

**Pulsed Flame Photometric Detector (PFPD)**  
**by Scion Instruments –**  
**Equimolar Responses for Sulfur Analytes**

by:

**Randall Bramston-Cook**

Lotus Consulting,

5781 Campo Walk, Long Beach, Ca 90803

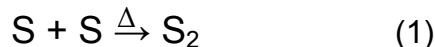
310/569-0128

[randy@lotusinstruments.com](mailto:randy@lotusinstruments.com)

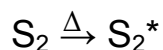
March 15, 2018



Organic sulfur compounds, especially mercaptans or thiols, and some inorganic sulfurs, such as hydrogen sulfide and carbon oxide sulfide, in gas samples, are best measured by gas chromatography with pulsed flame photometric detection. When these analytes elute from a column and are directed to the detector, their combustion in a hydrogen-rich flame break down these target molecules, and the sulfur atoms then react with each other to form sulfur dimers.



The hot flame then excites the dimer electrons to a higher energy state, and eventually photons are released, proportional to the sulfur concentration, as it returns to their ground states.

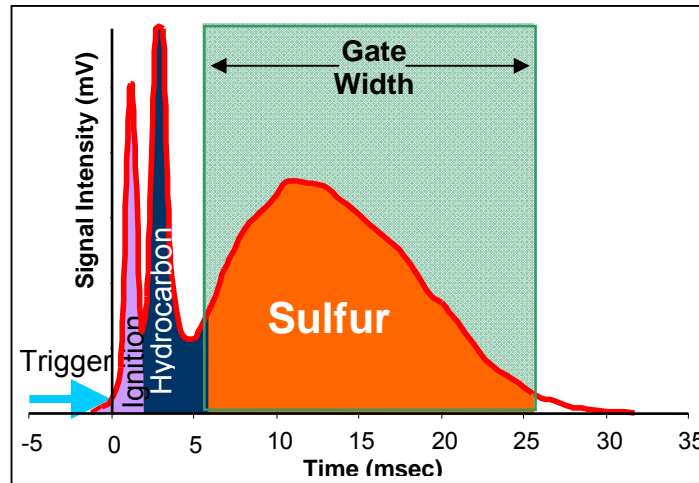


The wavelength of this photon emission is 394 nm. By monitoring this emission, the presence of sulfur compounds can be identified and quantitated. The reaction rate for the dimer formation becomes the product of the concentration of reactants in equation (1). Thus, the sulfur dimer concentration measured by the detector is the square of the sulfur atom concentration:

$$[S_2] = [S] * [S] = [S]^2$$

This yields the anticipated quadratic responses for sulfur concentrations.

