

Detection of Low-Level Sulfur Compounds in Spearmint Oil Using the Pulsed Flame Photometric Detector (PFPD)

FOOD & BEVERAGE SERIES



Introduction

Two species of spearmint are cultivated in the United States. In 2008, 1.09 million kilograms of spearmint oil were produced in the U.S.⁽¹⁾ Forty-five percent of U.S. spearmint oil is used to flavor chewing gum. One 55-gallon drum of mint oil can flavor 5,200,000 sticks of gum or 400,000 tubes of toothpaste.⁽²⁾

Sulfur compounds impart undesirable odors to essential oils used in flavor and fragrance products. Volatile sulfur compounds have extremely low olfactory thresholds. Detecting, indentifying, and eliminating sulfur compounds are important aspects of flavor and fragrance quality control.

This study examined the use of a Pulsed Flame Photometric Detector (PFPD) to locate and measure low-level sulfur compounds among the large number of hydrocarbon peaks present in a typical GC-FID chromatogram of neat spearmint oil. The analytical methodology employed in this rapid screening technique and chromatographic results are presented.



Figure 1. OI Analytical 5383 Pulsed Flame Photometric Detector

Experimental

Instrumentation used in this study was an Agilent 7890A GC equipped with an OI Analytical 5383 Pulsed Flame Photometric Detector (PFPD) shown in Figure 1 for detection of both Carbon and Sulfur species. Agilent Open Lab Software was employed for acquisition of C and S data. OI Analytical Pulseview Software was used to set up the analysis for C and S species. Setting the response factor (RF) between C and S compounds allowed display of widely different concentrations from the same output result. Pulseview Software was used to check each peak for the emission timing and characterize it as C and S with the filter and setup used.

Selective Detection of Sulfur Heteroatoms

The OI Analytical 5383 PFPD provides two independent channels of digitized output data. The integration gate for each data channel is set by using Pulseview Software to specify the start and stop times of each gate within the PFPD's 25-msec time domain.⁽³⁾

The emission times of hydrocarbons and heteroatoms often overlap. Figure 2 shows the emission profiles of hydrocarbon, phosphorus, and sulfur. Hydrocarbon emission exhibits little delay, phosphorus emission exhibits a slight delay, and the sulfur emission occurs over a significantly delayed time period. By analyzing a specific time slice of the emitted radiation, the selectivity of the detector can be enhanced significantly. For example, if the time slice from 10-24 milliseconds is analyzed, the majority of the emission is from sulfur with only a small contribution from phosphorus and no hydrocarbon contribution.

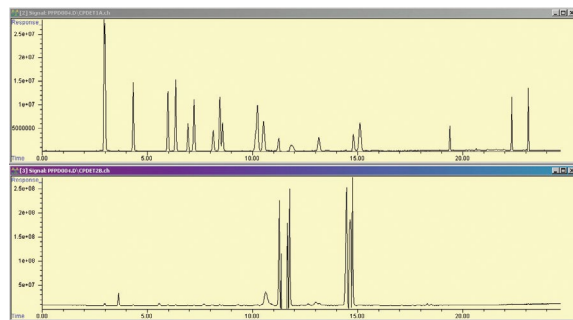


Figure 2. Hydrocarbon, Phosphorus, and Sulfur Emissions in the PFPD

Results and Discussion

Calibration

The peaks were very large and saturated the detector with a 1 μL injection and 200:1 split ratio. A 0.1 μL injection 70:1 split ratio was found to give good low level results without saturating the C element trace. Pulseview Software was used to compare the PFPD C element trace to the FID HC trace.

The C element trace is shown in green, and sulfur trace underneath it in blue, arranged on the same X time scale in Figure 3. Is there sulfur in this sample? The short answer is most probably, yes, from this first-glance data. More complete peak analysis is required to be certain.

