Calculation of Performance Factors for Agilent 6890 Detectors Using Different Data Handling Devices

Technology

Gas Chromatography

May 1997

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Abstract

There are multiple data paths available for the Agilent 6890 Series gas chromatograph (GC) system: GPIB and LAN interface for the Agilent ChemStation, analog interface, and INET interface. This technical note documents the relationships between the different data paths and the conversion factors needed for different performance calculations—with particular emphasis on the calculation of minimum detection limits for the flame photometric detector (FPD) and the micro-electron capture detector (micro-ECD).

Introduction

A previous Agilent Technologies technical note[1] describes the three different data paths available for the 6890 Series gas chromatograph (GC) and calculates system performance parameters. The objective of this technical note is to document further the data paths for two 6890 detectors, the flame photometric detector (FPD) and the micro-electron capture detector (micro-ECD).

Minimum Detection Limit Equations for the FPD

For the majority of GC detectors, the minimum detection limit (MDL) is defined as

$$MDL = 2 \cdot N_i/S_i$$

where N_i is the noise and S_i is the sensitivity. While the measurement of noise is straightforward, the calculation of sensitivity depends on the detector being used. For the FPD, the calculation of MDL depends on whether the phosphorus or sulfur mode is being used. If the phosphorus mode is used, the equation for MDL given above can be used.

In this case, the calculation for sensitivity in the phosphorus mode is straightforward using the equation

$$S_p = A_p/m_p$$

where A_p is the integrated area, m_p is the mass of phosphorus in the test substance, and S_p is the phosphorus sensitivity.

Combining equations gives

$$MDL(P) = 2 \cdot N_p \cdot m_p/A_p$$

In contrast, calculating the FPD response to sulfur compounds is more complex. When sulfur-containing compounds are introduced into the flame and under proper conditions, molecular band emission occurs because of the decay of S_2 from an excited state. The signal is proportional to the square of the sulfur concentration in the flame. This squared dependence leads to more complex calculations for MDL and sensitivity for sulfur.

$$MDL(S) = [2 \cdot N_s/S_s]^{1/2}$$

The calculation of sensitivity now includes the mass flow rate of the sulfur atoms in the test compound.

$$S_s = (A_s/m_s)\ (1/\mathbf{m}_s)$$

where N_s is noise, S_s is sensitivity, As is the integrated area, m_s is the mass of the sulfur in the test compound, and $\mathbf{m}_s$ is the mass flow rate of the sulfur in the flame as the test compound elutes.

Combining the equations gives

$$MDL(S) = [2 \cdot N_s \cdot m_s\ \ \mathbf{m}_s/A_s]^{1/2}$$

To calculate the sulfur MDL requires calculation of the mass flow, $\mathbf{m}_s$.

$\mathbf{m}_s$ is related to the width of the sample band eluting. In ASTM E 840(1), the sulfur mass flow rate is given by

$$\mathbf{m}_s = m_s/t_s$$

where ts is the peak width at half peak height. Substituting $w_{1/2}$ for t_s, the equation for sulfur MDL becomes

$$MDL(s) = \left[\frac{(2 \cdot N_s \cdot m_s \cdot m_s)}{(A_s\ w_{1/2})}\right]^{1/2}$$

MDL Equations for the Micro-ECD

For the ECD, sensitivity is calculated as follows:

$$S_i = A_i \cdot F_{det}/m_i$$

where A_i is the integrated area, m_i is the mass, and

$$F_{det} = F_{amb} \cdot T_{det}/T_{amb}$$

F_{det} is the detector flow rate at the detector temperature, T_{det}, and the flow and temperature at ambient levels are F_{amb} and T_{amb}, respectively. The equation for the micro-ECD becomes

$$MDL = 2 \cdot N_i \cdot m_i/(A_i\ \ F_{det})$$

Proper comparison of noise and area measurements, however, depends on the data handling device. Some data handling devices require conversion of noise and area measurements to comparable units before direct comparison can be made. The following segments discuss such conversions.