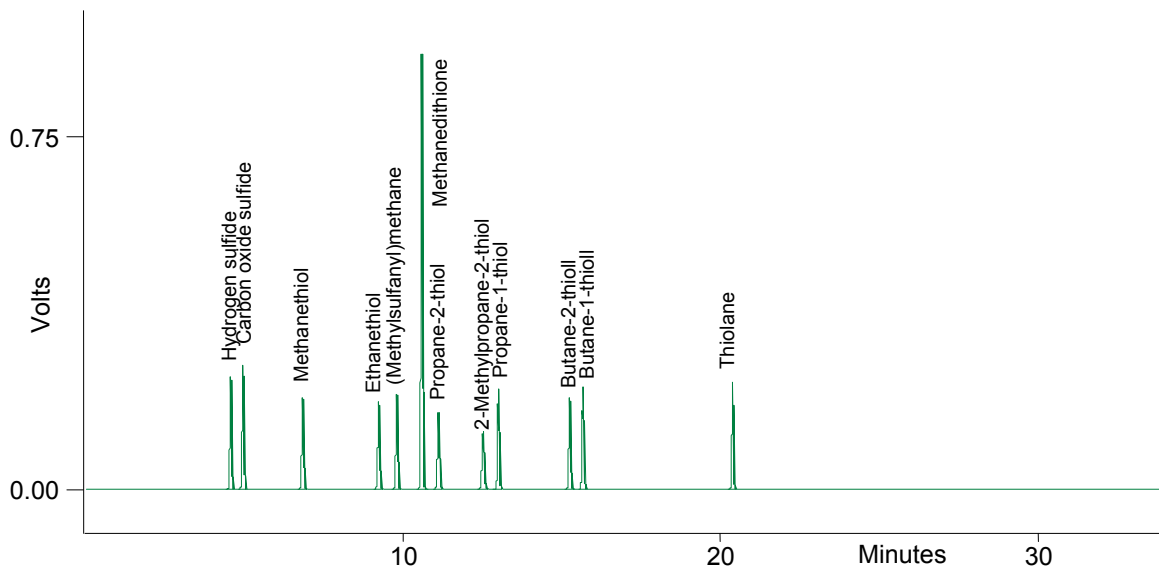
Possible interferences in this measurement are hydrocarbon species coeluting with the sulfur compounds. The C-H breakdown product in the flame emits a broad emission profile that overlaps the sulfur emission. Thus, the detector signal monitored can represent both sulfur and hydrocarbon emissions, and generate results that are biased high and variable from the coeluting hydrocarbons and also from the C-H bonds in the target molecules. Fortunately, they can be differentiated by their emission timing after excitation. C-H emission occurs between 2 and 6 msec after excitation, whereas the sulfur dimer emission occurs between 5 and 30 msec, as illustrated in Figure 1. When the flame is pulsed at typically 300 msec, and the emission profile is monitored after each pulse, the sulfur emission is differentiated from the hydrocarbon discharge by timing. An electronic gate is applied to the profile to exclude both the ignition and hydrocarbon signals and focus in on the sulfur emission. This operation becomes the primary advantage of the pulsed flame photometric detector over other flame photometric designs.



**Figure 1. Characteristic pattern of emissions from PFPD.**

Also, the exclusion of the hydrocarbon signal by the pulsating flame and electronic gate dramatically reduces the detected background. This improves the ability to measure sulfur concentrations as much as a factor of ten times lower levels than steady-state flame photometric detectors.

To illustrate the ability of the pulsed flame photometric detector to generate sulfur responses independent of the parent analyte, twelve common sulfur gases are chromatographically separated, and various data treatments are applied to the results and compared.



**Figure 2. PFPD chromatogram of twelve sulfur gases ( $\sim 5 \mu\text{mol/mol}$ ) was generated with the Scion 456 Pulsed Flame Photometric Detector.**

Chromatographic conditions:

Sample volume: 1 ml with gas sampling valve at 120 °C

Injector: split operations with tee, 50:1split

Flow: EFC25; initial 60 psiG, 2 min. hold, 2.00 min., 100 psiG/min, 20 psiG, hold 7.65min., 35 psiG, 1 psiG/min, hold 5.00 min.

Column: Supelco SPB-1, 60 m, 0.53 mm ID, 5.0 µm film

Column temperature program: Initial 35 °C, hold 4.00 min., 6 °C/min, 150 °C, hold 2.00 min, 12 °C/min, 180 °C, hold 0.00 min., 20 °C/min, 220 °C.

Detector: temperature 200 °C, range: 10, gate delay 6 msec., gate width 20 msec, PM voltage 600 volts, air #1 - 17 ml.min, H<sub>2</sub> - 13 ml/min, air #2 - 10 ml.min

Detector frequency: 5 Hz.

