

Keywords

PFPD
PFPDView
Pulp Mill Effluents
Sulfur
WinPulse

Measuring Light Sulfur Compounds in Pulp Mill Effluents with the Pulsed Flame Photometric Detector

Introduction

The presence of low molecular weight sulfur compounds in pulp mill effluents is often responsible for much of the unpleasant smell created during the pulping process. As a result, the pulp and paper industry is facing increasing demands to control the offensive odors in and around these facilities. Any analytical method developed for analyzing light sulfur compounds in pulp mill effluents must meet a number of criteria. It must be highly selective for sulfur to minimize the potential for false positives, it must be sensitive enough to allow for detection in the low ppb range, and it must not be subject to interference from the innumerable organic compounds present in the matrix. Ideally, the method should be adaptable to either a laboratory setting or to an on-line production stream. This application note describes the use of the OI Analytical Model 5380 Pulsed Flame Photometric Detector (PFPD) to speciate and quantify several light molecular weight sulfur compounds found in a pulp mill treatment pond influent.

Principle of PFPD Operation

Operation of the PFPD is based on a propagating flame that terminates within a glass combustor. The gas phase reactions produced by the propagating flame result in light emissions with specific luminescences and lifetimes. The differences in specific emission lifetimes, combined with the kinetics of the propagating flame, allow both time and wavelength information to be used to optimize the detector for sulfur selectivity. Because the carbon emission and sulfur emission lifetimes do not overlap (1.3 to 4 milliseconds for carbon compared to 6 to 25 milliseconds for sulfur), there is little, if any, interference from the organic compounds present in the effluent matrix. In addition, the use of gated electronics permits the rejection of noise occurring outside of the specified gate window. As a result, the PFPD is infinitely selective for sulfur with respect to carbon. Figure 1 shows the emission profile of a single PFPD pulse with the separate carbon and sulfur emission lifetimes identified.

The hydrogen and air gas flows for the PFPD are premixed, ensuring that there are no gas composition or temperature gradients within the flame. The constant gas mixture and temperature guarantee uniform flame conditions for all compounds, and the flame chemistry during excitation remains constant. The observed emission profile is characteristic of the uniform flame conditions when the sulfur dimer is excited, and the observed emission profiles for sulfur in different compounds are the



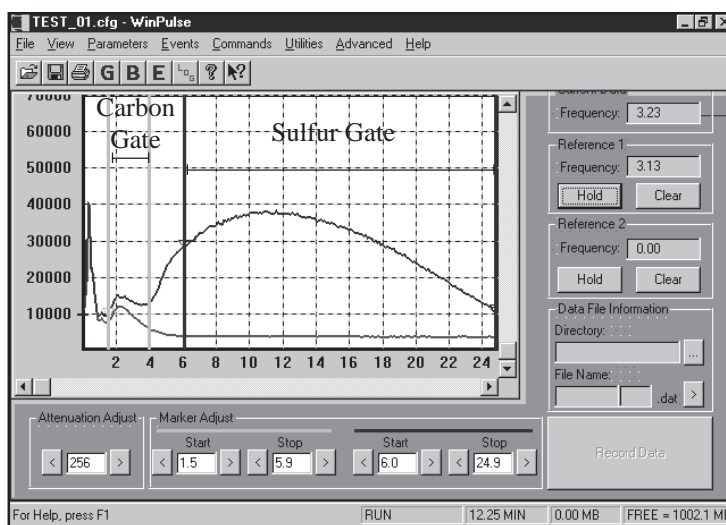


Figure 1. Sulfur and Carbon Emission Profiles of a PFPD Pulse

same. Since the flame chemistry is unchanged and the emission profile for sulfur remains constant regardless of the compound, the molar response of the emitting species is also constant, or equimolar. The concepts of infinite sulfur selectivity and equimolar response, as well detector linearity, are demonstrated below.