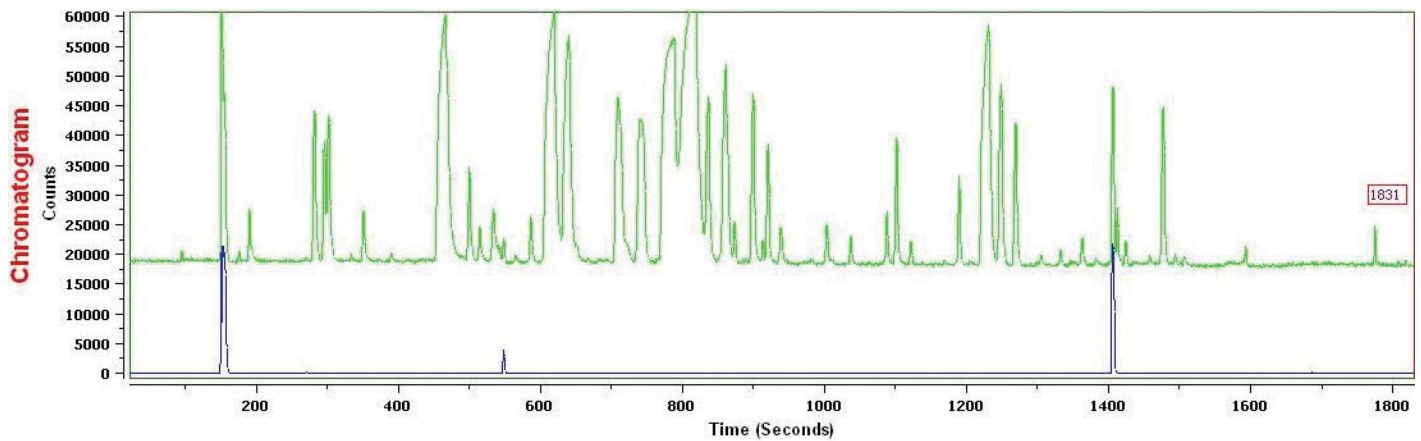


Figure 3. PFPD C and S Element Traces of a Spearmint Oil Sample

The carbon channel chromatogram in Figure 4 shows peak separation and the 65 peaks that could be labeled with retention times using Open Lab Software. The PFPD % area chromatographic response factors for major HC peaks in spearmint oil matched well with expected C percentages in FID chromatograms.⁽⁴⁾

The PFPD found nine S element peaks in this run. The PFPD sulfur channel chromatogram showing the retention times of peaks registered as sulfur compounds is shown in Figure 5.

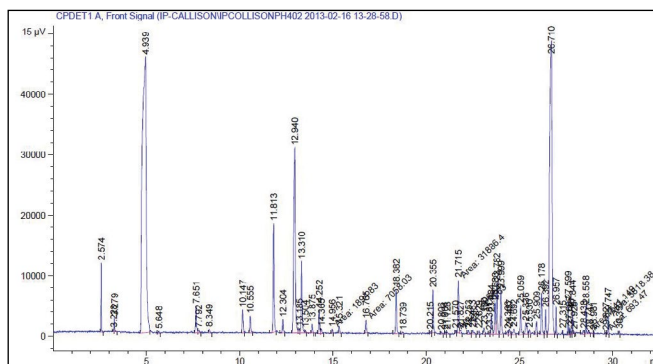


Figure 4. PFPD Carbon Channel Chromatogram of Spearmint Oil from Open Lab Showing 65 Peaks with Labeled Retention Times

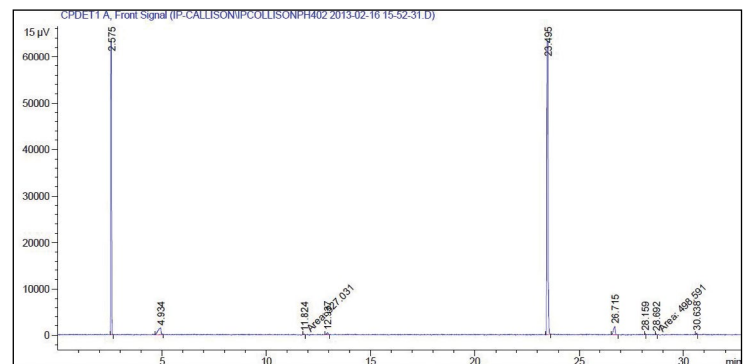


Figure 5. PFPD Sulfur Channel Chromatogram of Spearmint Oil

The next step was to confirm these peaks were not hydrocarbon or phosphorus compounds. Figure 6 shows the Pulseview response to a sulfur-containing species. This sequence provides an example of how emission times can be used to determine and confirm the validity of a sulfur peak. This sulfur peak begins with a rise at 6ms, then rises sharply without changing the C peak height and widening in the sulfur range out to 16ms (Figure 6 A, B, C). This peak extends past the phosphorus range and does not change the C height, confirming it is a sulfur species.

