Auto Gain with Pulsed Flame Photometric Detector on Varian CP3800

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The Short Story

With Varian CP3800 software ROM set Version 3.3.5B[1] (released May 13, 2003) and later versions, Varian added a user choice for the amplification of the sulfur signal inside the gate width into the list of parameters for the pulsed flame photometric detector (PFPD). This parameter allows the operator to set this gain to meet specific requirements for the measurement. On the Varian CP3800, the preset condition is with Auto Gain enabled such that the signal amplification is automatically determined based on the choice for the gate width, and this is the preferred mode.

Unfortunately, both Varian Star and Galaxie Chromatography Workstations[2] are preset with this Auto Gain ***disabled***. With Auto Gain turned off, the maximum signal processing is severely limited and the baseline noise can be excessive. These two combine to severely limit the operating range of the detector.

FOR PROPER OPERATIONS, THE AUTO GAIN FACTOR ALWAYS SHOULD BE ENABLED, unless very specific applications mandate a manual choice.

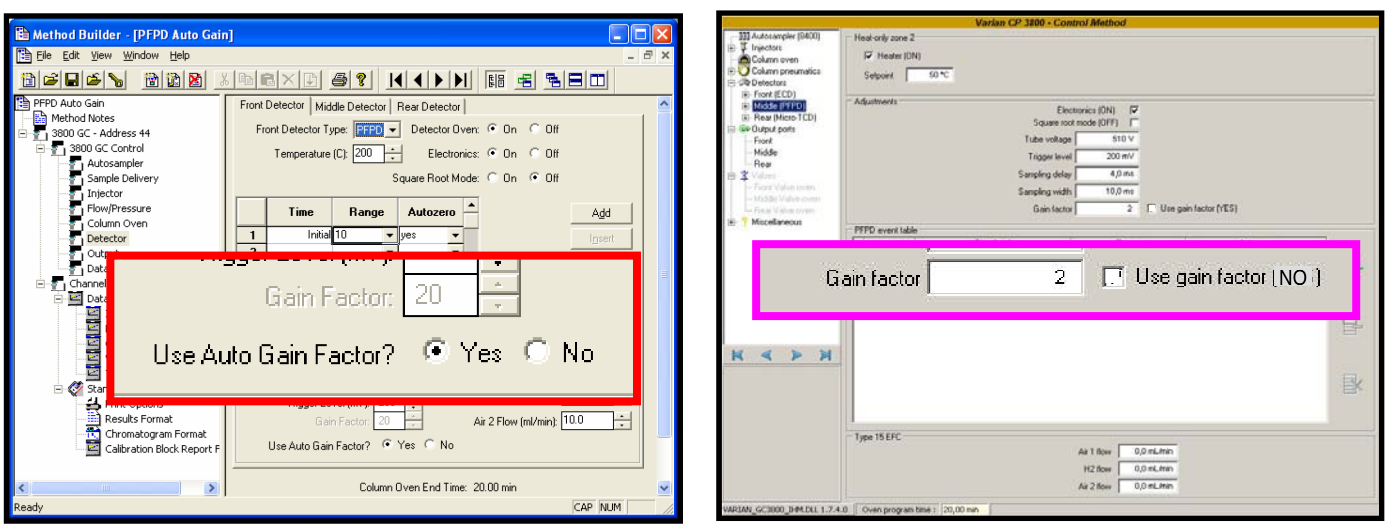

Figure 1. In Star method parameters for the PFPD (left), "Use Auto Gain Factor?" should always be set to "YES". With Galaxie (right), the "Use Gain Factor" should be *un*checked.

[1] The current ROM board update part number is P/N 03-925049-01, or P/N 03-925860-91 with release notes. The current version of Star upgrade to Version 6.41 is 03-910818-91.

[2] The "disabled" auto gain parameter occurs with Star Version 6 (including the last version 6.41) and Galaxie 1.9. Saturn Workstation Version 6.5 (and later releases) has had the preset value corrected to "Use Auto Gain Factor? – Yes".

The Long Story

Sulfur-containing compounds have a very useful property of emitting a characteristic wavelength when sulfur-containing compounds are broken down in a flame and then thermally exciting the resulting sulfur dimer - S_2. This principle has been the basis for conventional flame photometric detectors in use with gas chromatographs for well over twenty years.

