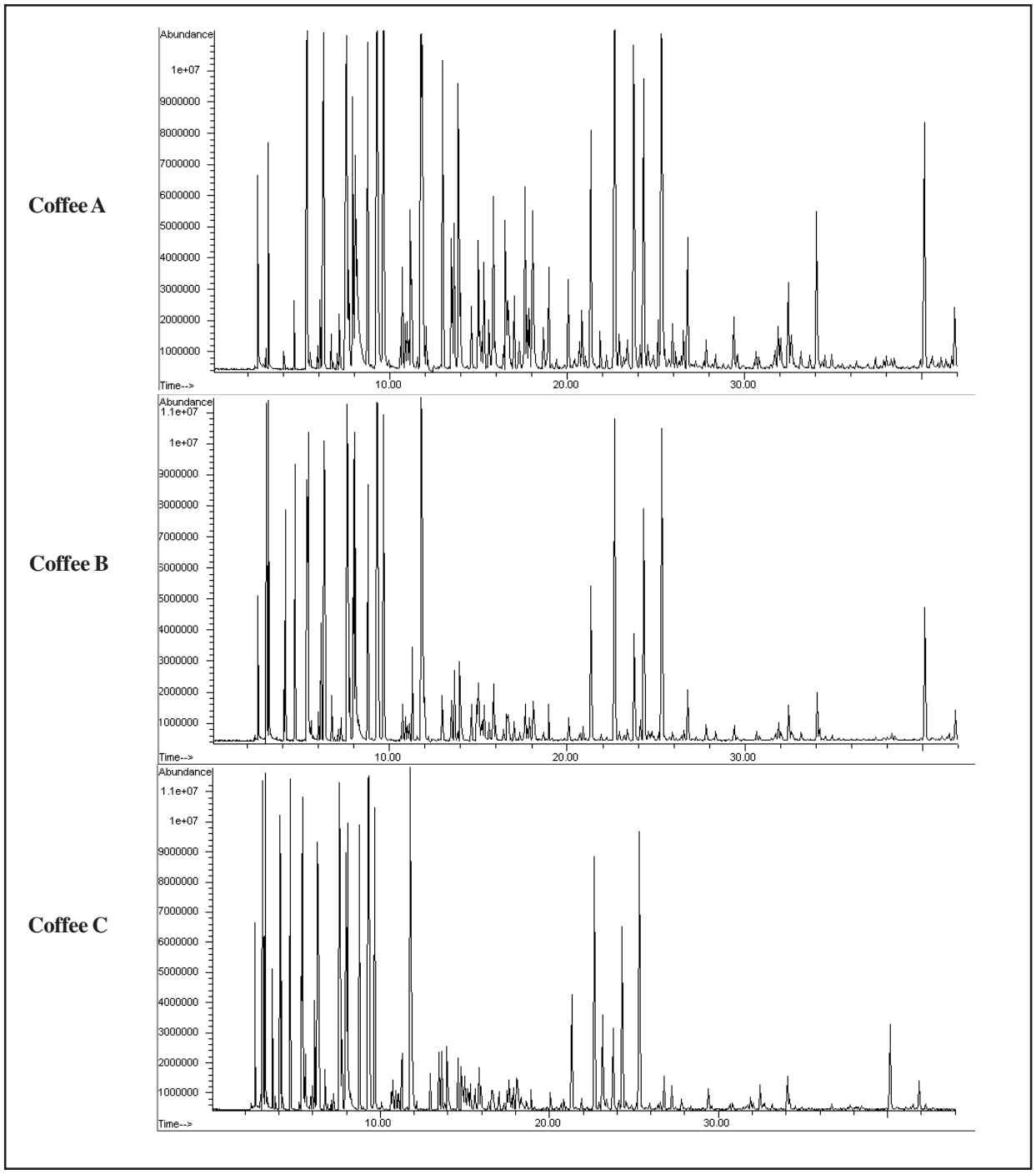

Figure 7. The PFPD sulfur chromatograms from analysis of three commercial coffee blends. Note the differences in the individual sulfur compounds present, which may be responsible for the characteristic flavors and aromas of the different coffees.

This technique of coupling a sulfur selective PFPD with a MS is not limited to analysis of sulfur in coffee. The method can be easily adapted for analysis of the sulfur content in any type of flavor or fragrance sample. Figures 8 and 9 illustrate how this approach was applied to the analysis of sulfur in two essential oils, fishwort oil and galbanum oil. When these two samples were analyzed using an FPD, no sulfur compounds could be detected in the fishwort oil and only four were seen in the galbanum oil. By contrast, the increased sensitivity of the PFPD allowed detection and identification of a wide range of sulfur species that otherwise would have been missed.