Experimental

The PFPD was configured for sulfur selective detection as detailed in Table 1. Initial injections of the treatment pond influent indicated that a split ratio of 49 to 1 gave the best on-scale signal for the concentration of sulfur compounds found in the influent. A six-point calibration curve was acquired by analyzing 1- μ L aliquots of the

Table 1. Instrument Settings for the Agilent 6890 GC and OI Analytical Model 5380 PFPD Sulfur Selective Detector

GC Parameter	Setting
Gas Chromatograph	Agilent 6890
Column	J&W DB-5MS, 30 m x 0.25 mm I.D. x 1.0 μ m film thickness
Column Mode	Constant flow; 1 mL/minute
Inlet Temperature	250°C
Inlet Mode	Pulsed split (20 psi for 0.5 minutes)
Split Ratio	49:1
Carrier Gas	Helium
Oven Program	35°C for 5 minutes 15°C/minute to 280°C Hold for 2 minutes
Detector Parameter	Setting
Detector	OI Analytical Model 5380 PFPD
Temperature	220°C
Analysis Mode	Sulfur
Combustor	2 mm
Optical Filter	BG-12 (sulfur)
Photomultiplier Tube	R1924
Sulfur Gate	6 to 24.9 msec
Square Root Mode	ON

individual calibration standards and using the 49 to 1 split ratio. Concentrations of sulfur in the calibration standards were 0.1 ppm, 0.2 ppm, 0.5 ppm, 1.0 ppm, 2.0 ppm, and 5.0 ppm. (All concentrations throughout this application note are reported as ppm or ppb of sulfur, rather than ppm or ppb of compound.) Thus, for the lowest calibration standard (1 μ L of the 0.1-ppm standard, split 49 to 1), approximately 2 μ g of sulfur were introduced to the PFPD. Using the same instrument conditions described in Table 1, 1- μ L aliquots of the preserved and unpreserved treatment pond influents, and one industry Laboratory Control Sample (LCS) were analyzed. A split ratio of 49 to 1 was used for all samples, except where noted in the chromatograms. No sample preparation or cleanup was attempted prior to injection.

Results and Discussion

The PFPD produces a quadratic response for sulfur over approximately two and a half orders of sample concentration, which is approximately five orders of magnitude signal response. Linearization of the quadratic output signal is also possible. Enabling the square root function when setting up the electronic gates for sulfur activates the calculation of the square root of the output signal. This feature is used to linearize the quadratic response signal associated with sulfur. For these analyses, the square root function was enabled and all quantitation was done using the linearized signal response from the sulfur gate. If desired, the PFPD can provide simultaneous signal outputs for both quadratic and linear response.

Calibration curves were generated using the peak areas from the linearized signal. Linear R^2 values ranged from 0.9991 to 0.9996 for the three sulfur compounds in the calibration mixture. (See Figure 2.) When the linearized peak areas are plotted as a function of sulfur concentration, the slope of the line is defined as the response factor. Since the detector response for sulfur is equimolar, the response factor or slope is expected to be the same for all compounds, as demonstrated by the equations in Figure 2. The coefficients of x for ethanethiol, methyl sulfide, and dimethyl disulfide were 1.0882, 1.004, and 1.0177, respectively. Discrimination in the volatility of the individual light molecular weight compounds in the mixture contribute to differences in the individual response factors, as they are lost at different rates during sample preparation and storage. Figure 3 shows the corresponding quadratic calibration curve for methyl sulfide.

Table 2 is a key to the individual sulfur species identified and quantified in the samples. In addition to the three compounds present in the calibration mixture, there were two additional target compounds detected and quantified in the analytical samples. Because of the equimolar response of the detector, it was not necessary to calibrate for all target compounds individually. The average response factor for methyl sulfide was used to quantify the sulfur concentration in hydrogen sulfide and methanethiol.