Gas standard details:

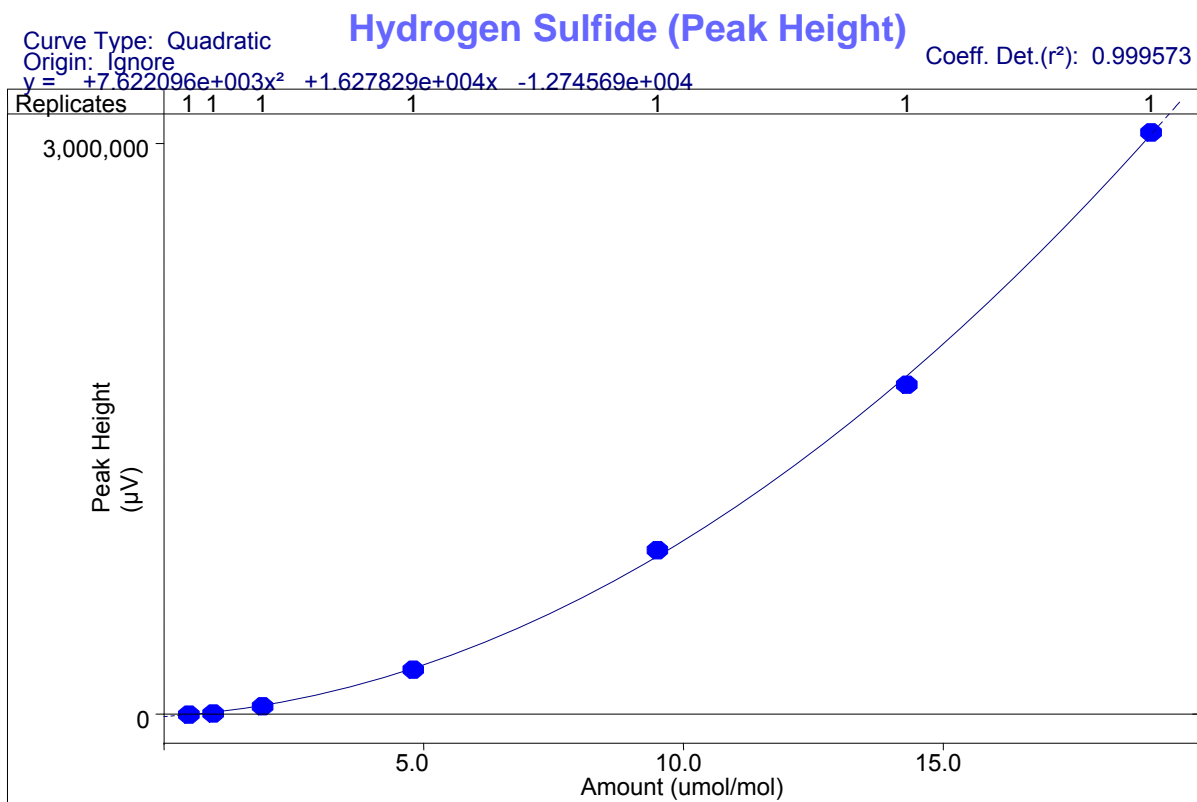
Label values - ± 5% of nominal 20 µmol/mol standard.

Multi-point calibration levels (7 points) achieved by serial dilutions into silico-coated canisters.

Common Name	IUPAC Label
Hydrogen sulfide	Hydrogen sulfide
Carbonylsulfide	Carbon oxide sulfide
Methylmercaptan	Methanethiol
Ethylmercaptan	Ethanethiol
Dimethylmercaptan	(Methylsulfanyl)methane
Carbon disulfide	Methanedithone
i-Propylmercaptan	Propane-2-thiol
t-butylmercaptan	2-Methylpropane-2-thiol
n-Propylmercaptan	Propane-1-thiol
s-Butylmercaptan	Butane-2-thiol
n-Butylmercaptan	Butane-1-thiol
Tetrahydrothiophene	Thiolane

**Table I. Conversion of analyte names from common tags to IUPAC labeling.**  
IUPAC labels are used in this discussion.

Since the sulfur response with this detector is proportional to the square of the sulfur concentration, special data treatment is required to properly quantitate sulfur in samples. Since sulfur response over a chromatographic peak is not linear, from the quadratic relationship to signal level, measurement of the peak sizes is often recommended to be performed by peak heights. Then the calibration curve can be plotted by peak heights versus concentration. This approach yields an anticipated quadratic curve, as shown in Figure 3. Hydrogen sulfide is selected for illustration in this discussion as typical plot performance for other sulfur analytes.

