Equimolar and Linear Carbon Response over 7 Orders of Magnitude for Alcohols, Ethers and Hydrocarbons

Application Note

Volatile Organic Compounds (VOCs)

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Abstract

The conversion of compounds to methane before detection by FID improves signal response and linearity over 7 orders of magnitude. The normalized response increases proportionally with the amount of carbon injected with a proportionality constant of one. The uniform detector response can lead to improved data integrity and simplified workflow when compared with other common detector technologies. A reduction in calibration can lead to time savings of over 58% with increased accuracy.

Introduction

The accuracy and precision of modern instruments allow for unprecedented analysis of molecules. Yet, as the sensitivity of these instruments increase, more care must be taken by scientists to ensure the accuracy of standards, the quantitative delivery of those standards to the detector, and the calibration of the variable detector response. The time and cost of these analyses can strain laboratories and sometimes prevent the analysis of more compounds.

Here, we compare the response of two common gas chromatography (GC) detectors, the flame ionization detector (FID) and the mass spectrometer (MS), with the Polyarc/FID sequential reactor-detector device. The large linear dynamic range with equimolar response allows for better data quality, accuracy and reliability.

Experimental

An Agilent 7890A GC equipped with a capillary-optimized FID, cool on-column inlet (Agilent G3454-64000), mass spectrometer (Agilent 5973), and Polyarc reactor (ARC PA-RRC-A02) were used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air (zero grade, Praxair) and H_2 (99.999%, Praxair) were supplied to the ARC electronic flow control module (PA-MFC-A09) and to the FID. The effluent of the GC column was sent to the various detectors in three different operational modes (Figure 1) one at a time. In the first mode, the GC column was connected directly to the inlet of the Polyarc reactor via a zero-dead volume union (PA-CPM-R46) and the reactor effluent was connected directly to the FID. Second, the GC column was connected to a retention gap column (Agilent, 160-2635-5, 2 ft., 0.1 mm ID), via a zero-dead volume union (PA-CPM-R46), which was connected to the MS. Third, the GC column was connected directly to the FID.

Samples were created from the dilution of a mixture of oxygenates (Restek, 30626, Lot A0116340) with toluene (99.9%, Sigma-Aldrich, 34866). All solvents, samples and vials were cooled to -3 °C to prevent vaporization and degradation. Chemicals were transferred using cooled glass pipettes and gravimetrically measured. Care was taken to avoid prolonged exposure to ambient conditions and samples were immediately recapped and stored in -3 °C temperatures after injections.

An on-column inlet was used to minimize inlet discrimination. The septum purge flow was turned off to ensure quantitative sample transfer to the column. The sample was injected using an automated sample handler and a 5 µL syringe.

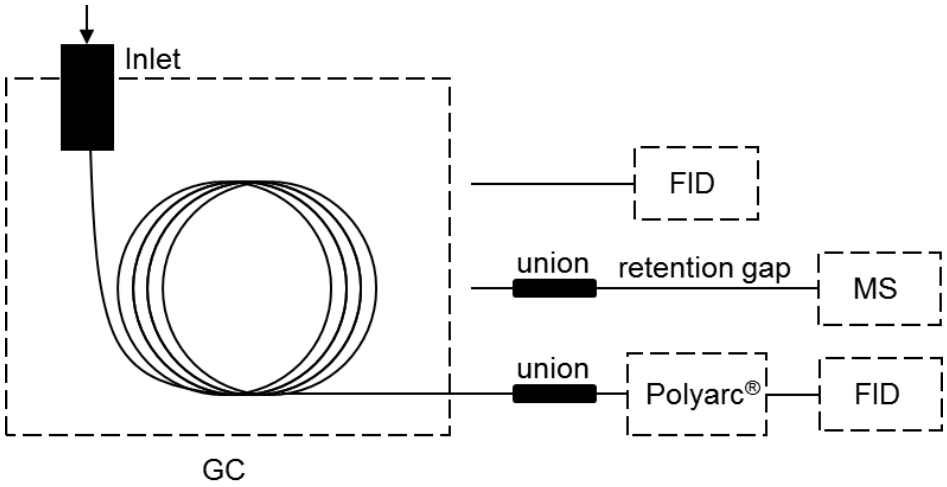


Figure 1. Diagram of GC setup with Polyarc/FID (mode 1), MS (mode 2) and FID (mode 3) options.