6890 Series GC Signal Paths

Table 1 shows the display units for the Agilent 6890 FPD and micro-ECD. The display units for the 6890 FPD differ from the display units for the 5890 FPD, which has a display unit of 100 pA. Even though the display unit for the 6890 FPD is larger than for the 5890 FPD, the least significant value for the 6890 FPD is still smaller than the 5890 FPD. Table 2 reproduces from the previous technical note1 the signal path reporting units and Least Significant Values (LSVs) for the 6890 data paths—with the addition of the FPD and micro-ECD.

Table 1. Display Units for the 6890 Detectors

Detector	Unit
FID	1 pA
NPD	1 pA
TCD	25 µV
ECD	5 Hz
FPD	150 pA
Micro-ECD	1 Hz

Table 2. Signal Path Reporting Units and LSVs 6890 Data Paths*

Detector	Data System	Height Units[a]	LSV (Height Unit)	Area Units[a]	Noise[b]
FID/NPD	ChemStation	1 pA	1.3×10^{-4} pA	1 pA-sec	0.038 pA
FID/NPD	SIGRange 0[c]	1×10^{-4} pA	1.3×10^{-4} pA	1×10^{-4} pA-sec	0.038 pA
FID/NPD	SIGRange 5[c]	3.2×10^{-3} pA	4.2×10^{-3} pA	3.2×10^{-3} pA-sec	0.038 pA
FID/NPD	Analog 1V[d]	1.25×10^{-4} pA	g	1.25×10^{-4} pA-sec	0.038 pA
TCD	ChemStation	25 μV	3.3×10^{-3} μV	25 μV-sec	1.43 μV
TCD	SIGRange 0[c]	2.5×10^{-3} μV	3.3×10^{-3} μV	2.5×10^{-3} μV-sec	1.43 μV
TCD	SIGRange 5[c]	0.080 μV	0.11 μV	0.080 μV-sec	1.43 μV
TCD	Analog 1V[d]	3.1×10^{-3} μV	g	3.12×10^{-3} μV-sec	1.43 μV
ECD	ChemStation	5 Hz	6.5×10^{-4} Hz	5 Hz-sec	0.285 Hz
ECD	SIGRange 0[c]	5×10^{-4} Hz	6.5×10^{-4} Hz	5×10^{-4} Hz-sec	0.285 Hz
ECD	SIGRange 5[c]	0.016 Hz	0.021 Hz	0.016 Hz-sec	0.285 Hz
ECD	Analog 1V[d]	6.25×10^{-4} Hz	g	6.25×10^{-4} Hz-sec	0.285 Hz
AIB[d,e]	ChemStation	15 μV	2.0×10^{-3} μV	15 μV-sec	< 5 μV[f]
AIB[d,e]	SIGRange 0[c]	1.5×10^{-3} μV	2.0×10^{-3} μV	1.5×10^{-3} μV-sec	< 5 μV[f]
AIB[d,e]	SIGRange 5[c]	0.048 μV	0.064 μV	0.048 μV-sec	< 5 μV[f]
AIB[d,e]	Analog 1V[d]	1.88×10^{-3} μV	g	1.88×10^{-3} μV-sec	< 5 μV[f]
Micro-ECD	ChemStation	1 Hz	1.3×10^{-4} Hz	1 Hz-sec	0.285 Hz
Micro-ECD	SIGRange 0[c]	$1 \times {}^{-4}$ Hz	1.3×10^{-4} Hz	1×10^{-4} Hz-sec	0.285Hz
Micro-ECD	SIGRange 5[c]	0.0032 Hz	4.2×10^{-3} Hz	0.0032 Hz-sec	0.285Hz
Micro-ECD	Analog 1V[d]	1.25×10^{-4} Hz	g	1.25×10^{-4} Hz-sec	0.285Hz
FPD	ChemStation	150 pA	1.95×10^{-2} pA	150 pA-sec	0.750 nA
FPD	SIGRange 0[c]	1.5×10^{-2} pA	1.95×10^{-2} pA	1.5×10^{-2} pA-sec	0.750 nA
FPD	SIGRange 5[c]	0.48 pA	0.623 pA	0.48 pA-sec	0.750 nA
FPD	Analog 1V[d]	1.875×10^{-2} pA	g	1.875×10^{-2} pA-sec	0.750 nA

[a] Value of one reported count. Analog 1V signal values only apply to Agilent integrator and 6890 Range 0

[b] Maximum noise per Agilent Technologies 6890 SOP[5].