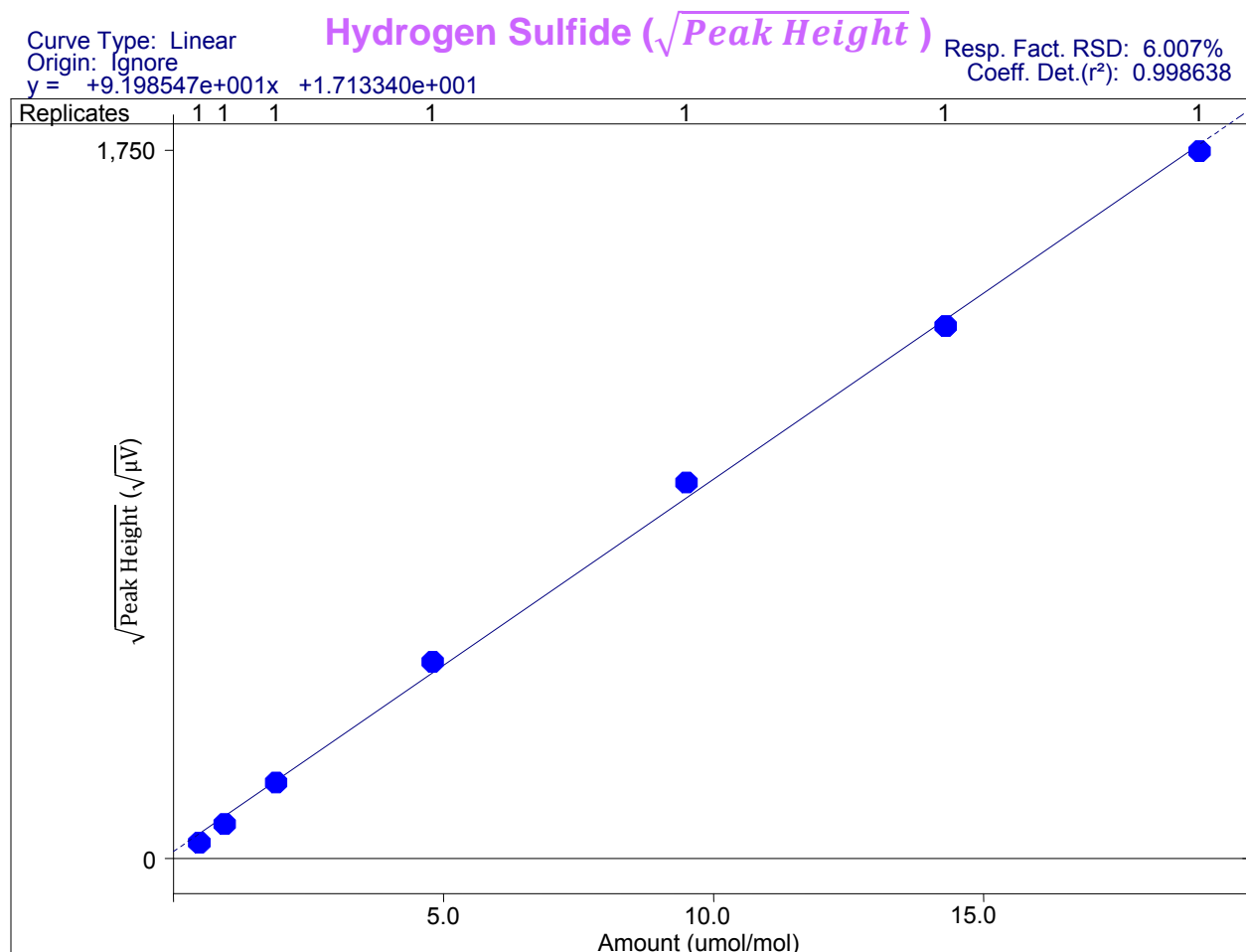


**Figure 3. Calibration plot of Peak Height vs Concentration for Hydrogen Sulfide for concentrations from 0.48  $\mu\text{mol/mol}$  to 19  $\mu\text{mol/mol}$ . Data fits nicely into the expected quadratic relationship, with a high  $r^2$  value.**