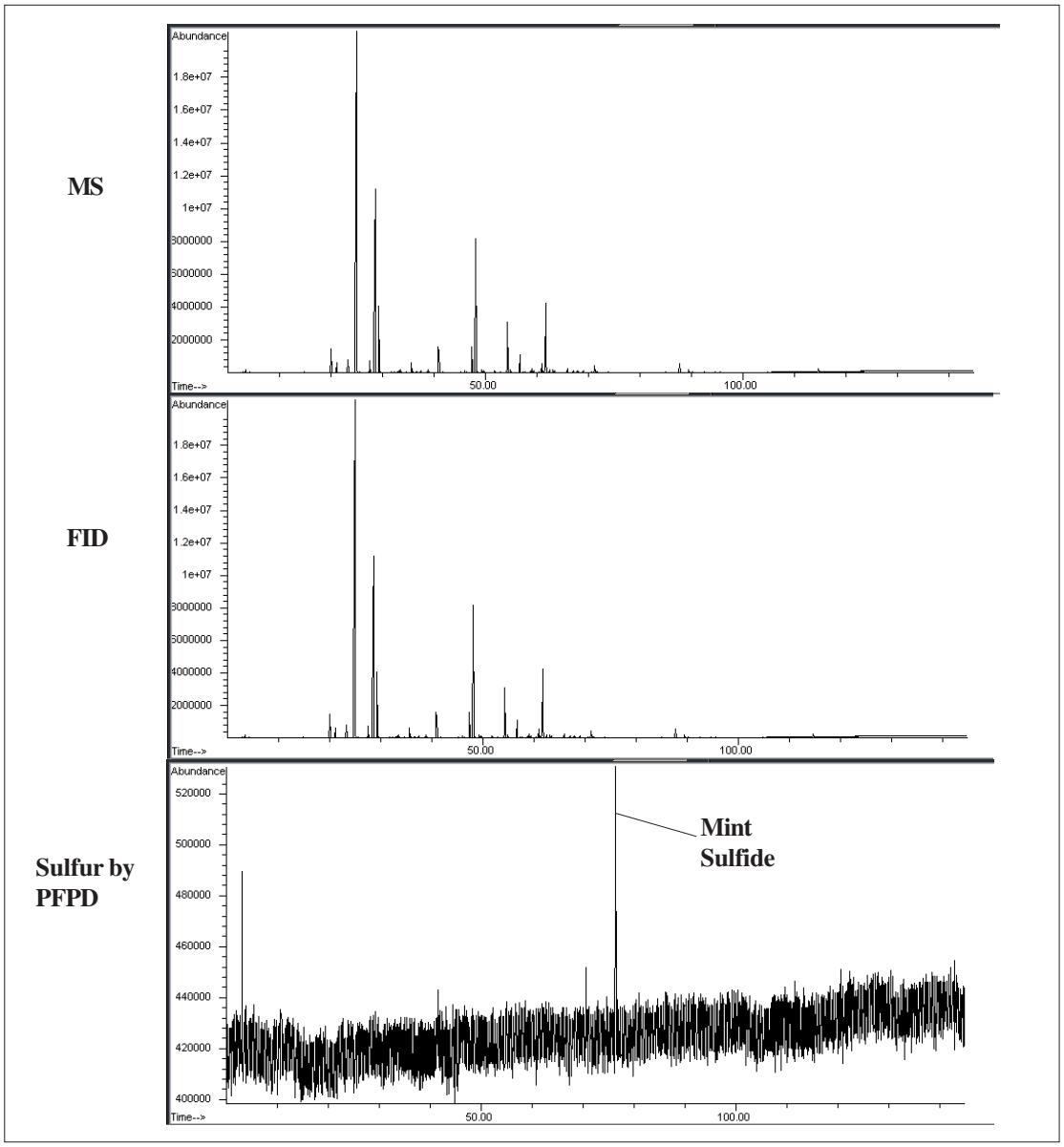

Figure 8. Simultaneous MS, FID, and PFPD chromatograms of fishwort oil. Fishwort oil is an essential oil distilled from the fishwort, or "Chinese Lizard Tail" plant. It has a destinctive correander lemon/ orange aroma and is used in the production of flavors. At these levels, mint sulfide is only detectable on the PFPD.