[c] With Agilent 3393 or Agilent 3396 integrator.

[d] Approximate values due to gain variation in analog circuitry.

[e] Analog input board (input non-Agilent detector signals).

[f] Typical noise value.

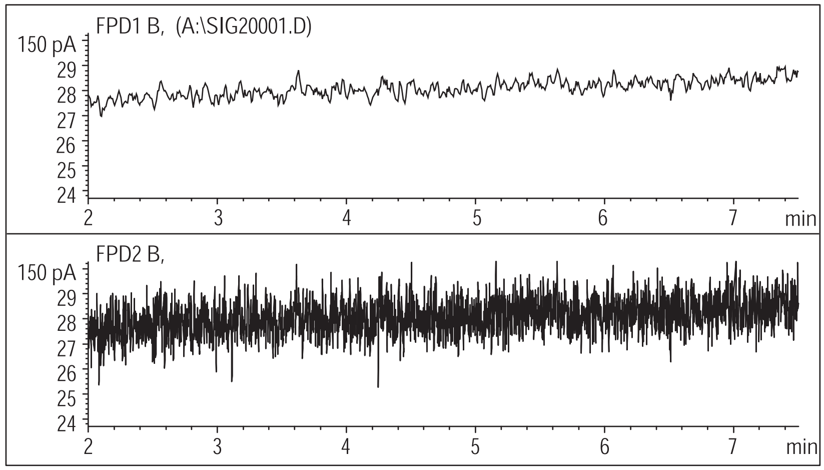
[g] Depends on analog circuitry and analog-to-digital rate of data handling device.

* Reproduced from Agilent Technologies Technical Note (23) 5964-0282E.[1]

Agilent ChemStation Data Path

The ChemStation is the easiest data handling device to use to calculate chromatographic performance factors for the 6890 detectors. The ChemStation, which has scaling equivalent to display units, further simplifies measurement and calculation by giving the user several tools. Noise can be determined automatically by setting up the appropriate time windows. This is accomplished by selecting the **Report/System Suitability/Edit Noise** windows in the Data Analysis View (full menu only).

The noise plot and report for an FPD test sample are shown in figure 1. Figure 2 presents a typical chromatogram and report for the FPD test sample run on sulfur mode under splitless conditions. Table 3 shows the results for the sulfur mode chromatogram.



Signal 1: FPD1 B, 2-Hz data rate

Noise Determination:

Time Range from [min]	to [min]	Noise (6*SD) [150 pA]	Noise (PtoP) [150 pA]	Noise (ASTM) [150 pA]
2.000	3.010	1.4234	1.2426	0.5669
3.000	4.010	1.4541	1.3721	0.5401
4.000	5.010	1.3648	1.1249	0.5170
5.000	6.010	1.4040	1.1924	0.5376
6.000	7.010	1.2432	1.3329	0.5054
2.000	7.500	1.3899	1.6584	0.5479

Signal 2: FPD2 B, 20-Hz data rate

Noise Determination:

Time Range from [min]	to [min]	Noise (6*SD) [150 pA]	Noise (PtoP) [150 pA]	Noise (ASTM) [150 pA]
2.000	3.010	3.6300	3.9362	2.9651
3.000	4.010	3.6534	4.5920	2.9347
4.000	5.010	3.8352	4.9654	2.9978
5.000	6.010	3.6968	4.0796	2.8884
6.000	7.010	3.6104	3.9215	2.8344
2.000	7.500	3.6020	5.1458	2.9007

Figure 1. ChemStation noise measurement.