Analyte	$x^2$	$x^2 / (\# \text{ sulfur})^2$	x	Intercept	Curve fit ( $r^2$ )
Hydrogen sulfide	7,622	5,507	16,278	-12,746	0.9996
Carbonylsulfide	7,043		6,468	1,193	0.9995
Methanethiol	6,244		1,857	-228.83	0.9998
Ethanethiol	5,807		-2,942	9,249	0.9996
(Methylsulfanyl)methane	6,363		-3,063	10,311	0.9995
Methanedithone	22,028		80,003	70,407	0.9998
Propane-2-thiol	5,256		-4,652	10,828	0.9997
2-Methylpropane-2-thiol	4,429		-4,628	9,540	0.9995
Propane-1-thiol	7,744		-12,524	24,730	0.9985
Butane-2-thiol	7,430		-8,556	19,196	0.9985
Butane-1-thiol	7,518		-11,432	26,269	0.9971
Thiolane	8,319		-15,236	32,210	0.9964
Average	6,606	Average		0.9990	
RSD	18%				

**Table II. Quadratic fit results based on peak height. Carbon disulfide has its  $x^2$  value four times the others, as it has two sulfur atoms per molecule.**

If the heights are converted to the square root of height, a linear calibration curve results, as in Figure 4.

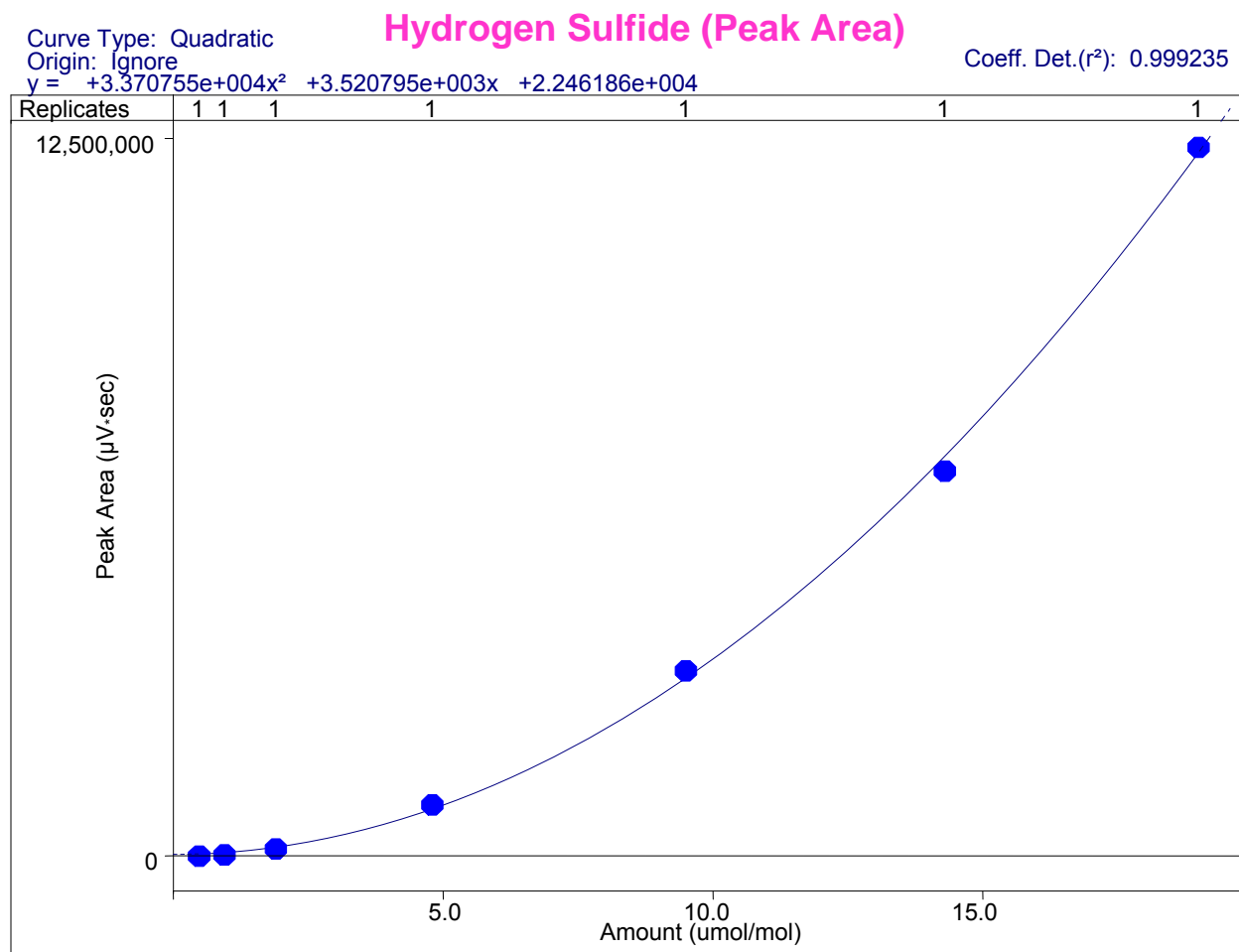


**Figure 4. Calibration plot of  $\sqrt{\text{Peak Height}}$  vs Concentration for Hydrogen Sulfide for concentrations from 0.48  $\mu\text{mol/mol}$  to 19  $\mu\text{mol/mol}$ .**

Analyte	x	x/ # sulfur	Intercept	Curve fit ( $r^2$ )	Resp Fact RSD (%)
Hydrogen sulfide	91.985		17.133	0.9986	6.0
Carbonylsulfide	84.969		22.208	0.9993	5.3
Methanethiol	79.424		5.5017	0.9998	2.3
Ethanethiol	74.917		7.7151	0.9997	3.3
(Methylsulfanyl)methane	78.330		10.664	0.9997	4.3
Methanedithione	162.72	81.36	54.205	0.9984	7.2
Propane-2-thiol	70.539		6.8849	0.9997	3.6
2-Methylpropane-2-thiol	64.451		4.8530	0.9996	3.4
Propane-1-thiol	83.983		4.4887	0.9991	3.1
Butane-2-thiol	83.001		9.2814	0.9991	3.7
Butane-1-thiol	82.760		10.028	0.9983	3.8
Thiolane	86.308		9.0914	0.9980	4.0
Average	80.169		Average	0.9991	4.1
RSD	9.2%				

**Table III. Quadratic fit results based on  $\sqrt{\text{Peak Height}}$ .** Carbon disulfide has its x value twice the others, as it has two sulfur atoms per molecule.

However, measurement of peak sizes by area can still generate adequate calibration curves, with an inherent advantage of inclusion of the entire peak shape. Figure 5 illustrates this approach. The quadratic response is evident.



