Quantification of Compounds with Low or Negligible Response in Traditional FID using the Polyarc® Reactor

Application Note

Low Sensitivity Compounds

Authors

Connor Beach and Paul Dauenhauer
University of Minnesota, Twin Cities
Amundson Hall
421 Washington Ave SE
Minneapolis, MN 55455

Charlie Spanjers and Andrew Jones
Activated Research Company
7561 Corporate Way
Eden Prairie, MN 55344
Andrew.Jones@activatedresearch.com

Abstract

The flame ionization detector (FID) is widely used in the field of gas chromatography because it is highly sensitive to many organic compounds and provides a linear response over many orders of magnitude. However, FIDs suffer from two main drawbacks: the response to analytes are variable (and therefore require time-consuming calibration) and the FID provides low or no response to highly functionalized molecules such as carbon monoxide, carbon dioxide, formic acid, formaldehyde, and formamide. In this application note, we show that an FID equipped with a Polyarc® reactor is not only highly sensitive to these compounds but also provides a response factor that is equivalent for all carbon-containing compounds, thus eliminating the need for time-consuming calibration. Compared to conventional FID-only systems, the Polyarc® reactor eliminates the need for a second detector to quantify carbon monoxide and carbon dioxide, improves accuracy in quantitative analysis, and saves time and money associated with calibrations.

Introduction

Quantification of molecules by GC/FID is often a time-consuming process, in part, because the response factors for every analyte must be determined before quantitative results can be obtained. Response factors (RF) correct the detector signal for differences in detector—analyte sensitivity and are typically defined with respect to the response of another molecule (i.e., the internal standard) as shown below:

$$RF\ (mol\ \%\ C) = \frac{area_1/mol\ C_1}{area_2/mol\ C_2}$$

where (1) and (2) refer to the analyte and internal standard, respectively, *area* is the GC/FID peak area (i.e., the integrated detector response), and *mol C* are the injected moles of carbon of the component (the concentration of the component in terms of carbon content in the sample could also be used).

Response factors in typical GC/FID analyses are dependent on the chemical structure of the molecule. Heteroatoms such as O, N, P, S, and Cl decrease the response of a given analyte in an FID detector, thus necessitating calibration. The reason for the decreased response factor is the diminished presence of CH and related hydrocarbon radicals. Ultimately, hydrocarbon radicals are thought to react with an oxygen atom to form the CHO^+ ion according to the following reaction:[1]

$$CH + O \rightarrow CHO^+ + e^-$$

The CHO^+ ion is responsible for the measured signal in the FID detector. Without the presence of CH, related hydrocarbon radicals, and ultimately the CHO^+ ion, there is no FID signal. This explains the experimental observation that molecules lacking C-H bonds such as carbon dioxide (CO_2) and carbon

monoxide (CO) are not detectable by conventional FID detectors.

Conversely, the Polyarc® reactor converts all organic compounds to methane prior to detection in the FID according to the following basic reaction:

$$\text{Carbon-Containing Compounds} + \text{Air} + H_2 \rightarrow \text{Methane } (CH_4) + \text{Non-Carbonaceous Byproducts}$$

Since all carbon-containing compounds are converted to methane, the response of the FID is equivalent for all molecules on a per-carbon atom basis and previously undetectable molecules such as carbon monoxide and carbon dioxide are easily quantified. Thus the response factors, as defined above, become unity for all carbon-containing molecules.

In this work, we demonstrate the quantitative analysis of carbon monoxide, carbon dioxide, formic acid, formaldehyde, and formamide using an FID equipped with a Polyarc® reactor. The results show that the Polyarc® setup allows for the sensitive analysis of these molecules (<30 ppm) without calibrations and in the presence of numerous other molecules.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet, a Polyarc® reactor (ARC PA-RRC-A02) was used for the analysis. Air (zero grade, Praxair) and H_2 (99.999%, Praxair) were supplied to the FID and to the ARC manual flow control module (PA-CAS-A07). Helium (99.999%, Praxair) was used as the carrier gas.

The system was configured with the column connected from the split/splitless inlet to the Polyarc®/FID and to the FID-only.