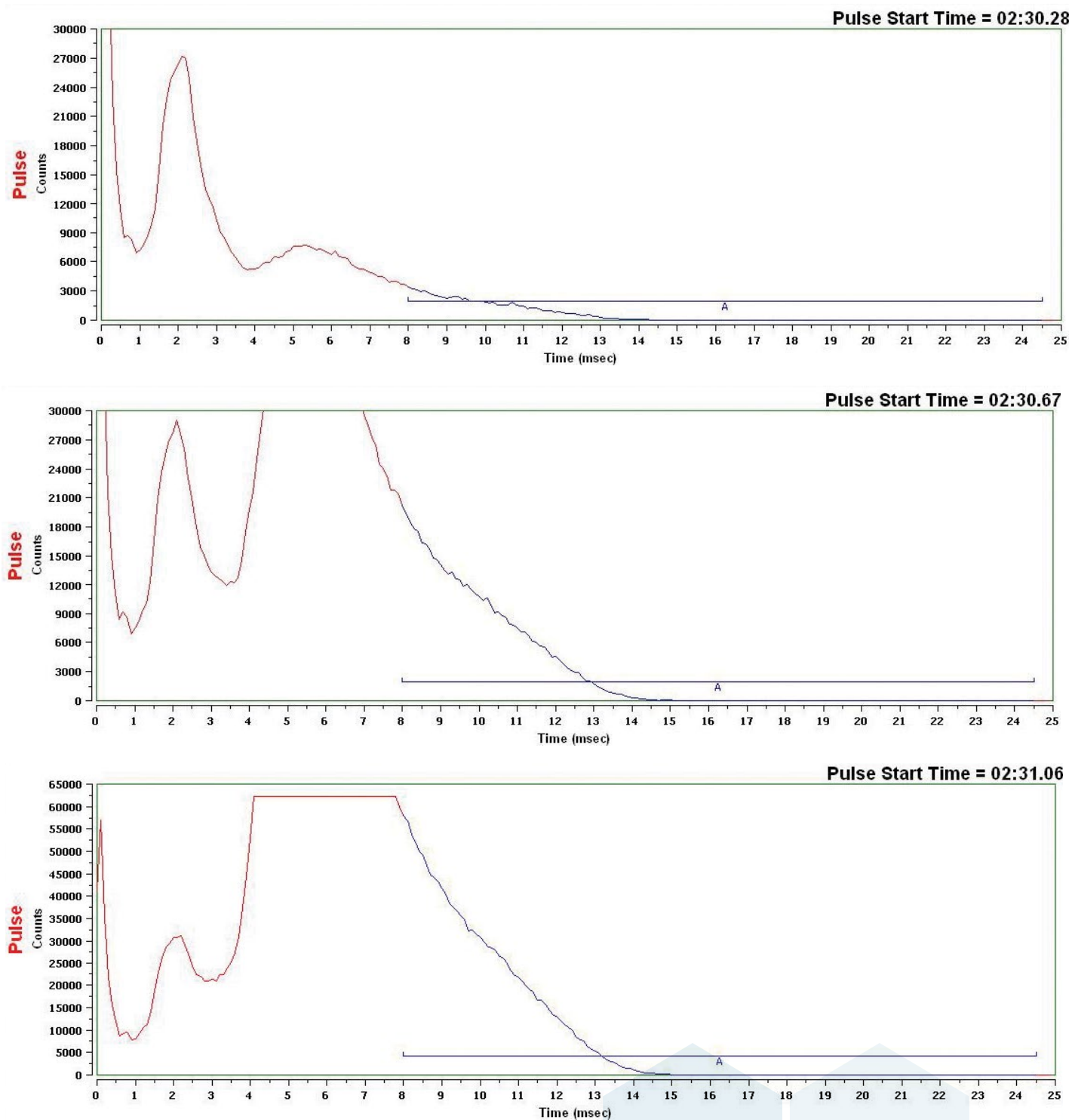


Figure 6. Emission Profile of a Sulfur Peak in a Spearmint Oil Sample

Confirmation of Sulfur Peaks in a Spearmint Oil Sample

Figures 7 and 8 show the response of low-level sulfur peak compounds using Pulseview Software. The intensity change occurring between 8-24.5 msec confirms the presence of sulfur.

An intensity increase at 8+ msec is a characteristic response for sulfur-containing compounds.

The sulfur channel chromatograms contain nine peaks at retention times reported in Figure 9. There were five confirmed sulfur peaks in this spearmint oil sample.