**Figure 5. Calibration plot of Peak Area vs Concentration for Hydrogen Sulfide for concentrations from 0.48 µmol/mol to 19 µmol/mol.**

Analyte	$x^2$	$\frac{x^2}{(\# \text{ sulfur})^2}$	$x$	Intercept	Curve fit ( $r^2$ )
Hydrogen sulfide	33,708	22,214	35,201	22,462	0.9992
Carbonylsulfide	29,883		11,485	16,944	0.9996
Methanethiol	27,951		-15,050	31,222	0.9996
Ethanethiol	26,664		-29,469	65,237	0.9994
(Methylsulfanyl)methane	27,511		-13,078	43,666	0.9996
Methanedithone	88,855		300,362	-277,964	0.9998
Propane-2-thiol	25,149		-24,209	56,045	0.9996
2-Methylpropane-2-thiol	23,849		-30,808	60,106	0.9993
Propane-1-thiol	30,820		-46,422	93,059	0.9986
Butane-2-thiol	31,987		-47,147	94,634	0.9982
Butane-1-thiol	31,297		-49,285	106,956	0.9976
Thiolane	30,799		-73,074	141,637	0.9957
Average	28,486		Average	0.9988	
RSD	12.4%				

**Table IV. Quadratic fit results based on Peak Area.** Carbon disulfide has its  $x^2$  value four times the others, as it has two sulfur atoms per molecule.



Then, plotting the square root of peak areas versus concentration produces a linear plot, as shown for Hydrogen Sulfide in Figure 6.