Despite the selectivity generated by filtering out the only the wavelength 465 nm for this emission, other species can generate an emission in the same wavelength region. Hydrocarbons passing through to this detector are also combusted and their products yield a chemilluminescence that coincides with the sulfur emission. This interference often yields false chromatographic peaks that could be quantified improperly as sulfur.

To save the day, another property of this sulfur excitation is the delay of the emission from when it is initially thermally decomposed. When the combustion process is pulsed, the emitting light will yield the chemilluminescence from hydrocarbons shortly after excitation, whereas sulfur is delayed longer. The pulsed flame photometric detector is designed to take advantage of this emission time difference. Figure 1 illustrates a snapshot of the process showing the emissions of the flame ignition, the hydrocarbon chemilluminescence and the desired sulfur emission.

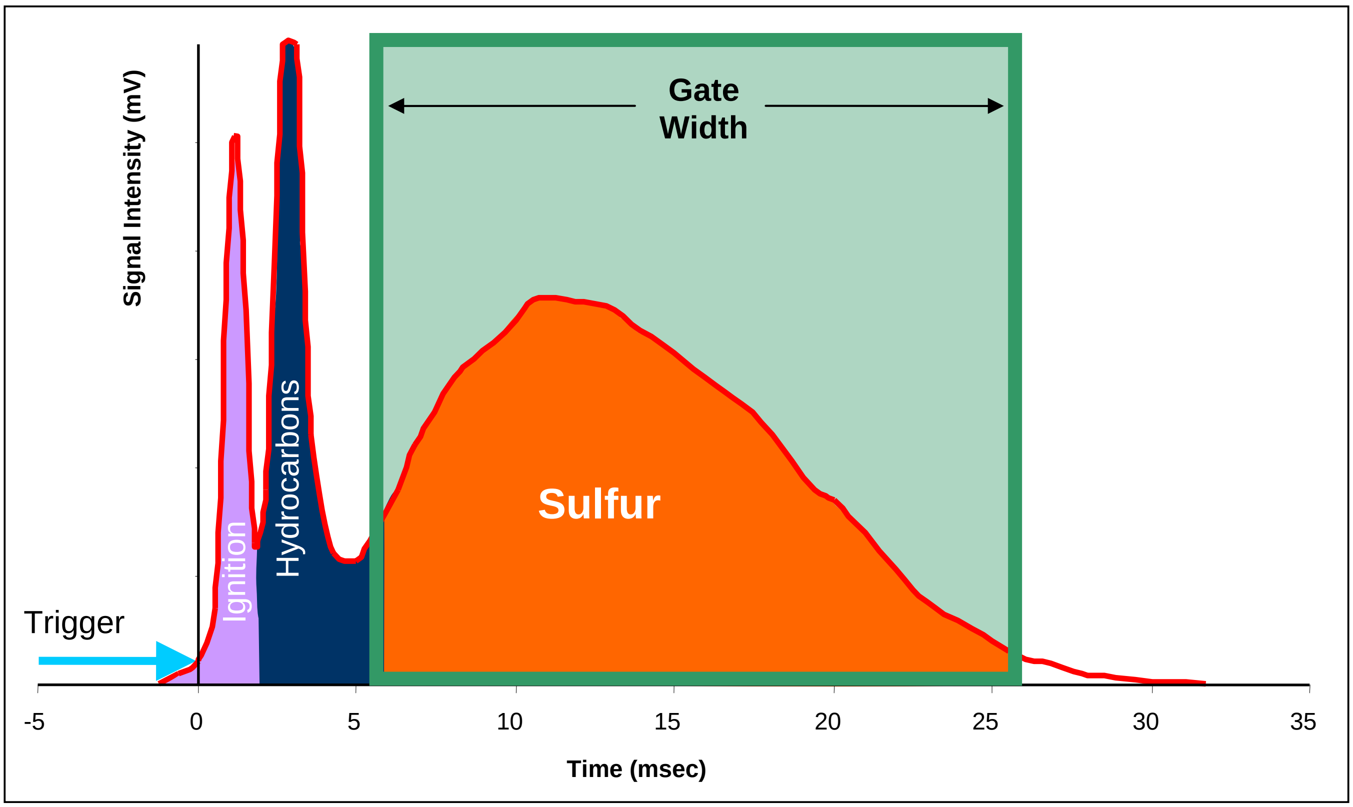

Figure 2. The pulsed signal from the PFPD separates the sulfur emission from ignition and hydrocarbons interferences. Only the signal emitted during the Gate Width timing is collected and processed.