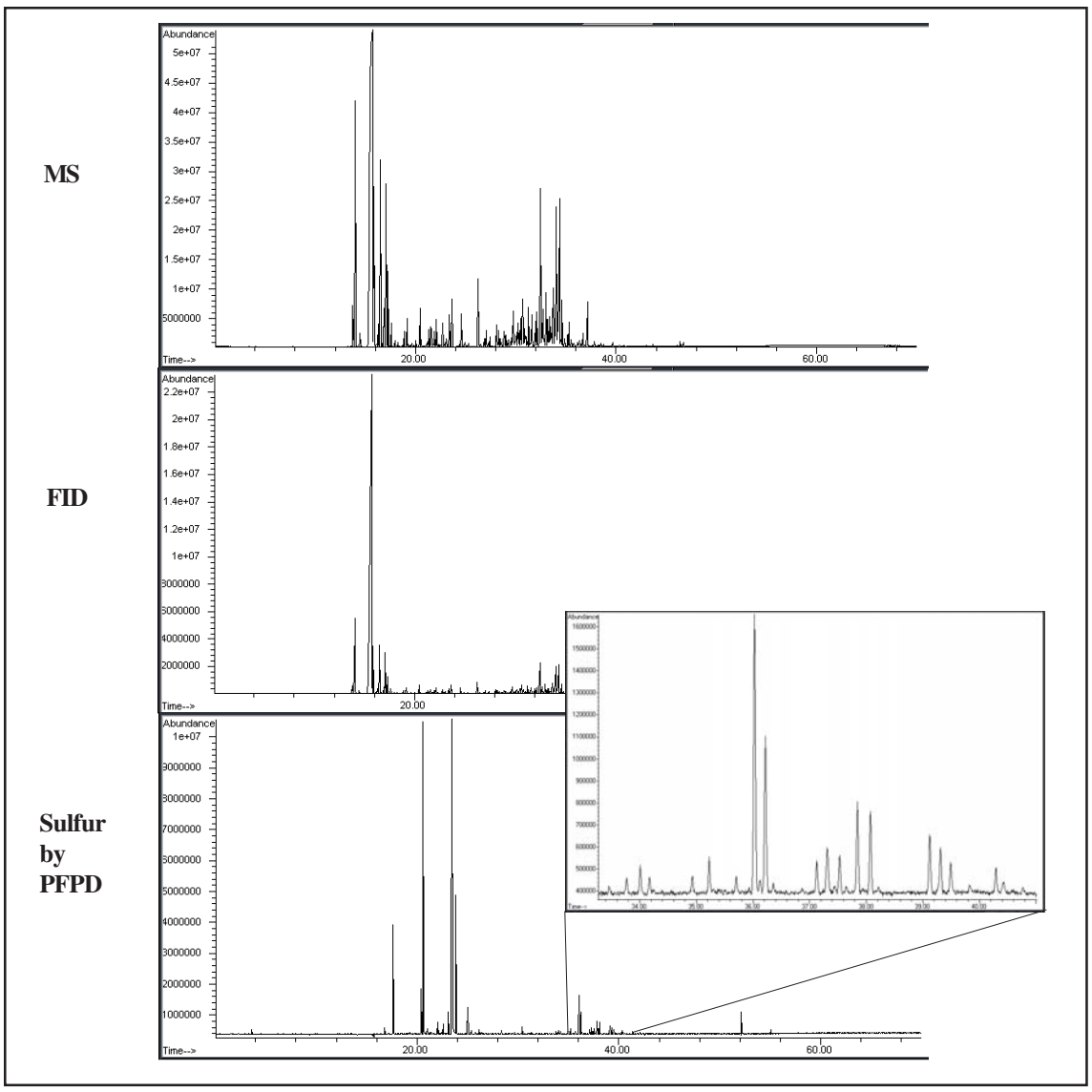

Figure 9. Simultaneous MS, FID, and PFPD chromatograms of galbanum oil. Only four sulfur peaks could be detected when the system was configured with an FPD. Galbanum oil is an essential oil distilled from the Galbanum plant. Its aroma is described as a green, fresh, leafy odor with dry, woody undertones and pine highlights and is usually used in the production of fragrances.

Conclusion

The Pulled Flame Photometric Detector (PFPD) can be used in parallel with a MS to identify the presence or absence of trace level sulfur compounds in complex flavor samples. The technique can be applied to a wide range of complicated flavor and fragrance sample matrices, and can be adapted for quality control or competitive analysis applications. Co-elution of flavor components that might mask the sulfur peaks or otherwise makes it difficult to locate the sulfur compounds in a complex chromatogram is not a problem for the PFPD, which responds only to the sulfur compounds in the mixture. Sensitivity of the MS can be further improved by increasing the portion of the carrier gas that is directed to that detector without a significant negative impact on the sensitivity of either the FID or the PFPD.

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