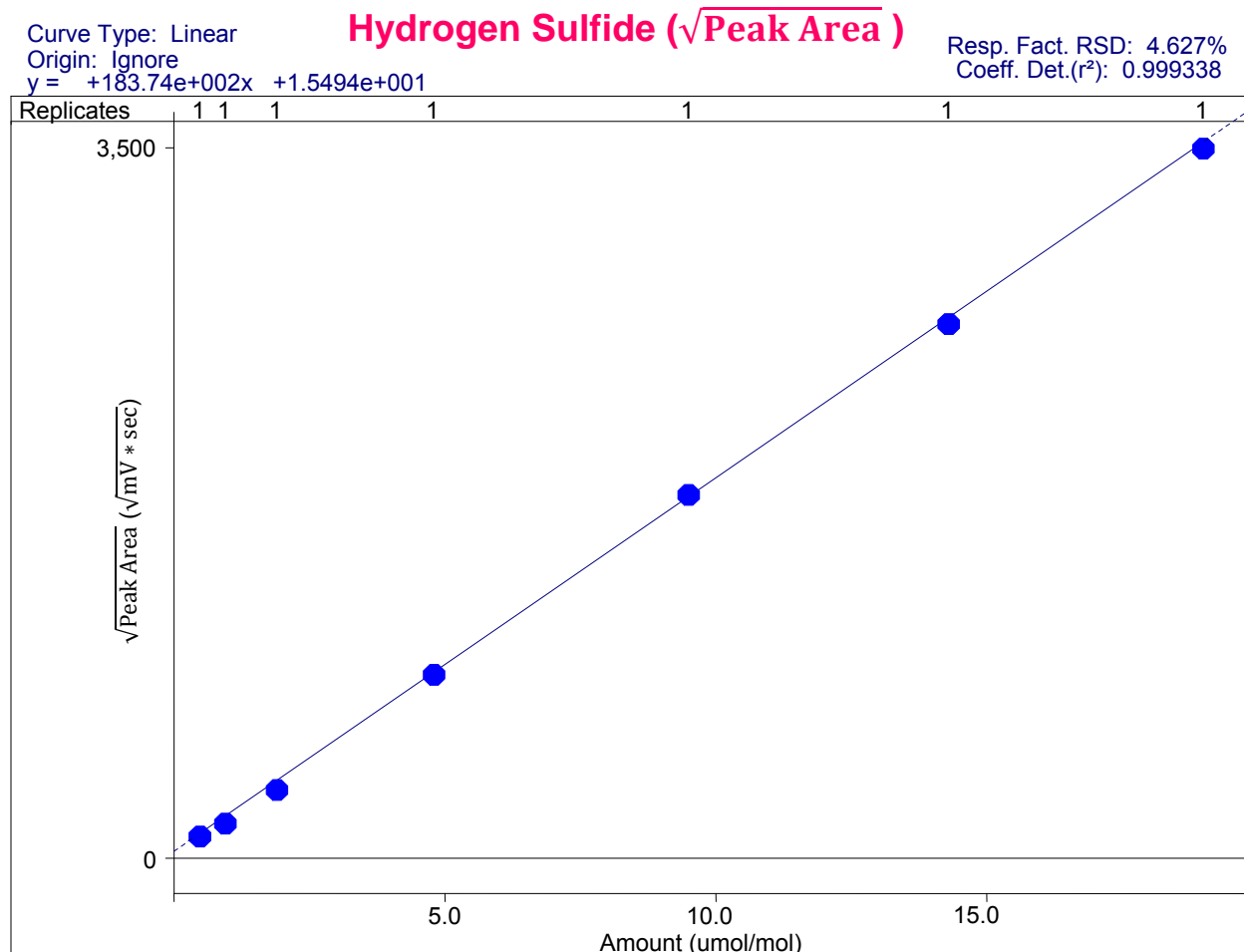


Figure 6. Calibration plot of  $\sqrt{\text{Peak Area}}$  vs Concentration for Hydrogen Sulfide for concentrations from 0.48  $\mu\text{mol/mol}$  to 19  $\mu\text{mol/mol}$ .

Analyte	x	x/ # sulfur	Intercept	Curve fit ( $r^2$ )	Resp Fact RSD (%)
Hydrogen sulfide	183.74	162.73	15.494	0.9993	4.6
Carbonylsulfide	173.22		32.848	0.9996	4.3
Methanethiol	164.35		12.133	0.9997	2.6
Ethanethiol	158.22		11.095	0.9996	3.0
(Methylsulfanyl)methane	162.95		21.189	0.9997	4.0
Methanedithone	325.47		92.599	0.9987	5.9
Propane-2-thiol	154.03		14.648	0.9997	3.4
2-Methylpropane-2-thiol	148.53		10.469	0.9996	3.7
Propane-1-thiol	168.12		8.6105	0.9992	3.2
Butane-2-thiol	170.81		13.921	0.9989	3.2
Butane-1-thiol	164.24	32.643	0.9992	4.2	
Thiolane	163.67	10.992	0.9976	3.6	
Average	164.55	Average	0.9992	3.8	
RSD	5.5%				

Table V. Linear fit results based on  $\sqrt{\text{Peak Area}}$ . Carbon disulfide has its x value twice the others, as it has two sulfur atoms per molecule.

## Summary

Computation Approach	Slope RSD for all Analytes	Curve Fit ( $r^2$ ) Average	Response Factor RSD
Peak Height	18%	0.9990	-- <sup>1</sup>