The combustion chamber inside this detector is carefully designed for hydrogen and air to premix and then build up inside the detector to a point that they detonate from the constantly glowing ignitor nearby. The resulting ignition propagates down the chamber and self-extinguishes at the bottom. The air/hydrogen mix fills up the chamber again and the process repeats. The setup causes the explosion to occur about every 350-400 milliseconds and lasts for about 2 millisecond, yielding a regular "popping" noise that is the audible characteristic of this detector. The hydrocarbon chemilluminescence occurs soon after the "pop", typically from 2 to 6 milliseconds after and is normally finished by the time sulfur specie starts emitting. A special electronic gate is set to selectively detect only the sulfur emission, normally from 6 to 26 milliseconds after ignition, with the ignition and hydrocarbon responses ignored by a delay in the activation of the gate. A trigger level is set to initiate the signal processing upon ignition of the flame so that the gate window for the sulfur signal is monitored consistently, despite slight changes in the pulse frequency of the flame. The process repeats typically near 3 hertz to generate a chromatographic peak for the sulfur compound. A special electronic circuit aids in smoothing out the pulsations to provide a contiguous curve displayed and computed for the detector response.

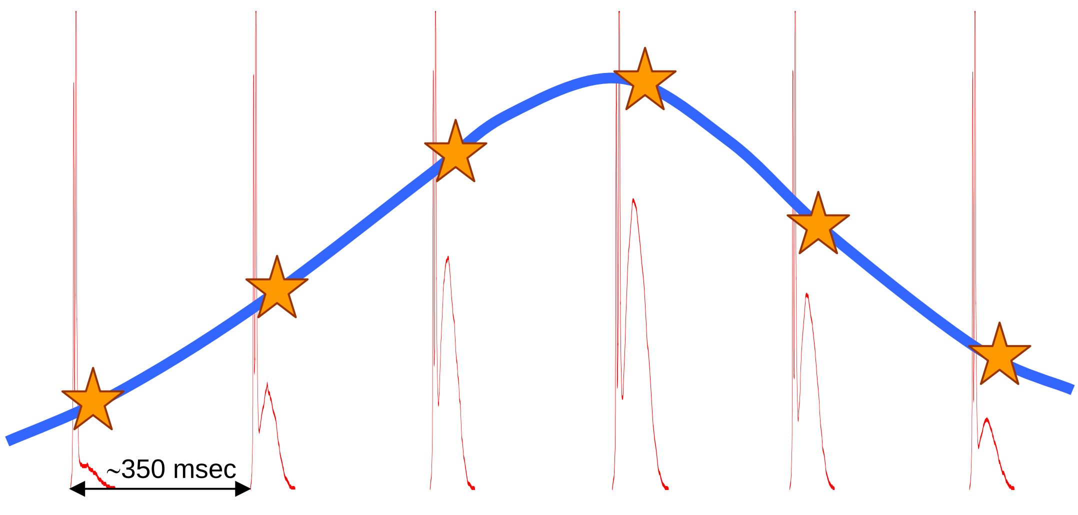

Figure 3. The characteristic "popping" noise at typically 3 hertz from the PFPD is the reoccurring momentary combustion of the flame so that the sulfur signal can be isolated from interferences as the chromatographic peak is eluting off the column.

Detector electronic processing sums up the responses detected within the Gate Width to generate the detector signal, presumably only for the sulfur response, if the Gate Delay and Gate Width are set up properly to reject hydrocarbon emissions. This integrator has a maximum value before it saturates and gives very non-linear responses at these high signal levels. A special parameter allows the signal to be amplified sufficiently to allow the integrator to maintain its optimum performance and still allow the smallest amount of sulfur to be detected. This Gain Factor becomes the adjustment for allowing huge signals to be attenuated to fit within the confines of the integration circuit and for permitting smaller signals to be amplified when appropriate. This Gain Factor must be adjusted as a function of Gate Width. Small Gate Widths will allow more amplification as the total signal is much less than with larger ones, where the total signal available could overwhelm the circuit.

