



Simultaneous Compound Identification and Quantification with Parallel Polyarc[®]/FID and MS

Application Note

Multi-detector Splitter

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Abstract

Quantification of unknowns with gas chromatography traditionally requires time-consuming and costly calibration steps including purchasing, preparing, and analyzing calibration standards, and applying the calibration results to determine analyte concentration. In this application note, we describe a method for identifying and quantifying unknowns in a single injection using a parallel Polyarc[®]/FID and mass spectrometer (MS) with a 10:1 split ratio.

Introduction

The mass spectrometer (MS) has long been the go-to instrument for qualitative identification of analytes in gas chromatography. Quantification, on the other hand, is most often performed with a flame ionization detector (FID) because of its linearity (over seven orders of magnitude) and its sensitivity to low-level organic analytes. The FID, however, does not provide a uniform response for different molecules, and therefore, requires detailed calibration of the detector response for accurate quantification. FID calibration is time consuming, and in many cases, impossible when standards do not exist or are prohibitively expensive. The Polyarc[®] system solves these problems by

converting all organic molecules to methane, water, and non-carbonaceous by-products for a uniform FID response. The response of the FID per carbon atom becomes identical for all carbon-containing compounds and calibrations are no longer necessitated. In this application note, we describe a method for configuring a Polyarc[®]/FID and MS in parallel leading to a single system that can identify and quantify unknowns in a single injection.

The simultaneous analysis of compounds with two or more detectors and a single inlet and column requires the use of a post-column flow splitter prior to detection. A constant split ratio as a function of temperature is necessary to obtain accurate results when using calibration-free methods. Keeping the split ratio constant requires the use of a pressurized splitter, such as the Agilent Two-Way CFT splitter. The configuration of a system utilizing a splitter is shown in Figure 1 below.

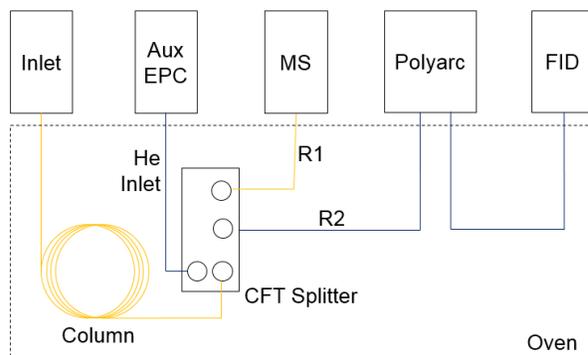


Figure 1. Configuration of a Polyarc[®]/FID and MS for simultaneous compound identification and quantification.

In this figure, it can be seen that the column connects directly to the port adjacent to the He inlet. The next port adjacent to the column inlet is fed to the Polyarc[®] via the metal capillary restrictor built-in to the Polyarc[®] (R2). The last port is connected to the MS via a fused silica capillary restrictor (R1). The restrictors provide backpressure for the added He flow at the CFT splitter and, control the split ratio between the two detectors,

and limit the flow to the MS. **Note:** If using a three-way splitter for configuring this method, the port adjacent the He inlet (the column port in Figure 1) should be plugged with a no-hole ferrule and the column should be attached at the port adjacent the plugged port.

Flow in capillary tubes is governed by the theory of ideal flow of compressible gases, as shown below:

$$F = \frac{60\pi r^4}{16\eta(T)L} \left(\frac{T_{ref}}{T} \right) \left(\frac{P_i^2 - P_o^2}{P_{ref}} \right) \quad (1)$$

where F is flow rate (sccm), r is the radius of the capillary tube (cm), $\eta(T)$ is the temperature-dependent viscosity of the gas (Pa·s), L is the length of the capillary tube (cm), P_i and P_o are the inlet and outlet pressures (Pa), respectively, T is the temperature (K), T_{ref} is the reference temperature (298 K), and P_{ref} is the reference pressure (101,300 Pa).