GC conditions

Front inlet	Cool on-column
Inlet temperature	Track oven (+3 °C)
Inlet pressure	11.27 psi
Septum purge flow	0 sccm
Oven	40 °C (2 min), 10 °C/min to 80 °C (1 min)
Column	HP-5 (30 m × 0.32 mm × 0.25 µm)
Syringe	5 µL
Injection volume	0.05 µL

MS conditions

Energy	70 eV
Scanning range	29-500 amu
Source temp.	230 °C
Quadrupole temp.	150 °C
GC inlet pressure	23.37 psi

FID conditions

Temperature	315 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	20 sccm (He)
Sampling rate	100 Hz

Polyarc reactor conditions

Setpoint	293 °C
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

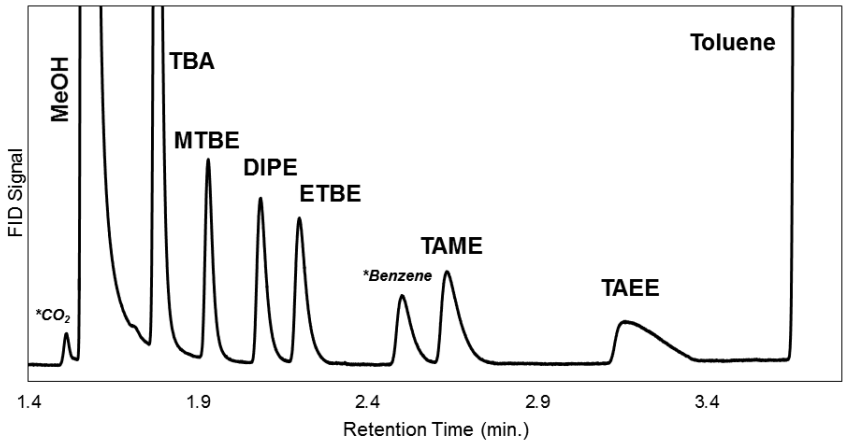
Table 1 shows the concentrations of toluene, methanol (MeOH), tert-butyl alcohol (TBA), methyl-tert-butyl ether (MTBE), diisopropyl ether (DIPE), ethyl-tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), and tert-amyl ethyl ether (TAEE) in each sample A through G. Concentrations were determined from the mass of oxygenates and toluene added, with the mixture density estimated from the pure component densities, assuming additive volumes,

$$\frac{1}{p_{mix}} = \sum_i \frac{x_i}{p_i}, \quad (1)$$

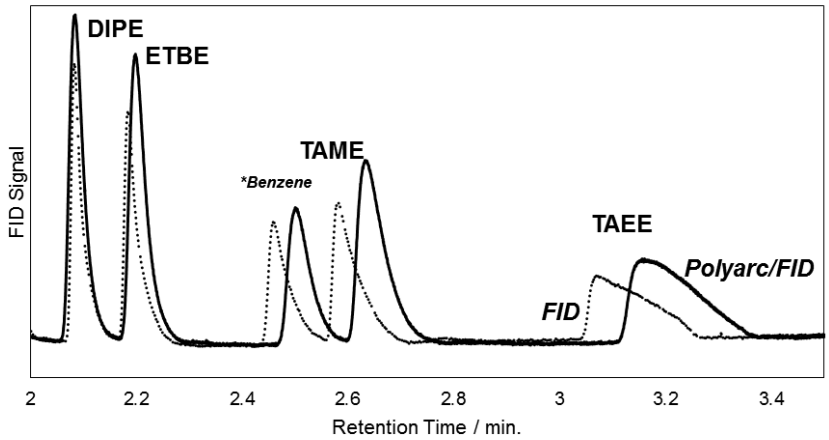
where p_i and x_i are the density and mass fraction of each pure substance, i, and p_{mix} is the mixture density. Concentrations in the samples range from 0.4 to 900,000 µg/mL (ppm), with a range of nearly 7 orders of magnitude (~6.3). For a 0.05 µL injection, the amount of sample injected ranges from 21 pg to 43,000,000 pg, or 1.2 pmol C to 3,300,000 pmol C.