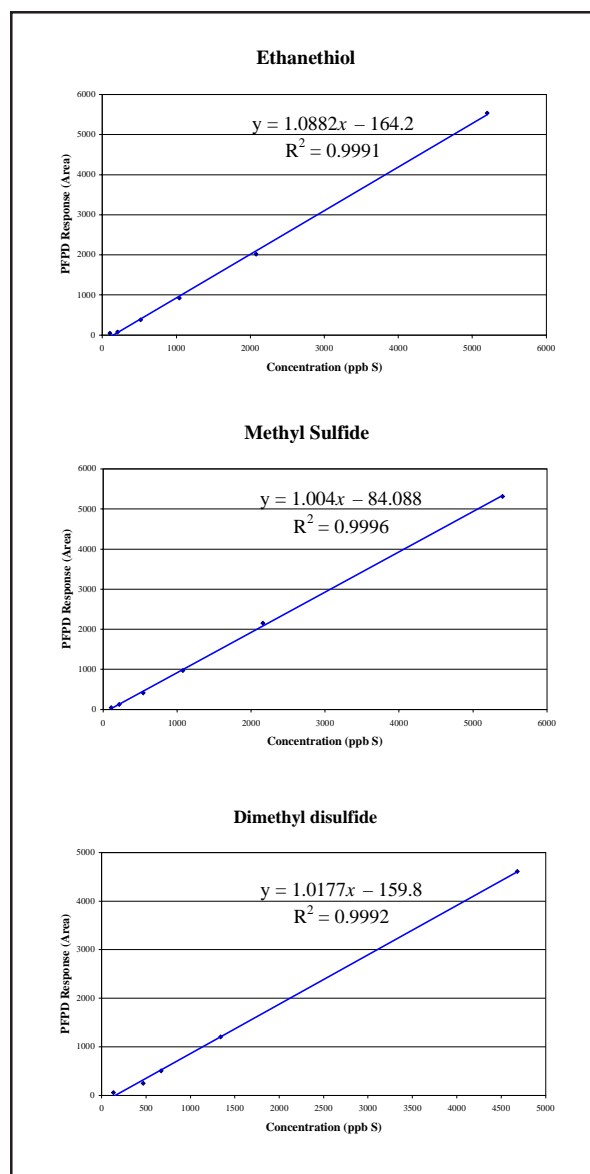


Figure 2. Calibration Curves for Three Light Sulfur Compounds by Direct Injection with PFPD. Calibration Curves Were Calculated Using the Linearized Peak Areas.

