O·I·Analytical

Options for Quantifying Sulfur Compounds by PFPD

Application Note 17110601

Keywords
Gas Chromatography
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The Pulsed Flame Photometric Detector (PFPD) is an inherently equimolar response detector; the sulfur's chemiluminescence response is independent of a compound's molecular structure. A fixed concentration of sulfur will give the same PFPD response regardless of the parent compound, and this feature allows quantitation of the sulfur content in complex samples. Calibration with a known concentration of a single sulfur compound will allow quantitation of the sulfur content in individual chromatographic peaks of unknown compounds. Examples of different approaches to quantitation using the equimolar sulfur response capability are described briefly below.

Total Sulfur Quantitation Using a Mix

1. Purchase a standard of known sulfur concentration in a matrix similar to the samples that will be analyzed (e.g., gasoline, diesel, fuel oil, etc.). The sulfur concentration in the standard should be approximately the same as that expected to be found in the samples.

2. If necessary, dilute the standard with clean, sulfur-free solvent to bring it to the approximate concentration range expected in the samples.

3. Analyze the standard under the same conditions that will be used for the samples. Be sure to acquire data with the square root function turned "ON".

4. Determine the total integrated peak area across the chromatogram and use it to calculate a response factor (RF) for sulfur as illustrated in Figure 1.

   RF = Total Peak Area/Sulfur Concentration

5. Acquire data for the unknown samples and determine the total integrated peak area across the chromatogram. Use the RF determined in step 4 to calculate the sulfur concentration in the sample.

   Sulfur Concentration = Total Peak Area/RF

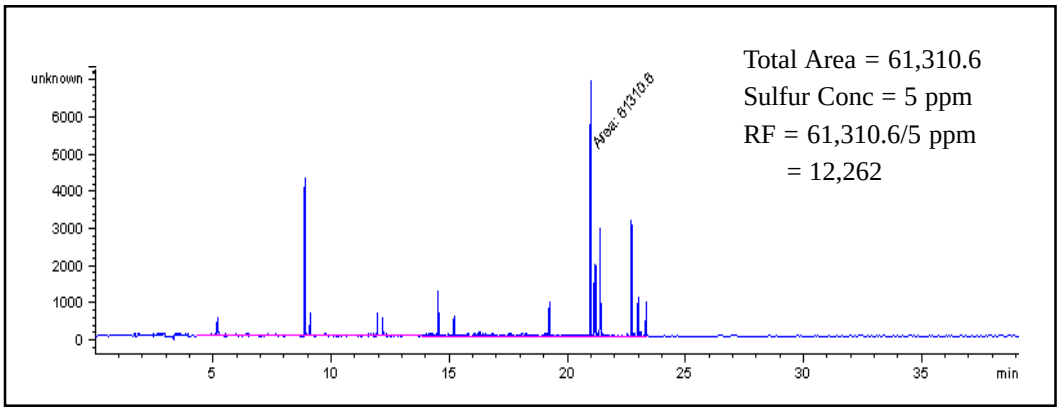

Figure 1. Calculation of Sulfur RF Using a Standard of 5 ppm Sulfur in Gasoline

Total Sulfur Quantitation Using a Single Compound

1. Select a single sulfur-containing compound with a molecular structure similar to those expected to be found in the matrix (e.g., thiophenes, sulfides, mercaptans, etc.)

2. Using the single compound, prepare calibration standards at several concentrations spanning the range of interest and analyze them under the same conditions that will be used for the samples. Acquire data in the linear mode with the square root function turned “ON”. (See Figure 2.)

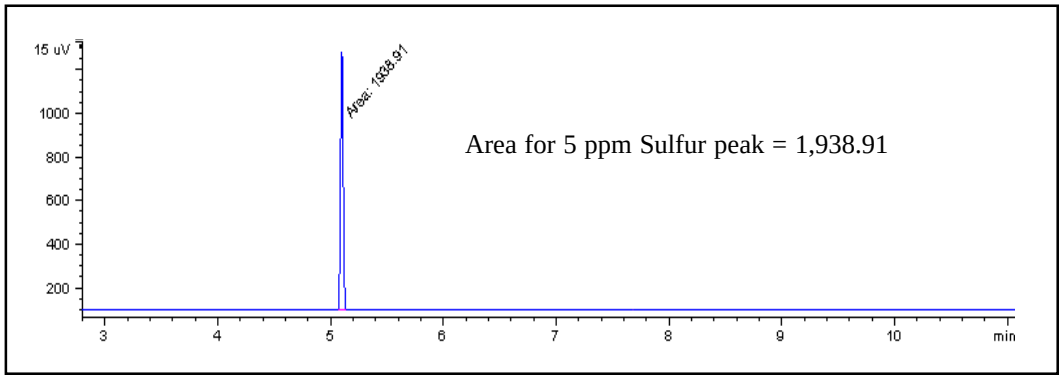

Figure 2. Integrated Area for a Single Sulfur Peak at 5 ppm

3. Prepare a calibration curve plotting PFPD response (peak area) as a function of the sulfur concentration, and determine the correlation coefficient (R^2) and equation for the line. Be sure to use the concentration of sulfur in the solution and not the concentration of the compound as illustrated in Figure 3.