Results

The response factors for five compounds that typically have low response or no response in FID detectors were determined with a conventional FID-only system and compared with the Polyarc® reactor. A bar chart comparing the response factors for FID-only and the Polyarc® reactor is shown in Figure 1 with the tabulated results presented in Table 1. The response factors for all compounds tested with the Polyarc® reactor are 1. CO and CO_2 showed no response in the FID-only system. The Polyarc® reactor is ~100 x more sensitive than FID-only to formic acid, ~10 x more sensitive to formaldehyde, and ~5 x more sensitive to formamide.

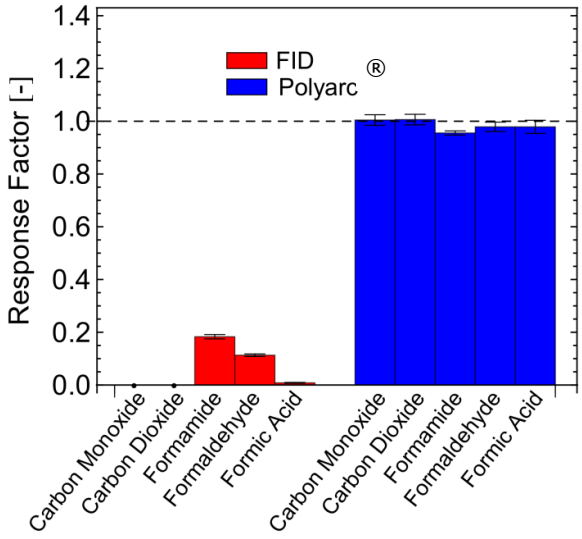

Figure 1. Comparison between the response factors using FID-only and the Polyarc® reactor for compounds that have very low responses in FIDs.

Chromatograms obtained for FID-only and the Polyarc® reactor are presented below for each of the compounds in Table 1. Furthermore, parity plots comparing the actual concentrations and measured concentrations assuming RF =1 are presented, showing the linearity of the Polyarc® reactor across a range of concentrations and the increased response over FID-only.

Table 1. Comparison between the response factors and limits of quantification using FID-only and the Polyarc® reactor for various molecules.

	Response Factor (RF)		Limit of Quantification[a] (ppm[b])		Limit of Quantification (pg C[c])	
Analyte	**FID**	**Polyarc®**	**FID**	**Polyarc®**	**FID**	**Polyarc®**
CO	0.00	1.00 ± 0.02	ND[d]	1.7	ND[b]	9
CO_2	0.00	1.00 ± 0.02	ND[d]	2.7	ND[b]	14
Formamide	0.18 ± 0.01	0.96 ± 0.01	211	29	62	8
Formaldehyde	0.11 ± 0.01	0.98 ± 0.02	155	26	68	11
Formic Acid	0.008 ± 0.002	0.98 ± 0.02	2138	27	620	8

[a]Limit of quantification (LOQ) defined as the concentration at 10x the standard deviation in baseline signal, obtained from linear extrapolation of peak height versus concentration for each analyte.
[b]PPM defined as mole of analyte per million moles of mixture for gaseous samples (CO and CO_2) and mg of analyte per kg of mixture for liquid samples (formamide, formaldehyde, and formic acid). Data is for comparative purposes only as no attempt was made to optimize LOQ by injecting large volumes at low split ratios.
[c]Picograms carbon of injected analyte.
[b]Not detected by FID; LOQ =∞.

Carbon Monoxide and Carbon Dioxide

Analysis Conditions – Carbon monoxide and carbon dioxide

Sample	Gas sample cylinder – 5 % CO, 5 % CH_4, 5 % CO_2, 5 % C_2H_4, 5 % C_2H_6, 5 % H_2, balance He
Column	Agilent GS-Carbonplot, 30 m, 0.32 mm ID, 3.0 micron film thickness
Carrier Gas	He at constant flow (2.0 std. cm^3 min^{-1})
Injection	100 µL split (10:1), 300 °C injection temperature, Agilent 5190-2295 inlet liner
Oven	35 °C (hold 2 min) to 100 °C @ 20 °C min^{-1} (hold 2 min)
Rctr. Gas	35 std. cm^3 min^{-1} H_2, 2.5 std. cm^3 min^{-1} air
Aux. Temp.	293 °C setpoint
FID Detector	315 °C, 1.5 std. cm^3 min^{-1} H_2, 350 std. cm^3 min^{-1} air