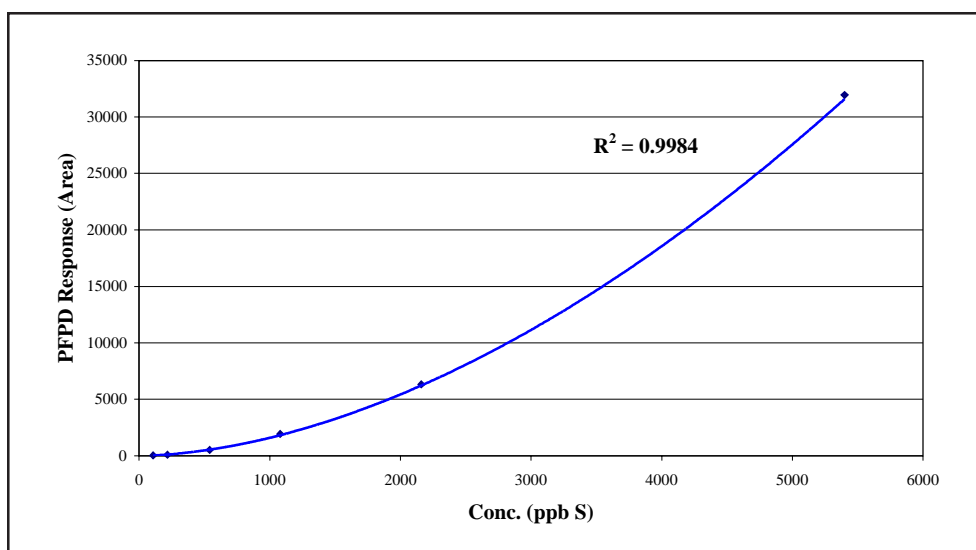


Figure 3. Quadratic Calibration Curve for Methyl Sulfide

Table 2. Compounds Identified in Figures 4, 5, 6, 7, and 8

Compound Name	Formula	RT (minutes)
Hydrogen sulfide	H ₂ S	1.40
Methanethiol	CH ₃ -SH	1.85
Ethanethiol	CH ₃ -CH ₂ -SH	2.50
Methyl sulfide	CH ₃ -S-CH ₃	2.68
Dimethyl disulfide	CH ₃ -S-S-CH ₃	8.32

Chromatograms of the 0.1-ppm calibration standard and the three analytical samples are shown in Figures 4, 5, 6, and 7. Measured concentrations for the industry LCS compared favorably to the expected values, with recoveries ranging from 95.8% for methyl sulfide to 127.3% for hydrogen sulfide. For the two influent samples, concentrations for all four target compounds were calculated using the linearized peak areas. All calculated concentrations are tabulated in Table 3. Concentrations ranged from 129.5 ppb sulfur (as H₂S) in the preserved influent, to 7853.1 ppb sulfur (as CH₃-S-S-CH₃) in the unpreserved influent. Lower concentrations in the LCS were easily quantified by reducing the split ratio. The industry LCS, which was analyzed with a 9 to 1 split ratio, had a measured concentration of 54.2 ppb sulfur for methanethiol, with a signal-to-noise ratio of 15:1. Using these conditions, measured concentrations of sulfur at the single-digit ppb range are possible. If detection of even lower concentrations of sulfur is desired, introduction of the sample using the static headspace technique is an option. Figure 8 shows a chromatogram of a 1-ppb standard run by the static headspace technique and using a 0.5-mL sample loop and a 9 to 1 split ratio.

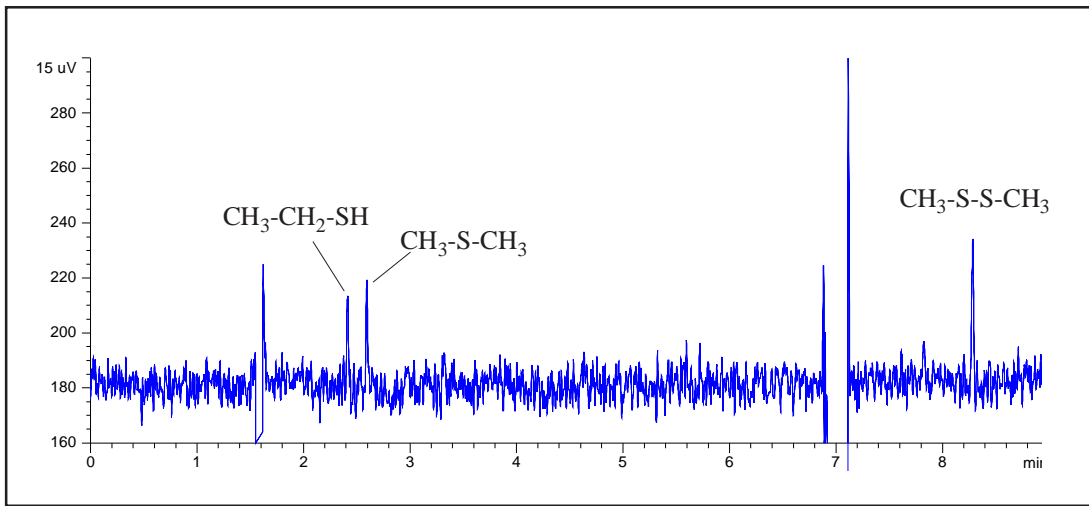


Figure 4. 0.1-ppm Calibration Standard by Direct Injection with PFPD (1- μL injection, split 49:1, approximately 2 pg S on column)

