Enhanced Chromatographic Analysis with Polyarc® Ultra

Application Note

Product Note

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Abstract

An enhanced version of the Polyarc reactor, the Polyarc Ultra, has been developed to improve (decrease) solvent tailing with certain solvents and improve peak shapes of active compounds. Here we demonstrate a reduction in solvent tailing of dichloroethane by up to 250% with the new reactor design, improving quantification of compounds that elute on the solvent tail.

Introduction

The Polyarc is a catalytic microreactor that is added after the column and before the FID, through which all organic compounds are converted to methane in a two-step catalytic reaction:

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

As a result of only ionizing methane in the FID, the response-per-carbon in the FID becomes equivalent for all molecules. Thus, the relative response of the FID to a single internal standard (or an external standard) can be used to quantify all other components in the mixture, without the need for calibration factors.

Due to the added volume of the inlet transfer line and reactor body, roughly 5-10% peak broadening is to be expected with the standard Polyarc. Some peak tailing for higher concentrations of compounds is also to be expected. The Polyarc Ultra was designed to address this issue for analyses that require better resolution in these cases by modifying the internal reactor morphology, catalyst microstructure, and flow-path surface chemistry.

In this application note, it is shown how the Polyarc Ultra (Figure 1) can be used to analyze compounds with a uniform response and improved tailing relative to the standard Polyarc.

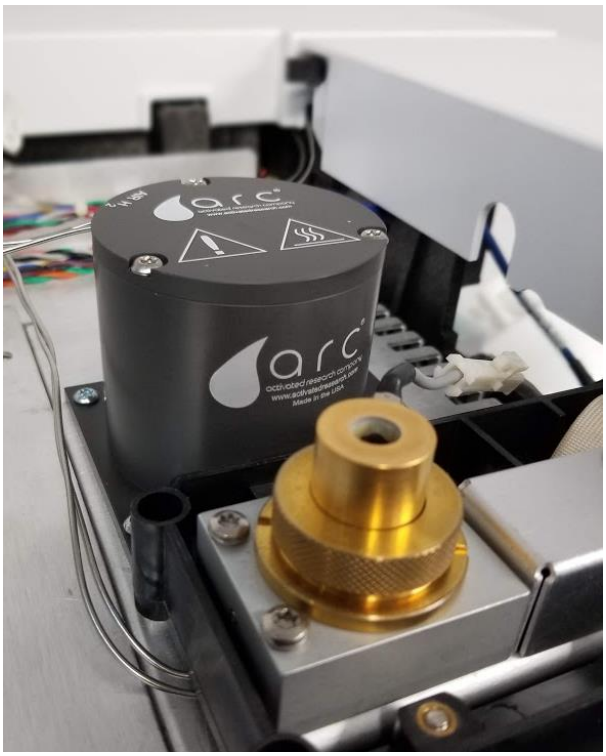

Figure 1. Polyarc Ultra on an Agilent 7890 GC.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet (Agilent G3454-64000), capillary-optimized FID, and Polyarc® Ultra reactor with electronic flow control (ARC PA-SYS-UEF) or standard Polyarc® reactor with electronic flow control (ARC PA-SYS-EFC) was used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air purified with an ARC CO_2 trap (ARC PA-COT-R31) and H_2 (99.999%, Praxair) were supplied to the ARC electronic flow control module and to the FID. The inlet capillaries to the Polyarcs were connected directly to the column with an Agilent Ultimate Union (Agilent G3182-60581).

GC conditions

Front inlet	Split/splitless
Inlet temperature	250 °C
Inlet linter	Agilent 5190-3165
Carrier gas	He; 2.6 sccm constant flow
Septum purge flow	3 sccm
Oven	40 °C (hold 5 min) to 150 °C at 10 °C/min to 250 °C at 25 °C/min
Column	HP-5 (30 m × 0.32 mm × 0.25 µm film)
Syringe	10 µL
Injection volume	1.0 µL

FID conditions

Temperature	315 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	5 sccm (He)

Polyarc® System conditions

Setpoint	450 °C
H_2	35 sccm
Air	2.5 sccm

Analysis Procedure

Peak half-widths were measured at 10%, 5%, 1%, and 0.1% of the total peak height to compare peak tailing on the solvent (dichloroethane) peak for the Polyarc Ultra and the standard Polyarc. The standard peak tailing calculation such as the USP <621> definition was not used because the solvent peak greatly overloads the column and outweighs the peak symmetry calculation.