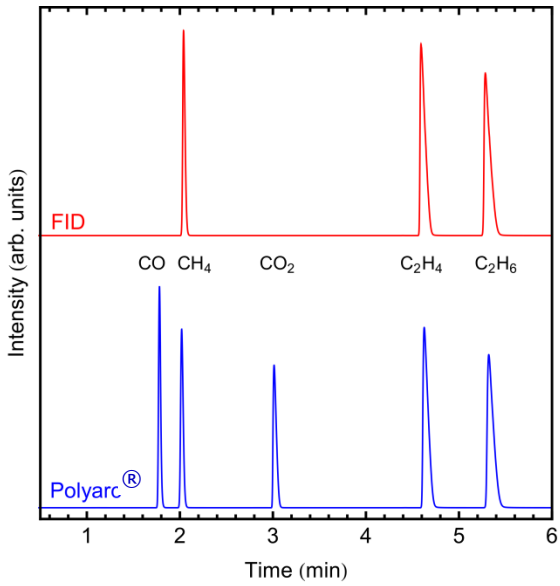

Figure 2. Comparison between the chromatograms obtained for FID-only and the Polyarc® reactor.

Formamide

Note – DMSO should not be injected with larger injection volumes or with lower split ratios than those shown below to prevent sulfur poisoning.

Analysis Conditions – Formamide	
Sample	0.5 to 17 wt. % formamide (neat) in DMSO (neat)
Column	Agilent DB-5, 30 m, 0.32 mm ID, 0.25 µm film thickness
Carrier Gas	He at constant flow (2.5 std. cm^3 min^{-1})
Injection	0.1 µL split (100:1), 325 °C injection temperature, Agilent 5190-2295 inlet liner
Oven	100 °C (hold 2 min) to 140 °C @ 10 °C min^{-1}
Rctr. Gas	35 std. cm^3 min^{-1} H_2, 2.5 std. cm^3 min^{-1} air
Aux. Temp.	293 °C setpoint
FID Detector	300 °C, 1.5 std. cm^3 min^{-1} H_2, 350 std. cm^3 min^{-1} air

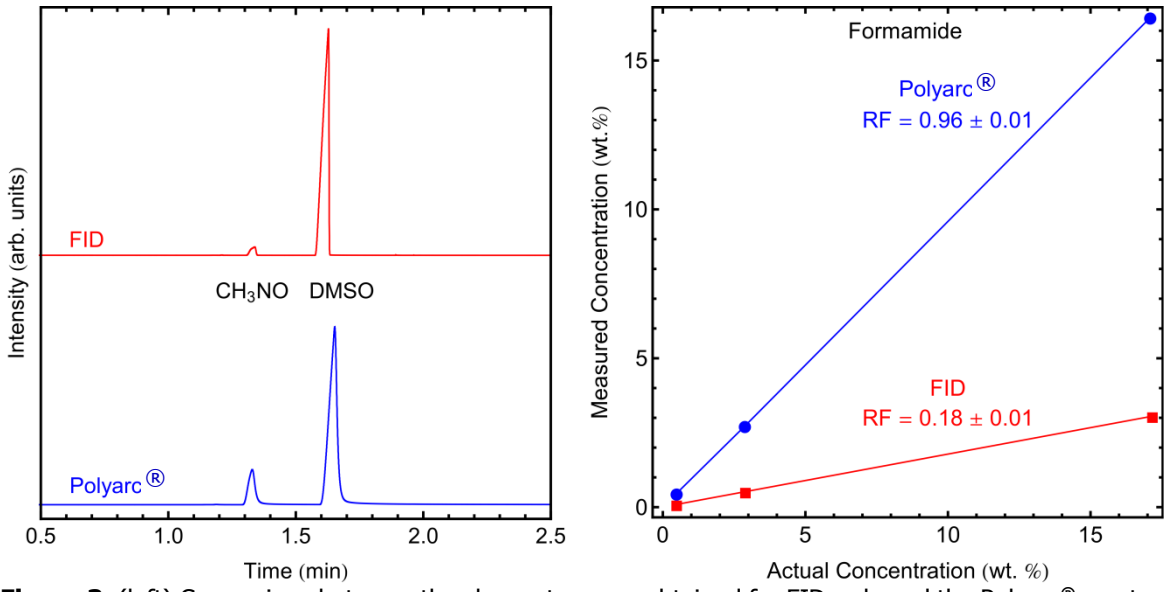

Figure 3. (left) Comparison between the chromatograms obtained for FID-only and the Polyarc® reactor; (right) actual versus measured concentrations (calibration-free, RF = 1) for the Polyarc® reactor and FID-only.