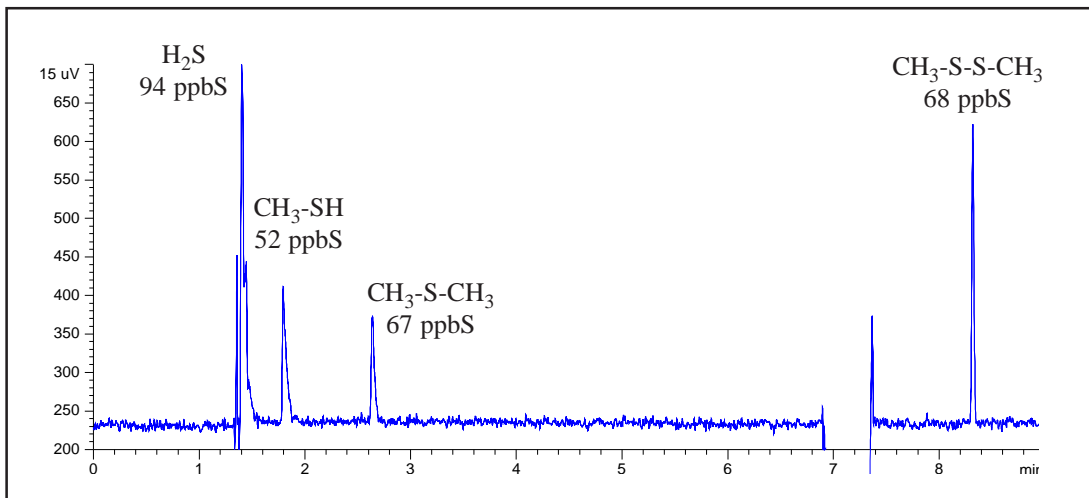


Figure 5. Industry LCS by Direct Injection with PFPD (1- μL injection, split 9:1, approximately 5.2–9.4 pg S on column)

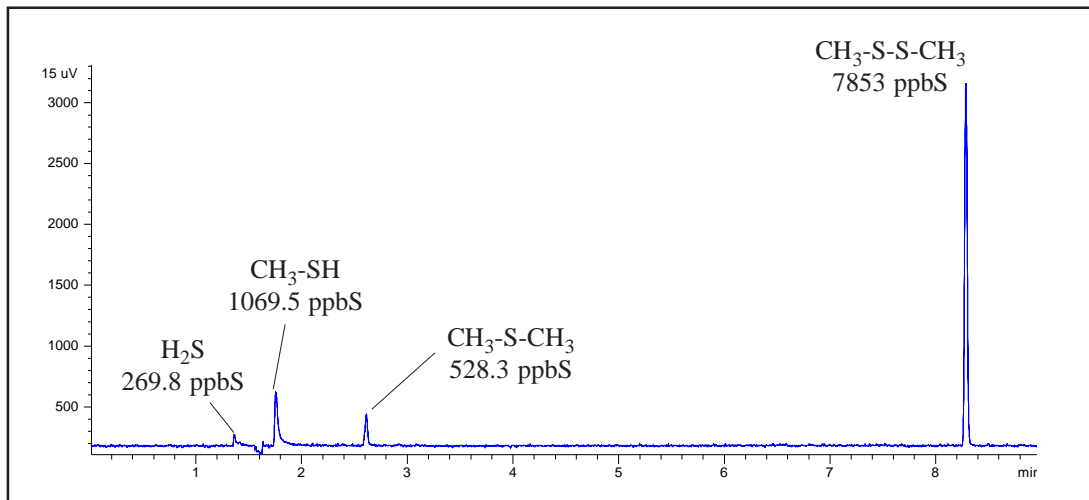


Figure 6. Unpreserved Treatment Pond Influent by Direct Injection with PFPD (1- μL injection, split 49:1)