Table 1. Sample compositions.

	Concentration in sample (µg/mL or ppm)						
	A	**B**	**C**	**D**	**E**	**F**	**G**
Toluene	0.0	646439.7	729420.4	778235.6	857590.9	865387.5	866829.6
MeOH	764192.9	194406.7	121265.7	78238.9	8293.4	1421.3	150.2
TBA	10057.5	2558.6	1596.0	1029.7	109.1	18.7	2.0
MTBE	2136.1	543.4	339.0	218.7	23.2	4.0	0.4
DIPE	2184.6	555.8	346.7	223.7	23.7	4.1	0.4
ETBE	2136.1	543.4	339.0	218.7	23.2	4.0	0.4
TAME	2097.2	533.5	332.8	214.7	22.8	3.9	0.4
TAEE	2103.4	535.1	333.8	215.4	22.8	3.9	0.4



(a)



(b)

Figure 2. Chromatogram of sample E with (a) GC-Polyarc/FID and (b) GC-FID (dotted) with GC-Polyarc/FID (solid) comparison.

Figure 2 shows the FID signal after Polyarc reactor conversion to methane of MeOH, TBA, MTBE, DIPE, ETBE, TAME, and TAEE in sample E (8000 to 23 ppm). Baseline separation was obtained for all species. Solvent interactions with TAEE in the GC column led to poor peak shape of TAEE in samples B through G. Benzene, ethyl benzene and xylene impurities came from toluene solvents and did not co-elude with analytes. The small peak before MeOH is believed to be the air peak containing CO_2 because of its retention time, however, only O_2 was observed in the mass spectrometer.

Figure 3 shows the integrated detector responses of the Polyarc/FID and FID as a function of the amount of carbon injected in the form of alcohols, ethers and toluene. Each sample injection was repeated a total of four times (28 total injections), leading to 224 data points for each detector. The Polyarc/FID signal is higher for all compounds, because the methane generated in the Polyarc burns more efficiently in the FID than alcohols, ethers and toluene [1]. The Polyarc/FID also improves the linearity of the FID response from an R^2 of 0.9055 (FID) to 0.9986 (Polyarc/FID), because of the uniform response of all compounds when they are converted to methane. The log-log plot hides some of the major discrepancies; these are highlighted further in Figure 6.

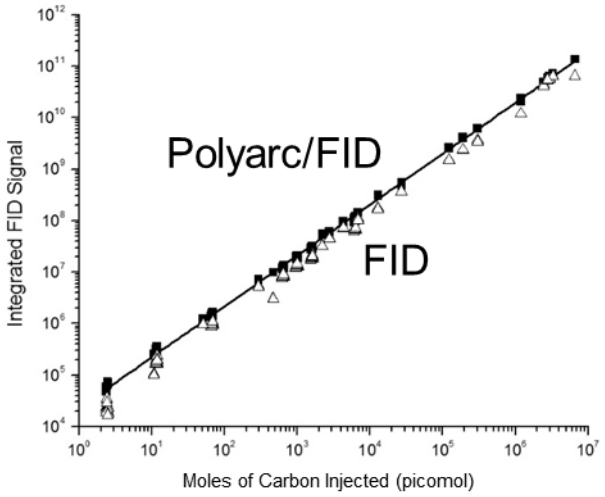


Figure 3. Polyarc/FID (solid squares) and FID (open triangles) response to alcohols, ethers and toluene in samples A through G as a function of the amount of carbon injected. Linear regression (line) of Polyarc/FID response gives a slope of 21051, an intercept of $-3 \cdot 10^7$ and an R^2 of 0.9986.

Figure 4 shows the integrated response of the mass spectrometer to the various alcohols and ethers in the samples (the ion source was turned off during the larger methanol and toluene peaks to avoid source damage). The linear dynamic range of the mass spectrometer was about 3-4 orders of magnitude less than the Polyarc/FID and FID. The average RSD for all modes were similar at about 3%, 4% and 4% for the Polyarc/FID, FID, and MS, respectively. A large amount of scatter in the MS response demonstrates the large variability in sensitivity of the detector to various molecules.