The split ratio (S) between MS and Polyarc® detectors is defined as the ratio of the gas flows to each detector, as shown below (complete derivation is in the Appendix):

$$S = \frac{F_{Polyarc}}{F_{MS}} = \frac{\frac{r_{R2}^4}{L_{R2}} (P_{split}^2 - P_{Polyarc}^2)}{\frac{r_{R1}^4}{L_{R1}} (P_{split}^2)} \quad (2)$$

where F_{MS} is the flow rate to the MS, $F_{Polyarc}$ is the flow rate to the Polyarc®, P_{split} is the pressure of the splitter, P_{MS} is the pressure of the MS ($P_{split}^2 \gg P_{MS}^2$, so that $P_{split}^2 - P_{MS}^2 \approx P_{split}^2$), $P_{Polyarc}$ is the pressure of the Polyarc®, r_{R1} and r_{R2} are the inner radii of restrictor R1 and R2, respectively, and L_{R1} and L_{R2} are the lengths of the restrictor capillaries R1 and R2, respectively.

P_{split} is controlled by the Aux EPC and should be programmed to remain constant throughout all runs. $P_{Polyarc}$ is the pressure inside the Polyarc® and will vary slightly with temperature. However, the variation is small.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet, capillary-optimized FID, 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 H₂ (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 connected to an Agilent 3-way CFT splitter (G3183-60500) according to Figure 1. Because a 3-way splitter was used to perform a 2-way split, the port adjacent to the He inlet was plugged with an Agilent no-hole ferrule to minimize dead volume. The MS was connected to the splitter via a retention gap column (Agilent, 160-2635-5, 0.61 m, 0.1 mm ID), labeled R1 in Figure 1. The inlet capillary to the Polyarc® was connected directly to the splitter according to Figure 1. The splitter was controlled by an EPC (with restrictor frit removed) to set up a 10:1 split (FID:MS). It is very important that the restrictor frit is *removed* from the EPC to maintain a constant pressure at the splitter.

GC conditions

Front inlet	Split
Split ratio	10:1
Inlet temperature	250 °C
Column flow	3 sccm
Septum purge flow	3 sccm
Inlet liner	Agilent 18740-80190
Oven	40 °C (5 min), 15 °C/min to 125 °C (0 min), 25 °C/min to 250 °C (2 min)
Column	DB-5MS UI (30 m x 0.25 mm x 1 µm)
Syringe	10 µL
Injection volume	0.5 µL

MS conditions

Energy	70 eV
Scanning range	29-500 m/z
Source temp.	230 °C
Quadrupole temp.	150 °C
Transfer line temp	250 °C
Transfer line length	0.6 m
Transfer line diam	0.1 mm ID

FID conditions

Temperature	300 °C
H ₂	1.5 sccm
Air	350 sccm
Makeup	5 sccm (He)
Sampling rate	100 Hz

Polyarc® reactor conditions

Setpoint	293 °C
H ₂	35 sccm
Air	2.5 sccm

Results and Discussion

The theory above was verified by analyzing an 8-component mixture of alcohols and alkanes (250 ppm each in dichloroethane: Restek Polar ISO) to ensure the split ratio remains constant with changing oven temperature. The average error in concentration was 1.5% , consistent with the typical acceptance criteria of this mixture of 3%.

An application of the parallel Polyarc®/FID and MS to the analysis of E85 gasoline is shown in Figure 2. Quantification of ethanol with a single injection without calibration yields a measured concentration of 88 wt. % ethanol. The actual concentration of the sample measured by ASTM D5501 methods is 86 wt. %. The small error between the two methods of 2.3% is within the accuracy of calibrations and the co-elution of some minority species.