Aniline peak tailing was quantified using USP <621> tailing factor (A_S), defined as follows, where $W_{0.05}$ is the width of the peak at 5% height and f is the distance from the peak maximum to the leading edge of the peak, the distance being measured at a point 5% of the peak height from the baseline:

$$A_S = {W_{0.05}}/{2f}$$

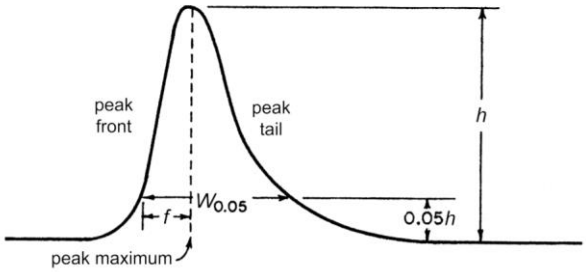

Figure 2. Asymmetrical Chromatographic Peak

Accurate quantification was also verified on both reactors. Concentrations were calculated using the following equation. Methane produced from combustion-reduction reactions in the Polyarc is measured with the FID resulting in an equimolar carbon response. The concentration of each analyte can therefore be calculated from the concentration/area ratio of an arbitrary standard using the following equation:

$$C_A = C_s \left(\frac{Area_A}{Area_S}\right)\left(\frac{\#C_S}{\#C_A}\right)\left(\frac{MW_A}{MW_S}\right)$$

where:

C_A = Mass concentration of analyte
$Area_A$ = Integrated peak area of the analyte
Mw_A = Molecular weight of the analyte
Mw_S = Molecular weight of the standard
$\#C_S$ = Number of carbon atoms for standard
$\#C_A$ = Number of carbon atoms for analyte

More Details can be found within the "Quantification with the Polyarc.pdf" on the web at https://www.activatedresearch.com/documents/

Results and Discussion

Figure 3 shows the improvement in solvent tailing with the Polyarc Ultra (black) over the standard Polyarc (blue). Note the two small peaks on the standard chromatogram before the first impurity are an FID spike and a small impurity not present in the sample, so they are not present in the Ultra runs. This tailing is quantified in Table 1, showing the percent improvement calculated relative to the half width of the Polyarc Ultra.

Table 1. Comparison of Half-Widths

	Standard Polyarc	Polyarc Ultra	Percent Difference
Half-Width, 10% (min)	0.0125	0.0080	56%
Half-Width, 5% (min)	0.0148	0.0094	57%
Half-Width, 1% (min)	0.0219	0.0125	75%
Half-Width, 0.1% (min)	0.1395	0.0385	262%

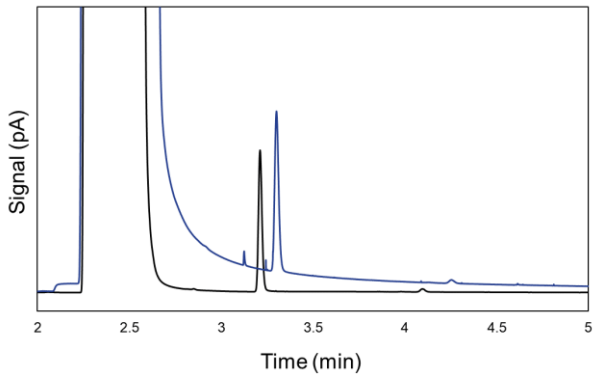

Figure 3. Dichloroethane Solvent Peak tails

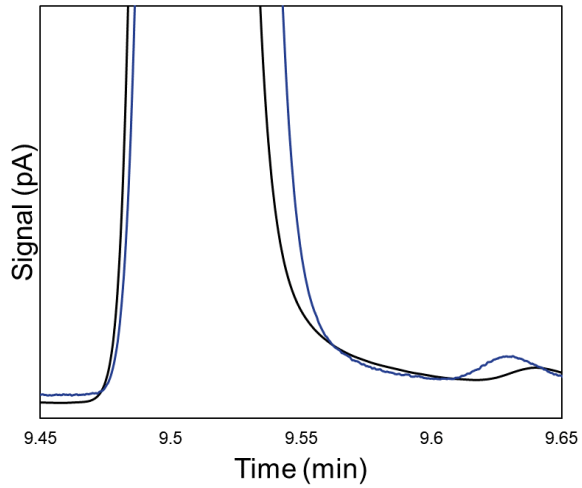

Figure 4. Aniline Peak Tails

Figure 4 shows the peak shape of aniline at 250 µg/mL for both reactors (standard in blue, Ultra in black). Tailing for this peak is relatively unchanged, with the standard reactor's USP tailing being 0.98 and the Polyarc Ultra USP tailing factor being 1.04.

Quantitation was tested on both versions of the Polyarc with the Polyarc Test Mix (PA-PTM-R73), a quantitative standard used to validate performance of each Polyarc. Table 2 shows percent errors relative to gravimetric values for the standard Polyarc and Polyarc Ultra. Errors are within expected values and encompass contributions from the entire GC system.

Table 2. Quantification Results

Analyte	Standard Polyarc % Error	Polyarc Ultra % Error
Aniline	-3.6%	-0.1%
2-Chlorophenol	-3.0%	0.0%
1-Octanol	-6.6%	-2.8%
2-Nonanone	0.0%	1.9%
2-Dodecanol (IS)	N/A (IS)	N/A (IS)
Methyl Laurate	3.3%	1.9%
n-Heptadecane	1.3%	-1.4%
n-Nonadecane	-1.4%	-6.1%

Conclusions

The Polyarc Ultra showed significant improvement in solvent peak tailing, while maintaining accurate quantification of a known standard and good peak shape for aniline. This reduction in solvent tailing improves sensitivity and accuracy near the solvent, allowing analysts to expand their capabilities and be more accurate. The standard Polyarc is confirmed to be as accurate under the same conditions for quantification not near the solvent peak.

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, www.activatedresearch.com.

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