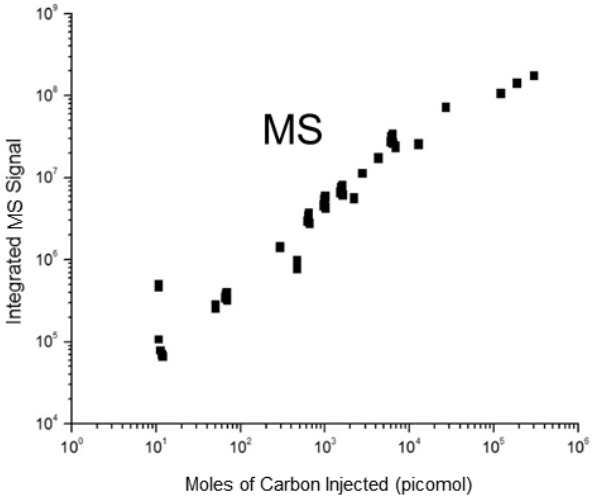


Figure 4. Mass spectrometer response to compounds in samples A through G as a function of the amount of carbon injected.

Next, we normalize the Polyarc/FID response using toluene as an internal standard to (1) assess the relative response of carbon and (2) eliminate injection-to-injection variability. Figure 5 shows the normalized response. The response of the FID to all molecules is equivalent and linear over ~7 orders of magnitude. The slope of the line formed by the points is 1 with an R^2 of 0.999996. The universal response of the detector is the direct result of the full conversion of all compounds, or the carbon contained therein, to methane before their detection by FID. Thus, the concentration of any carbon species could be determined from its relative response to an internal standard or from an appropriate external calibration curve such as the one in Figure 3.

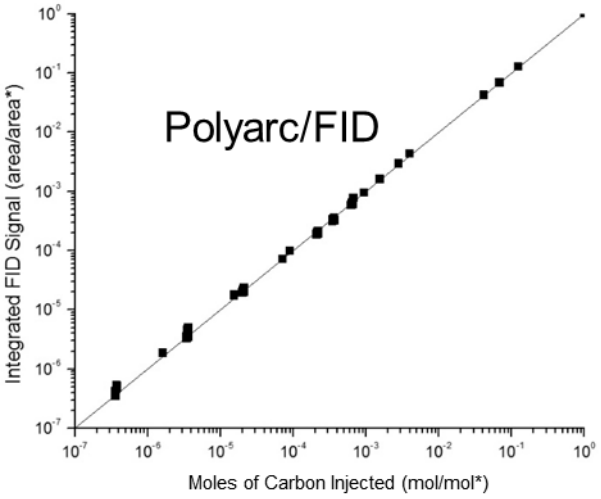
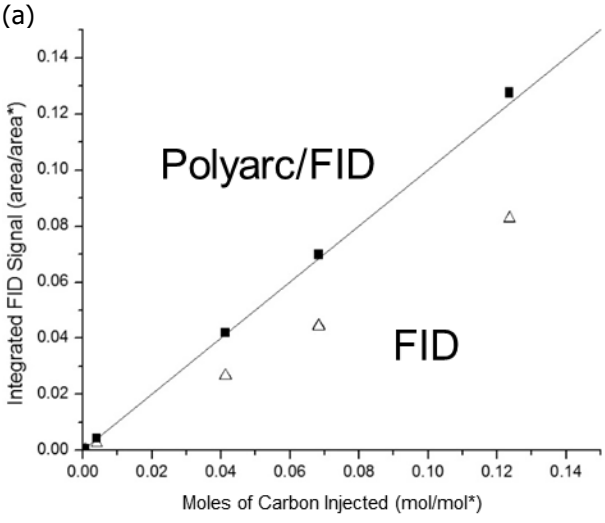


Figure 5. Polyarc/FID response to alcohols and ethers normalized by the toluene response in the same injection. Solid line is the diagonal. Linear regression through the origin yields a slope of 1.00011 and an R^2 of 0.999996.

The differences between the responses of the Polyarc/FID and the FID are more apparent on a linear scale (Figure 6). In Figure 6a, the different slopes indicate the lower response of the FID than the Polyarc/FID to MeOH (by 67%). Figure 6b shows a similar difference for MTBE (68%). The value of this difference depends on the functionality of the molecule because different molecules burn differently in the FID. The different burning efficiencies of some molecules have been tabulated, and heuristics have been made for their theoretical calculations [2,3], however, the poor accuracy of these calculations have led to little use in practice. The benefit of converting molecules to methane with the Polyarc/FID is the resulting uniform and universal carbon response shown in Figure 5, which minimizes errors and enables the diagnosis of GC problems.