Formaldehyde

Note – DMSO should not be injected with larger injection volumes or with lower split ratios than those shown below to prevent sulfur poisoning.

Analysis Conditions – Formaldehyde	
Sample	0.2 to 6.2 wt. % formaldehyde/methanol (37.5 %/12.5 % in H_2O) in DMSO (neat)
Column	Agilent DB-5, 30 m, 0.32 mm ID, 0.25 µm film thickness
Carrier Gas	He at constant flow (2.5 std. cm^3 min^{-1})
Injection	0.1 µL split (100:1), 250 °C injection temperature, Agilent 5190-2295 inlet liner
Oven	100 °C (hold 2 min) to 140 °C @ 10 °C min^{-1}
Rctr. Gas	35 std. cm^3 min^{-1} H_2, 2.5 std. cm^3 min^{-1} air
Aux. Temp.	293 °C setpoint
FID Detector	300 °C, 1.5 std. cm^3 min^{-1} H_2, 350 std. cm^3 min^{-1} air

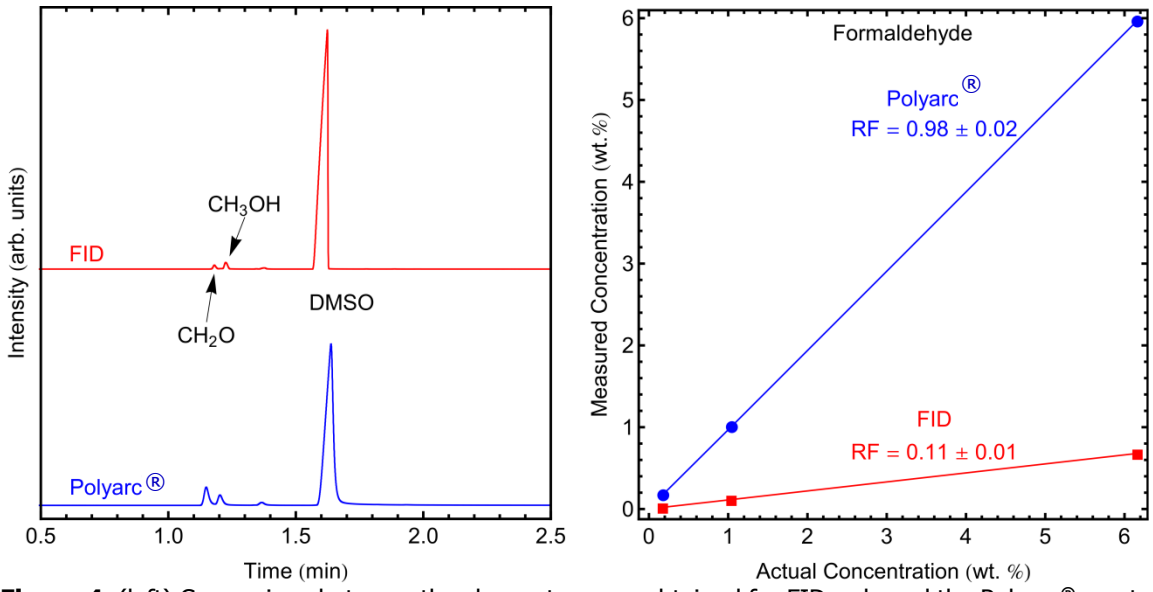

Figure 4. (left) Comparison between the chromatograms obtained for FID-only and the Polyarc® reactor; (right) actual versus measured concentrations (calibration-free, RF = 1) for the Polyarc® reactor and FID-only.

Formic Acid

Note – DMSO should not be injected with larger injection volumes or with lower split ratios than those shown below to prevent sulfur poisoning.