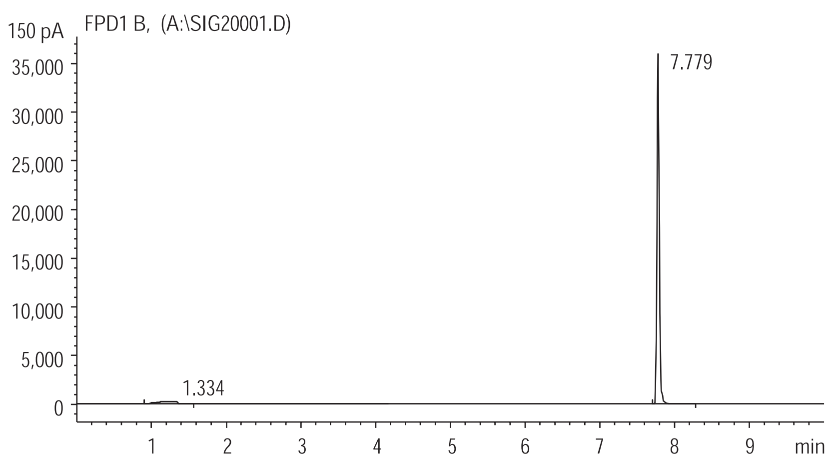


Figure 2. Chromatogram for FPD sulfur mode using checkout sample and standard operating conditions.

Table 3. Results for Sulfur Mode Chromatogram

2 Hz data rate

Peak No.	RetTime (min)	Width Type	Area (min)	Height 150 pA*s	Area (150 pA)	%
1	1.334	BB	0.2130	4800.48437	272.49585	5.57318
2	7.779	BB S	0.0338	8.13350e4	3.60195e4	94.42682
Totals :				8.61355e4	3.62920e4	

20 Hz data rate

Peak No.	RetTime (min)	Width Type	Area (min)	Height 150 pA*s	Area (150 pA)	%
1	1.327	BB	0.2100	4805.04248	269.51349	5.57968
2	7.767	BB S	0.0280	8.13118e4	4.31541e4	94.42032
Totals :				8.61169e4	4.34236e4	

The noise report shows three different noise values. For the purpose of calculating the MDL in this example, an average of the 1.01-minute time window noises was taken. (In our experience, the ASTM noise correlates well with the analog noise measurement on the 3396 integrators.) The data rate was set to 20 Hz.

N_S = 2.90 du

A_S = 81311 du-sec

m_S = 3168 pg sulfur

$w_{1/2}$ = 0.0267 min * 60 sec/min
= 1.602 sec

$$MDL = \left\{\frac{(2 * 2.90 * (3168)^2)}{(81311 * 1.602)}\right\}^{1/2}$$

MDL = 21 pg / sec

If the data rate is changed to 2 Hz, the area remains essentially the same (81335 du-sec) while the peak width increases slightly to 0.0338 min. The noise is significantly reduced from 2.9 du to 0.548 du. Recalculating the MDL :

$$MDL = \left\{\frac{(2 * 0.548 * (3168)^2)}{(81335 * 2.028)}\right\}^{1/2}$$

MDL(@2Hz) = 8.16 pg / sec

The choice of the data rate affects the MDL that can be achieved on most detectors. The data rate also influences the FPD's ultimate detection limit for the sulfur mode.

Agilent 6890 Integrators

Analog Data Path

When compared to other detectors, the FPD is quite noisy and is normally operated at range 5 on the analog signal path. The noise is typically measured at range 5. For higher concentrations of analyte, the range may have to be increased. The micro-ECD will also require changes from the Range 2^0, Attn 2^0 operation typical of the other detectors when measuring the noise.

Figures 3 and 4 and table 4 show the data for the following MDL calculation based on analog measurements:

Area (lindane) = 1805665
@ Range = 2^6

Flow = 60 mL/min with detector temperature at 300 °C

Noise = 10.6 mm @ Range = 2^0
and Attn = 2^3

Noise = 10.6 * 2^0 *2^3 * 0.00677

N_i = 0.574 du

$F_{det} = F_{amb} \cdot T_{det} / T_{amb}$

F_{det} = 60*[(273.15 + 300) /
(273.15 + 25)]

F_{det} = 115.34 mL/min

Converting the area counts to display units gives

Area = 1805655 * 0.000125 * 2^6

Area (du-sec) =14445

The mass of lindane is 33 pg. From this, the MDL can now be calculated.