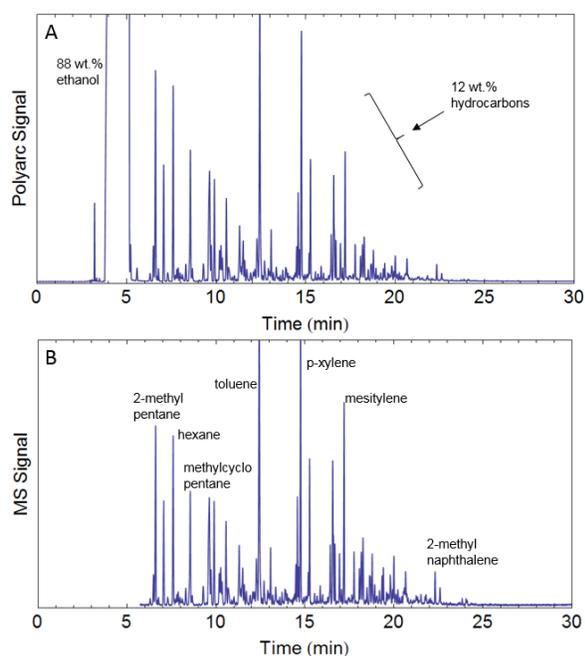


Figure 2. Parallel Polyarc®/FID (A) and MS (B) for the quantification and identification of the components of E85 gasoline

Basic steps for system configuration (contact ARC for more information):

Parts needed for an Agilent 7890 configuration (contact ARC for other systems):

- Polyarc System with Electronic Flow Control (PA-SYC-401)
- Polyarc MS Split Kit (PA-SPL-KT7)
- Agilent Aux 3-Channel EPC (PA-EPC-3C7)

Configuration instructions on an Agilent 7890 (contact ARC for other systems):

1. Install an Agilent 3-Channel EPC.
Important: Remove the restrictor frit from the EPC module.
2. Install an Agilent 2-way CFT splitter and connect the input to the EPC.
3. Connect the column to the CFT splitter (see Figure 1).
4. Install the Polyarc system with electronic flow control, following the installation manual.
5. Connect the inlet of the Polyarc directly to the CFT splitter according to Figure 1 (do not change the length of the Polyarc inlet transfer capillary).
6. Install a 0.6 m, 0.1 mm ID transfer line (Agilent, 160-2635-5) to the MS.
7. Configure the Aux EPC, and set the EPC pressure to 4 psi in all runs.
8. Configure the GC method with the configuration above to ensure column flow rates are set correctly.

Notes:

1. Ensure that the splitter is properly installed and configured in the method.
2. The flow control frit in the EPC flow module must be removed or replaced with a zero resistance tube (removal of the frit ensures the pressure at the splitter is equal to the pressure set by the EPC).

Conclusions

The combined Polyarc[®]/FID and MS system proves to be a highly useful tool for identification and quantification of analytes in a single injection. A constant split ratio with oven temperature ramps can be obtained with a constant splitter pressure controlled by an EPC. This allows for the unparalleled simultaneous quantification and identification without the need for calibration using equimolar carbon response of the Polyarc/FID and fragmentation databases for the MS.

Contact Us

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

Please visit our [website](#) for details and [additional technical literature](#).

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Appendix

Derivation of Eq. (2):

$$S = \frac{F_{Polyarc}}{F_{MS}} = \frac{\frac{60\pi r_{R2}^4}{16\eta(T)L_{R2}} \left(\frac{T_{ref}}{T}\right) \left(\frac{P_{split}^2 - P_{Polyarc}^2}{P_{ref}}\right)}{\frac{60\pi r_{R1}^4}{16\eta(T)L_{R1}} \left(\frac{T_{ref}}{T}\right) \left(\frac{P_{split}^2 - P_{MS}^2}{P_{ref}}\right)} = \frac{\frac{r_{R2}^4}{L_{R2}} (P_{split}^2 - P_{Polyarc}^2)}{\frac{r_{R1}^4}{L_{R1}} (P_{split}^2 - P_{MS}^2)} = \frac{\frac{r_{R2}^4}{L_{R2}} (P_{split}^2 - P_{Polyarc}^2)}{\frac{r_{R1}^4}{L_{R1}} (P_{split}^2)} \quad (2)$$