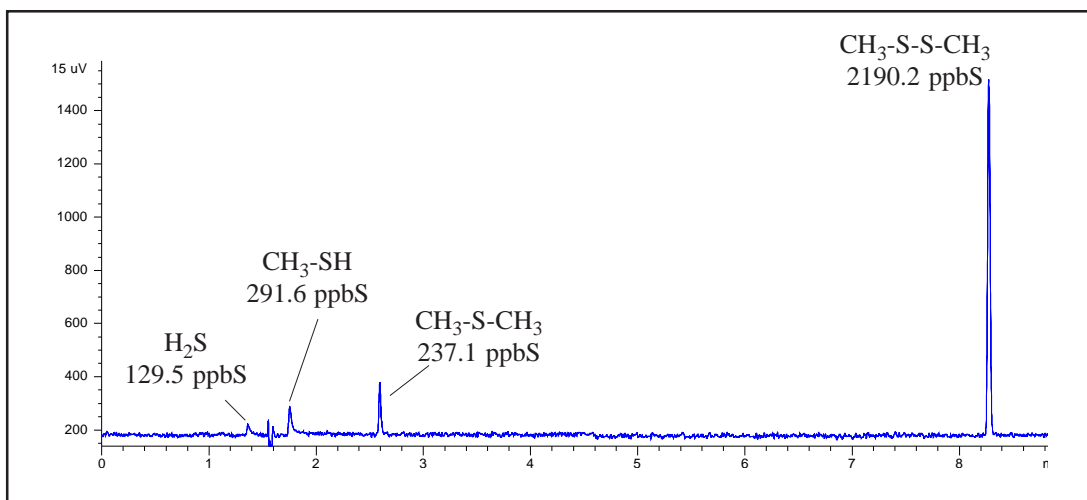


Figure 7. Preserved Treatment Pond Influent by Direct Injection with PFPD (1- μ L injection, split 49:1)

Table 3. Results from Direct Injection of One Industry LCS and Two Treatment Pond Influent with Detection by PFPD (concentrations reported as ppb S)

Compound Formula	Industry LCS			Unpreserved Influent	Preserved Influent
	Conc. (as ppb S) Expected	Conc. (as ppb S) Measured	% Recovery	Conc. (ppb S)	Conc. (ppb S)
H ₂ S	94	119.7	127.3	269.8	129.5
CH ₃ -SH	52	54.2	104.2	1069.5	291.6
CH ₃ -S-CH ₃	67	64.2	95.8	528.3	237.1
CH ₃ -S-S-CH ₃	68	66.1	97.2	7853.1	2190.2

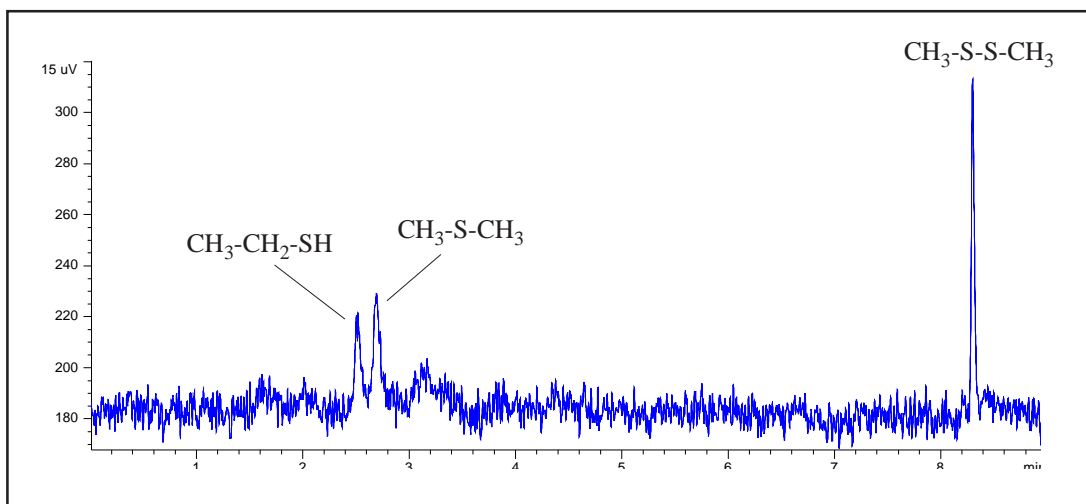


Figure 8. 1-ppb Calibration Standard by Static Headspace with PFPD (0.5-mL sample loop, split 9:1)