4. Acquire data for the unknown samples and determine the total integrated peak area across the chromatogram.

5. Use the linear equation from step 3 to calculate the total concentration of sulfur in the unknown samples.

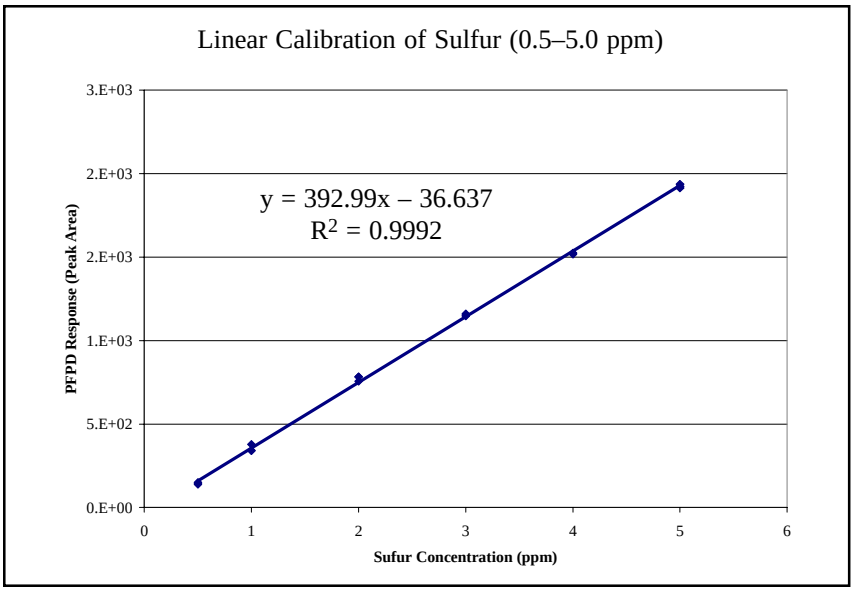

Figure 3. Calibration Curve Plotting Peak Area as a Function of Sulfur Concentration

Speciated Sulfur

1. Purchase or prepare a stock standard solution containing all of the sulfur compounds of interest at a single concentration.

2. Using the stock solution, prepare calibration standards at several concentrations spanning the range of interest and analyze them under the same conditions that will be used for the samples. Acquire data in the linear mode with the square root function turned “ON”. (See Figure 4.)

3. Prepare a calibration curve for each compound, plotting PFPD response (peak area) as a function of the sulfur concentration. Determine the correlation coefficient (R^2) and equation for each line. For speciated sulfur, either the concentration of sulfur in the solution or the concentration of the compound can be used for the calibration curve.

4. Acquire data for the unknown sample and determine the integrated peak area for each peak with retention time matching those in the standard. Use the linear equations from step 3 to calculate the concentration for each peak.

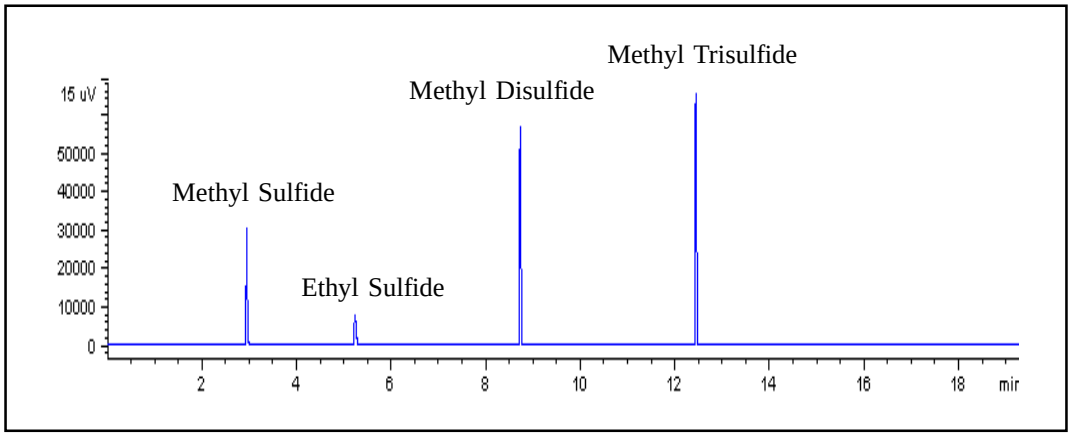

Figure 4. Chromatogram of Sulfur Standard Containing Four Different Sulfur Species

5. To calculate the sulfur content of an unknown peak, use the equation for a compound of similar structure and peak width. Be sure that the calibration curve has been created using the concentration of sulfur rather than the concentration of the compound.

Notes

- To take advantage of the PFPD's equimolar response capability for sulfur, the detector must be operated in the linear "Square Root ON" mode, and all responses must be measured as peak areas, not peak heights.

- The GC/PFPD determination of total sulfur concentration measures only those organic sulfur compounds that can be easily passed through and separated by a gas chromatographic column. Sulfur content determined by other techniques, such as AA, XRF, microcoulemetric, etc., might not necessarily match concentrations determined by GC due to the differences inherent in the instrumentation.

- Like other flame photometric detectors, the PFPD sulfur signal can be "quenched" (decreased) when the sulfur peak is coeluting with a large (e.g., > 50 ng) hydrocarbon peak. Therefore, it is important to ensure that chromatographic separation exists between the sulfur compounds and any large matrix hydrocarbon peaks in the sample.

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