The limit of quantification (LOQ) is calculated as the concentration that would lead to a peak height that is 10x the standard deviation in baseline signal. The LOQ values for the various detectors were determined from the injections of sample F (Polyarc/FID and FID) and sample E (MS). The LOQ values of MTBE and TAEE are shown in Table 2. TAEE has a high LOQ value due to the poorer peak shape in all cases. The Polyarc/FID has the lowest LOQ value for TAEE and a similar LOQ value for MTBE as the FID. The mass spectrometer LOQ values were more than 10-fold higher, however, these could be improved with selected ion mode.

(a)



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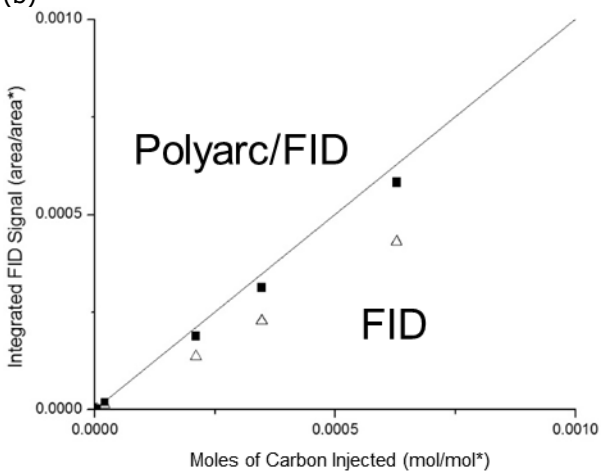

Figure 6. Polyarc/FID and FID responses to (a) MeOH and (b) MTBE normalized by the response of toluene. Solid line is the diagonal.

Table 2. Limits of quantification (LOQ).

	LOQ (µg/mL or ppm)		
	Polyarc/FID	**FID**	**MS**
MTBE	1.1	0.9	43.7
TAEE	5.1	8.0	130.3

Next, we test the stability of the Polyarc/FID response over time; 0.1 µL of sample E was injected into the GC-Polyarc/FID sequentially for a total of 100 injections over 16 hours. The larger injection volume of 0.1 µL instead of 0.05 µL was used to minimize sample-to-sample injection variability, which can be a larger problem for lower injection volumes. Figure 7 shows baseline corrected chromatograms for injection numbers 1, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100. The baseline increased with sequential runs, but decreased again after allowing the oven and inlet to sit at 300 °C for 30 min. This indicates the presence of larger species building up in the column at the low temperatures of these runs. Absolute peak areas decreased (~10% loss in TBA area), but some relative peak areas (e.g., TBA/toluene) were constant (within 2%) over the course of the runs indicating a uniform detector response. The lower absolute areas could be the result of sample degradation (e.g., preferential vaporization of some compounds through the punctured septum, or adsorption on carbon in the column) or the aforementioned baseline drift.

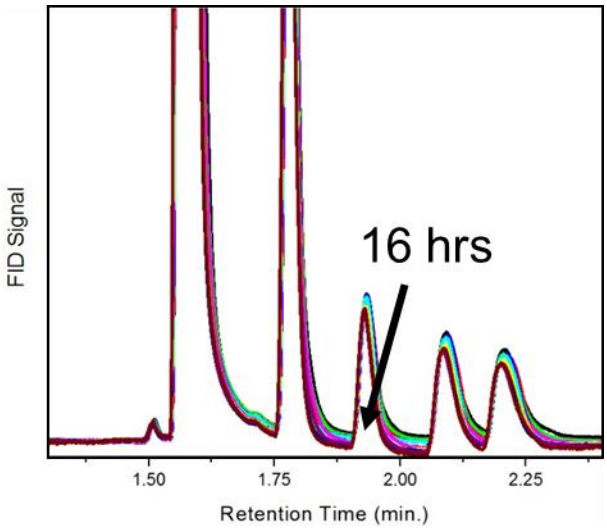

Figure 7. Polyarc/FID chromatograms of 100 injections (0.1 µL) of sample E over 16 hours showing MeOH, TBA, MTBE, DIPE, and ETBE (left to right).