1. Peak at 2.57 is a high RF sulfur peak with 63246 height counts. This peak contains multiple sulfurs.
2. Peak at 23.49 is also a high RF sulfur peak with 63189.2 height counts. This peak contains multiple sulfurs and has a very high area % of sulfur (over 55% of the total) and 5000:1 signal-to-noise ratio.
3. Peak at 28.15 is a low RF sulfur peak. The low intensity indicates the peak contains one or two sulfurs.
4. Peak at 28.69 is a low RF sulfur peak. The RF indicates the peak contains only one or two sulfurs and a signal-to-noise ratio of 10:1.
5. Peak at 30.63 is a low RF sulfur peak. It appears to contain only one or two sulfurs.

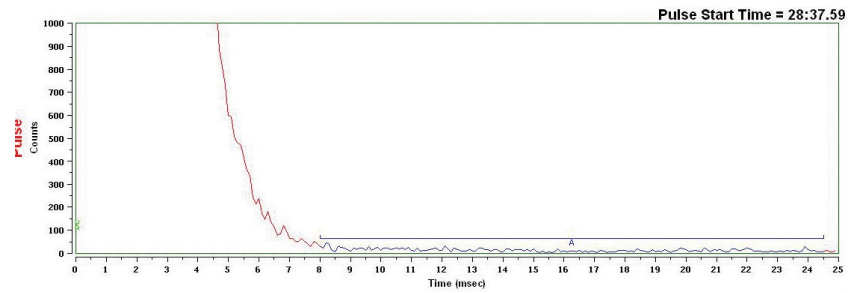


Figure 7. Signal Intensity Change of a Low-Level Sulfur Peak in Spearmint Oil

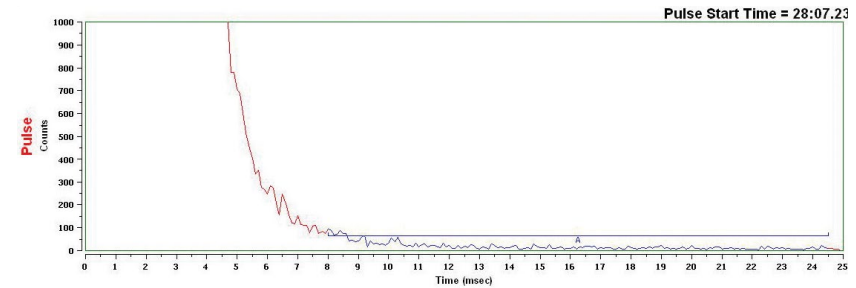


Figure 8. Signal Intensity Change of a Low-Level Sulfur Peak in Spearmint Oil

Signal 1: CPDET1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [15 μ V*s]	Height [15 μ V]	Area %
1	2.575	BB S	0.0476	1.81984e5	6.32469e4	37.97473
2	4.934	BB	0.1307	1.47555e4	1438.49646	3.07903
3	11.824	MM	0.0456	527.03076	192.47113	0.10998
4	12.937	BB	0.0612	2454.14575	492.19568	0.51211
5	23.495	BB S	0.0671	2.65788e5	6.31892e4	55.46209
6	26.715	BB	0.0828	1.17823e4	1837.53552	2.45862
7	28.159	BB	0.0235	496.28030	331.43024	0.10356
8	28.692	MM	0.0315	498.59137	263.84778	0.10404
9	30.638	BB	0.0355	938.56250	371.43814	0.19585

Figure 9. Response Factor Nine Peaks in Sulfur Channel Chromatogram of Spearmint Oil



Summary & Conclusions

The results of this study demonstrate that low-level sulfur compounds can be detected in spearmint oil using a PFPD detector, dual integration time gates, and comparative carbon peak matching with FID chromatograms. The PFPD C trace matched the FID HC trace for major peaks that have the same number of C atoms as HC bonds.

Five confirmed sulfur peaks were found in each of the spearmint oil samples. The percent total sulfur of the smallest peak that could be detected and confirmed was .00206%.

Response differences between the sulfur peaks show a linear dynamic range of 3+ for S elements. The lowest response for sulfur in the spearmint oil sample was the 28.69 RT peak with a 263.8 height and 10:1 signal-to-noise ratio.

References

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3. OI Analytical Application Note #1127, Using Dual Gate Subtraction to Enhance the Selectivity of a Pulsed Flame Photometric Detector, 1999.

OI Analytical, a Xylem brand
PO Box 9010
College Station, TX 77842-9010

+1.979.690.1711
xylem-lab@xylem.com
oico.com



oico.com/5383PFPD