$\sqrt{\text{Peak Height}}$	9.2%	0.9991	$\pm 4.1\%$
Peak Area	12.4%	0.9988	--
$\sqrt{\text{Peak Area}}$ <sup>2</sup>	5.5%	0.9992	$\pm 3.8\%$

Performing calculations for conversion of pulsed flame photometric detector response to concentrations is best performed with either  $\sqrt{\text{Peak Height}}$  or  $\sqrt{\text{Peak Area}}$ , with very satisfactory curve fits and standard deviations for response factors. These results show that the pulsed flame photometric detector has a nearly equimolar response to sulfur, for a variety of sulfur gases.

---

<sup>1</sup> Response Factor RSDs are not reported for quadratic fits as they are meaningless in non-linear calculations.

<sup>2</sup> All four computation approaches can be employed with Scion CompassCDS. With Scion MS Workstation, only modes available are peak height,  $\sqrt{\text{peak height}}$ , or peak area.



Copyright 2018 Lotus Flower, Inc.

---

**Lotus Consulting**

310/569-0128 Fax 714/898-461  
Email: [randy@lotusinstruments.com](mailto:randy@lotusinstruments.com)



5781 Campo Walk  
Long Beach, California 90803  
Website: [lotusinstruments.com](http://lotusinstruments.com)