$MDL = 2 \cdot N_i \cdot m_i / (A_i \cdot F_{det})$

MDL = 2 * 0.574 * 33 * 60 /
(14445*115.34)

MDL = 0.00136 pg/mL

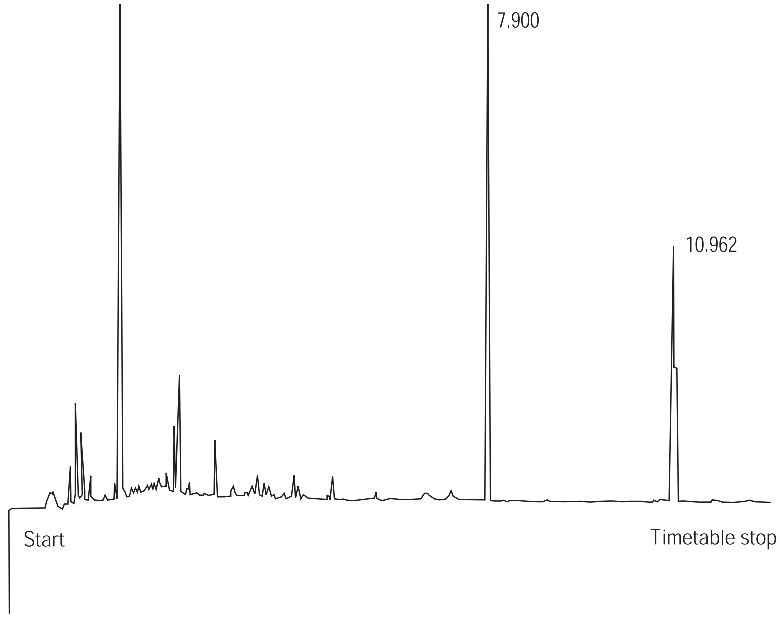


Figure 3. Chromatogram for micro-ECD using checkout sample and standard operating conditions.

Table 4. Results for Micro-ECD Chromatogram

Area (%)

Retention Time	Area	Type	Width	Area (%)
1.816	1076715	SBB	.018	22.47286
7.900	1908801	SPB	.032	39.83989
10.962	1805665	VB	.064	37.68726

Total Area = 4791181
Mul Factor = 1.0000E = 00

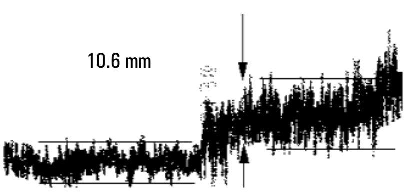


Figure 4. Analog noise measurement.

INET Data Path

The MDL calculation for the FPD's phosphorus mode illustrates the calculations for the INET data path.

$MDL(P) = 2 \cdot N_p \cdot m_p/A_p$

The noise was measured by plotting the signal in plot mode. The INET data path includes the range for the 3396. The default integrator range (known as SIGRANGE) is set at SIGRANGE = 2^5. Because the comparable measurement for the analog signal is typically measured at range = 5, it is not necessary to change from the default setting. The setting of the SIGRANGE value is discussed in more detail in Technical Note (23) 5964-0282E. Neither the range value nor the attenuation at the 6890 affect the INET data path.

For the following example calculation, the data are shown in figures 5 and 6 and table 5.

Noise: N_p = 24.0 mm @Attn 2^0 and SIG1RANGE = 5

Converting the noise measurement to display units (du),

N_p = 24.0 mm * 0.00542 pA/mm * (2^range * 2^attn)

Np = 24.0 mm * 0.00542 du/mm * (2^5 * 2^0)

N_p = 4.16 du

Area: A_i = 14234056 counts @ SIG1RANGE = 5

A_p = 14234856 counts * 0.0001 du-sec/count * (2^Range)