Using the Windows®-based post-acquisition processing software, PFPDView, examination of the recorded emission profiles revealed that the carbon emissions from organic species present in the matrix did not interfere with the sulfur emission profiles and confirmed sulfur selectivity for these samples. Only “clean,” characteristic sulfur emissions were observed, indicating that there was no contribution to the chromatographic peaks from the carbon emission, and thus no false positives reported, as seen in Figure 9.

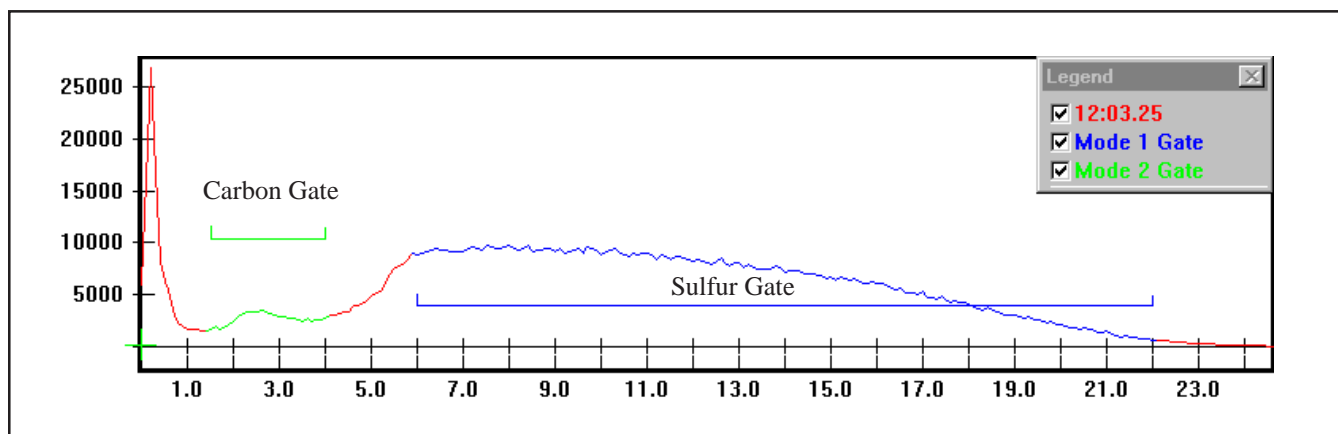


Figure 9. Emission Profile of a Single PFPD Pulse with the Electronic Gates for Carbon and Sulfur Identified Using OI Analytical PFPDView Software (This emission profile was taken from the methanethiol peak at 1.85 minutes in the chromatogram for the unpreserved treatment pond influent.)

Conclusion

The OI Analytical Model 5380 Pulsed Flame Photometric Detector is capable of detecting and accurately quantifying light sulfur compounds in pulp mill effluents at concentrations in the low ppb range. Using different introduction techniques such as static headspace will allow for quantitation down in the sub-ppb range. No sample preparation was necessary, and no interference from carbon emission of the many organic species present in the matrix was observed, confirming sulfur selectivity. Calibration response factors confirmed detector linearity and equimolar response for sulfur. Little or no maintenance is required for the PFPD, making it an ideal choice for on-line and at-line applications.



P.O. Box 9010
College Station, Texas 77842-9010
Tel: (979) 690-1711 • FAX: (979) 690-0440 • www.oico.com