Workflow

Next, we assess the potential time and cost savings of using the Polyarc/FID. Because the Polyarc/FID results in a uniform response in carbon of all molecules, the concentration of any species can be determined from a single external calibration curve (Figure 3), a single-point calibration with an internal standard, or the relative response to an internal standard with no calibration,

$$concentration = \frac{area}{area_{standard}} concentration_{standard} \quad , \quad (2)$$

where concentration is that of carbon (e.g., mol C/mL) and area is the integrated detector signal. This equation is merely the result of Figure 5, or the relative response factor equation with an RF of 1. The highly linear and predictable response can lead to better data quality, but also to significant time and cost savings because of the minimization of calibrations.

To compare the time savings with the Polyarc/FID vs. FID, let's assume that sample 'C' is a mixture with an unknown composition of 7 components and toluene as an internal standard of known concentration. In order to quantify the composition of the mixture with the FID, we must calibrate the FID signal (or risk errors of more than 30%) using 1 to 5 calibration points for each compound (i.e., 7 to 35 different points). If we are lucky enough to purchase a standard that contains all the compounds of interest, then it is just a matter of diluting the mixture. This is rarely the case, but it serves as an optimistic time estimate (7-fold decrease in time) we will use for this example. If we use the data points from samples B, D and E to form a 3-point calibration curve we can estimate the composition of compounds in sample C with an average error of 2.4 %.

To determine the composition of sample C with the Polyarc/FID, we could (Figure 8) either (a) repeat the same 3-point calibration as the FID and achieve a lower average error of 1.4 %; (b) reduce the number of calibration points from three to one and achieve a lower average error of 2.0 %; or, (c) use Eq. (2) without any calibrations and trade accuracy for time savings with an average error of 6.1 %. Note that these errors describe deviations from the gravimetrically measured concentrations, which are also prone to errors. Method (c) may lead to concentrations that are closer to the actual concentrations injected despite its deviations from gravimetric values reported by the vendor.

The time requirements for each of the scenarios are depicted in Figure 8. The following conservative estimates are used for the analysis. The preparation time for the dilution and gravimetric measurements of samples B, D and E is ~20 minutes each. Sample injections take ~10 min. of instrument time including cooling time. Analysis and data workup take ~10 min. Method (a) results in higher accuracy, but with the same time requirements of the FID. Method (b) results in a 58% time savings and an increase in accuracy from the FID. Method (c) results in an 88% time savings and simplified workflow, but with concentrations that are 6.1% different from the gravimetric concentrations. The Polyarc/FID allows the user the choice of continuing to operate as usual with an increased accuracy, or to reduce the calibration workload, and even analyze samples without calibration standards. The increased accuracy of analysis is even more important when considering the error of creating multi-component standards and possible interferences with the sample matrix.

Figure 8. Workflow comparison of FID (orange) and Polyarc/FID (blue; from top to bottom correspond to methods (a), (b) and (c) from the text) analysis of sample C. Personnel and instrument time requirements are shown in black and red, respectively.

These results suggest that time savings between 58% and 88% are possible because of the simplified and reduced workflow requirements of the Polyarc/FID. In addition, significant cost savings are possible because of the reduced instrument time and labor requirements. The following describe areas where the introduction of a Polyarc/FID can add value to a laboratory environment:

- Decrease instrument time
- Decrease instrument maintenance
- Decrease labor time
- Minimize purchase and use of standards
- Quantitation of unknowns and samples without standards
- Mass/carbon balance closure
- Higher quality products from increased analysis accuracy
- Quicker turnaround times for projects
- Reduce error in multicomponent calibrations

Conclusions

The Polyarc/FID yields a linear and uniform response to alcohols, ethers and toluene over 7 orders of magnitude. The improved signal response and uniformity provides key benefits to the scientist including:

1. Better data quality
2. More data reliability
3. Time savings
4. Simplified workflow

To obtain peak performance of the reactor, care should be taken to minimize,

1. Inlet discrimination
2. Sample degradation
3. Improper/incomplete integration

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