A_i = 14234856 * 0.0001 * 2^5

A_i = 45551 du-sec

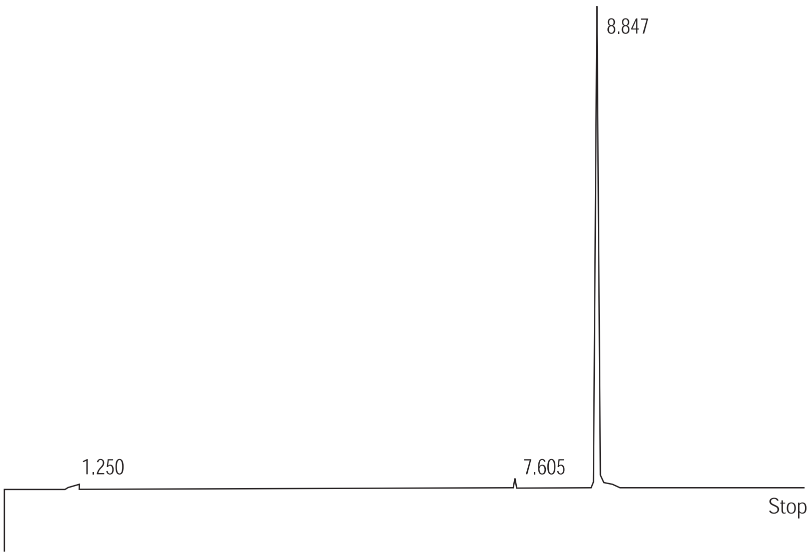


Figure 5. Chromatogram for FPD phosphorus mode using FPD checkout sample and standard operating conditions.

Table 5. Results for Phosphorus Chromatogram

Area %

Retention Time	Area	Type	Width	Area (%)
1.250	1335327	PP	.247	8.40486
7.605	317372	PB	.030	1.99761
8.847	14234856	PB	.033	89.59754

Total Area = 1.5888E + 07

Mul Factor = 1.0000E + 00

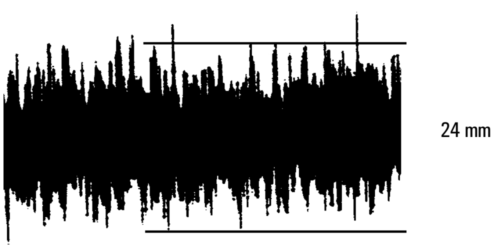


Figure 6. INET Noise measurement.

The mass of the phosphorus is 2331 pg phosphorus for a 1.0-µL injection.

$$\mathrm{MDL(P)} = \frac{2 * 4.16 \text{ du} * 2331 \text{ pg}}{45551 \text{ du} * \text{sec}}$$

$$\mathrm{MDL(P)} = 0.43 \text{ pg/sec}$$

Summary

The calculation of performance factors must take into account the data handling device and data path scaling factors. The previous technical note[1] discusses the scaling factors in more detail. This note has described the calculation of MDL for the new Agilent 6890 detectors and show that the conversion to display units facilitates the calculations.

References

1. P. Larson, S. O'Kane, B. Rhodes, and T. Stark, "Calculation of Performance Factors for the 6890 Gas Chromatograph Using Different Data Handling Devices," Agilent Technologies, Technical Note, Publication 5964-0282E, August 1996.
2. 1993 Annual Book of ASTM Standards, Vol. 14.02, General Test Methods, Nonmetal; Laboratory Apparatus; Statistical Methods; Forensic Sciences; Chromatography, E840-91, "Standard Practice for Using Flame Photometric Detectors in Gas Chromatography," pp 258-268, 1993.
3. 1993 Annual Book of ASTM Standards, Vol. 14.02, General Test Methods, Nonmetal; Laboratory Apparatus; Statistical Methods; Forensic Sciences; Chromatography, 697-91, "Standard Practice for Use of Electron-Capture Detectors in Gas Chromatography," pp 203-213, 1993.
4. L. Bilen, G. Jackaway, M. Klee, and T. Stark, "ChemStation for Gas Chromatography: Reporting Units, Significant Digits, and Threshold Values for 5890, 6890, and 35900 Data," Agilent Technologies, Technical Note, Publication 5965-1640E, July 1996.
5. *6890 Series Gas Chromatograph Standard Operating Procedures*, Agilent Technologies, part number G1530-90380, November 1995.
6. *6890 Series Gas Chromatograph Operating Manual*, pp 266-7, Agilent Technologies, part number G1530-90310, May 1995.
7. *3396 Series III Integrator Operating Manual*, Agilent Technologies part number 03396-90540, January 1995.

Printed in the USA 4/2000
5965-8901E

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