Analysis Conditions – Formic acid	
Sample	0.4 to 16 wt. % formic acid (88 % in H_2O) in DMSO (neat)
Column	Agilent DB-5, 30 m, 0.32 mm ID, 0.25 µm film thickness
Carrier Gas	He at constant flow (2.5 std. cm^3 min^{-1})
Injection	0.1 µL split (100:1), 250 °C injection temperature, Agilent 5190-2295 inlet liner
Oven	100 °C (hold 2 min) to 140 °C @ 10 °C min^{-1}
Rctr. Gas	35 std. cm^3 min^{-1} H_2, 2.5 std. cm^3 min^{-1} air
Aux. Temp.	293 °C setpoint
FID Detector	300 °C, 1.5 std. cm^3 min^{-1} H_2, 350 std. cm^3 min^{-1} air

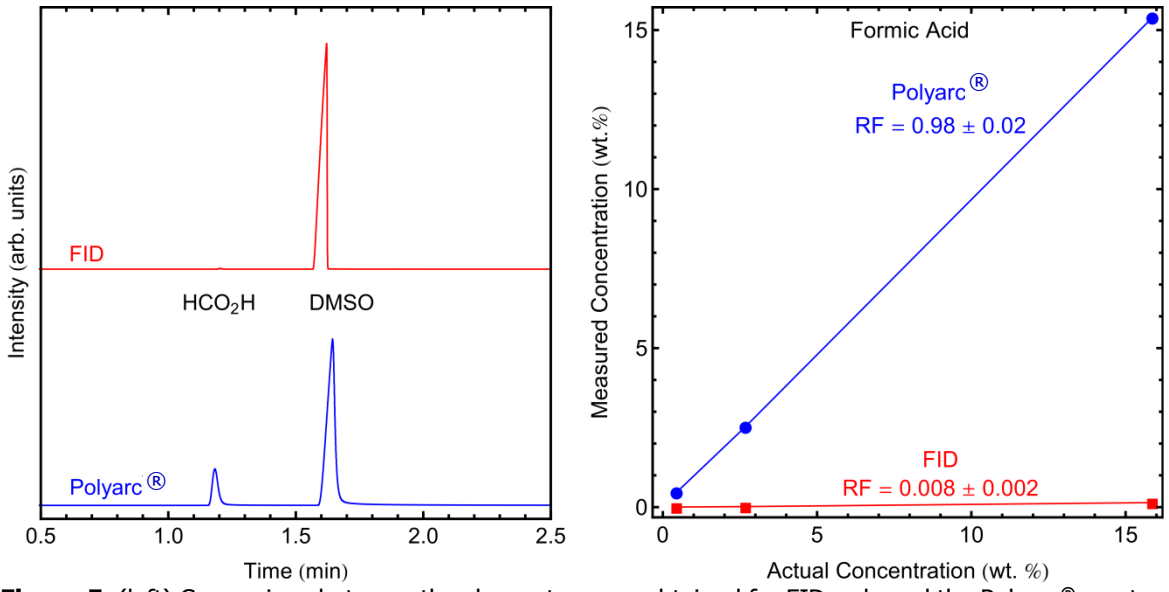

Figure 5. (left) Comparison between the chromatograms obtained for FID-only and the Polyarc® reactor; (right) actual versus measured concentrations (calibration-free, RF = 1) for the Polyarc® reactor and FID-only.

Conclusions

The Polyarc® reactor is highly sensitive and provides a uniform response to compounds that are undetectable in standard FID detectors such as carbon monoxide and carbon dioxide. Furthermore, the Polyarc® reactor is also highly sensitive to compounds that have a very low response in FIDs such as formic acid, formaldehyde, and formamide. The sensitivity and robustness of the Polyarc® system mark a first of its kind in the field of analytical chemistry – other reactor-based technologies such as methanizers are incapable of producing a high and uniform response to all organic molecules. In summary, the Polyarc® reactor saves time, improves analysis sensitivity and accuracy, and eliminates the need for a second detector for molecules that have no or low response in traditional FID detectors.

References

1. Jorgensen, A.D., Picel, K.C., and Stamoudis, V.C., *Analytical Chem.*, 62 (1990) 683-689.

Contact Us

For more information or to purchase a Polyarc® system, please contact us at 612-787-2721 or contact@activatedresearch.com.

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