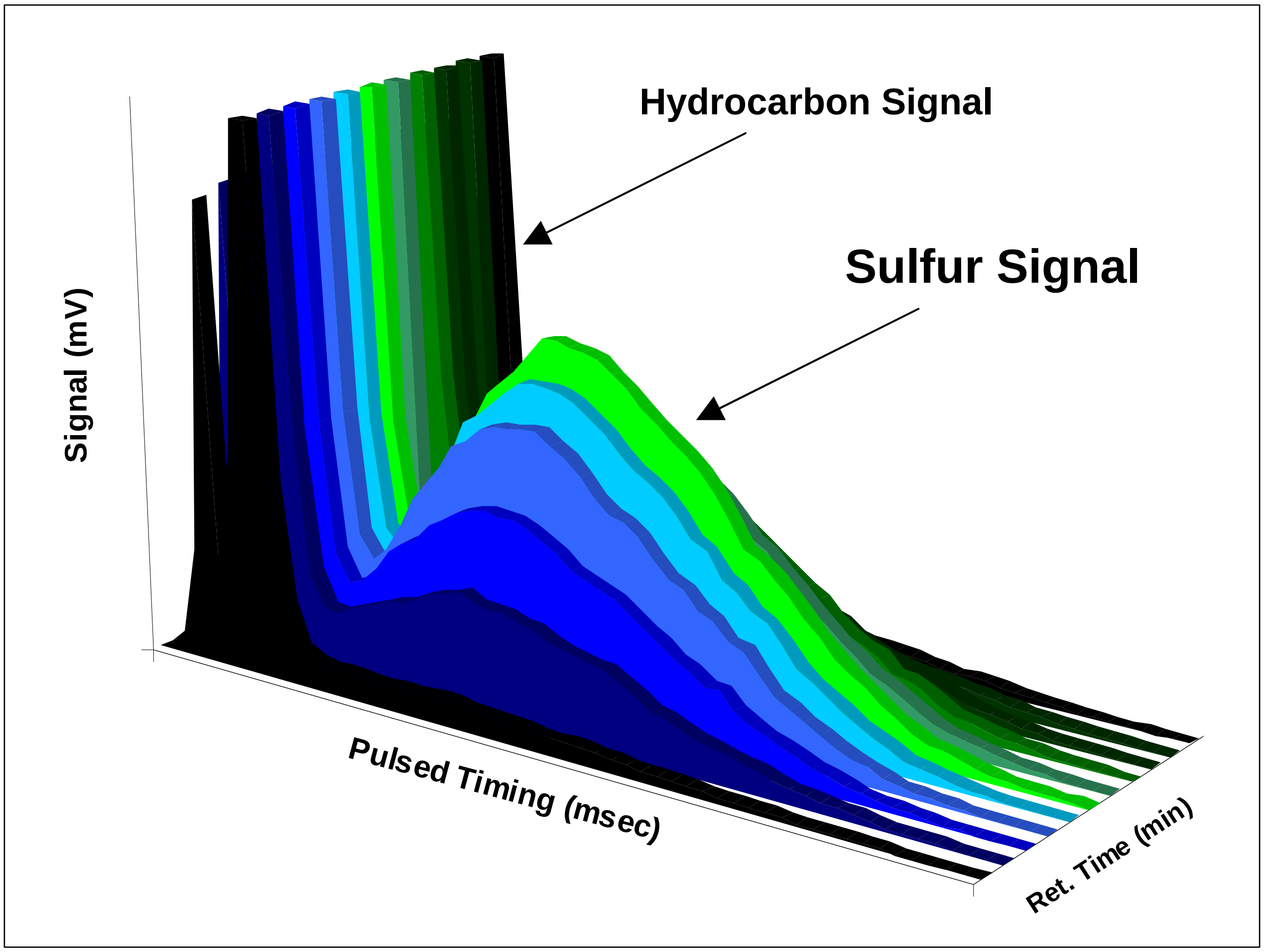

Figure 4. Signals generated from the PFPD can be displayed in a three-dimensional graph illustrating the sulfur response separated from potential interferences by time.

Automatic Gain Factor

To prevent overloading this circuit, a special Automatic Gain Factor parameter sets the Gain Factor based on the chosen Gate Width. This process ensures that the maximum signal is generated without severely overloading the circuitry and still provides good detection for low sulfur levels. The preferred operating mode for routine measurements is with Automatic Gain Factor enabled.

The preset parameter on the Varian 3800 Gas Chromatograph is set with Automatic Gain Factor "On". Unfortunately, both Varian Star and Varian Galaxie Workstations have this setting turned off, and the Gain Factor is fixed by the related entry value. The favored entry is to turn on the Automatic Gain Factor (see Figure 1). This allows the photometric signal to be optimally enhanced without overloading the electronic signal processing.