Quantification of Liquid Hydrocarbons with Large Boiling Point Range using the Polyarc® Reactor

Application Note

Hydrocarbon Ladder

Authors

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

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

Abstract

The conversion of analytes to methane before their detection with a flame ionization detector (FID) using gas chromatography (GC) gives more uniform analyte response. In this application note, we use the Polyarc® reactor to convert C5 to C18 n-alkanes to methane in order to quantify their concentrations. The Polyarc® reactor allows for accurate quantification (average error of 0.9%) of the hydrocarbons studied here. The Polyarc® reactor maintains high separation efficiency with only a 9% increase in peak width compared to an FID-only analysis. We demonstrate that low inlet pressures can lead to discrimination in the vaporization of hydrocarbons in the inlet, especially those with large differences in boiling points, and we describe methods for the optimization of inlet conditions to avoid these issues.

Introduction

Modern scientific analysis instruments allow for highly sensitive analyses of organic compounds. Identification of unknown compounds is often performed with a mass spectrometer and can be done on the fly without the need for standards. Quantification, on the other hand, is often time consuming, as it requires creating a calibration curve for each compound.

Here, we demonstrate use of the Polyarc®/FID for quantitative analysis of hydrocarbons without the need for calibration standards. While pure hydrocarbons can also be analyzed on an FID without calibration, we show here that the Polyarc®/FID does not lead to degradation in performance compared to FID-only for these compounds. We also show how to mitigate inlet issues that can lead to analysis inaccuracies.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet and 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. A C5 to C18 n-alkane standard (2.4 to 21.1 wt.%, Agilent 5080-8786, Lot CG-3720A) was used without further modification. The sample was injected into the split/splitless inlet in splitless mode.

GC conditions

Front inlet	Split/Splitless
Inlet temperature	360 ºC
Inlet pressure	6.64 psi
Septum purge flow	0 sccm
Oven	35 °C, 15 °C/min to 245 °C
Column	Rtx-2887, 10 m, 530 µm, 2.65 µm film thickness
Syringe	10 µL
Injection volume	0.1 µL splitless

FID conditions

Temperature	360 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	0 sccm (He)
Sampling rate	50 Hz

Polyarc reactor conditions

Setpoint	293 °C
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

A solution of 13 n-alkanes with known concentrations was analyzed with the Polyarc ® reactor to determine its ability to quantify analytes without the need for calibration. The chromatogram obtained using the Polyarc® reactor is shown in Figure 1. Corresponding peak areas and peak widths are displayed in Table 1. N-decane was used as an internal standard to determine the concentrations of the analytes assuming relative response factors per carbon of unity. The maximum error between the actual concentrations and the concentrations determined with the Polyarc® reactor is 2.4%, and the average error is 0.9%. The average full width at half maximum (FWHM) of the peaks increases by ca. 9% using the Polyarc® reactor compared to an FID-only analysis.
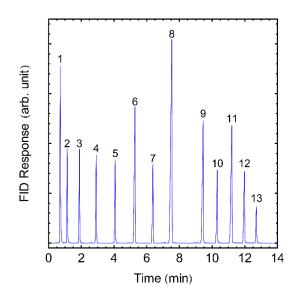

Figure 1. Analysis of C5 to C18 n-alkanes using the Polyarc® reactor.

Table 1. Peak properties and concentrations of C5 to C18 n-alkanes using the Polyarc® reactor.

#	Analyte	Peak Area	FWHM[a] (min)	Calculated Conc. (wt. %)	Actual Conc. (wt. %)	Percent Error
1	n-pentane	9171	0.043	8.62	8.83	2.4
2	n-hexane	4994	0.044	4.67	4.65	0.4
3	n-heptane	5221	0.046	4.87	4.83	0.8
4	n-octane	5348	0.050	4.97	4.97	0.0
5	n-nonane	5493	0.055	5.10	5.06	0.7
6	n-decane	11118	0.068	N/A[b]	10.3	N/A[b]
7	n-undecane	5661	0.059	5.24	5.23	0.1
8	n-dodecane	22622	0.092	20.91	21.1	0.9
9	n-tetradecane	11470	0.078	10.58	10.8	2.0
10	n-pentadecane	5832	0.066	5.38	5.42	0.8
11	n-hexadecane	11609	0.082	10.70	10.9	1.9
12	n-heptadecane	5882	0.068	5.42	5.47	1.0
13	n-octadecane	2610	0.059	2.40	2.42	0.7

[a]Full width at half maximum.
[b]Not applicable as n-decane was used as the internal standard.

The accurate analysis of sample composition requires that the ratio of components in the injected sample remains constant during the injection onto the column and to the detector. Preferential vaporization of components in the injector of the GC can result in analysis inaccuracies. Traditional calibrations can absorb some of these errors, but only when similar mixtures are used for calibration, which is rarely the case. These errors go unnoticed with traditional analysis and calibration techniques. However, with the Polyarc® reactor it is possible to both detect and fix this problem by measuring the FID response to a sample with analytes that have a large range in boiling temperatures and known concentrations.

The relative response of the FID with the Polyarc® reactor per C atom for high inlet pressure (proper inlet conditions; 6.64 psi constant pressure) are contrasted with those for low inlet pressure (poor inlet conditions; 3.33 psi constant pressure) in Figure 3 with a splitless injection. At low inlet pressures, and correspondingly low column flow rates, compounds with the highest volatility have a systematically lower detector response because these compounds are preferentially vaporized and purged from the inlet rather than injected onto the column. At higher pressures, response factors of unity are found for all analytes consistent with the injection of the entire sample onto the column and the complete conversion of all hydrocarbons to methane. We find, not surprisingly, that higher pressures and corresponding flow rates are required to ensure the absolute injection of compounds onto the columns. The specific flow rates required will depend on the inlet and column conditions and the vapor pressures of the molecules injected. Thus, by analyzing a standard mixture with the Polyarc® reactor, it is possible to detect inlet problems and fix them by altering injection parameters until the standard gives equal relative responses per carbon atom in the sample. Leaks in column fittings or the injection system can also be diagnosed with this method (Figure 3). In this case, a leak in the column connection fitting resulted in the preferential loss of compounds with high volatility; however, this may be due to fittings that leak only at the lower temperatures of elution for these molecules (n-pentane, n-hexane, and n-heptane).
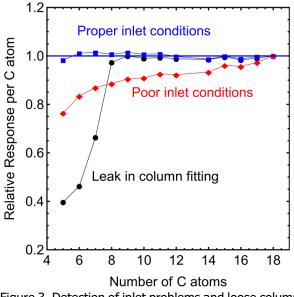

Figure 3. Detection of inlet problems and loose column fittings using the Polyarc® reactor.

Conclusions

The Polyarc® reactor allows for the accurate and facile quantification of hydrocarbons with a wide range of boiling points and carbon content. The accuracy of the Polyarc® system to analyze compounds without calibration is unparalleled in the field of analytical chemistry, making this tool useful for a variety of industries where accuracy is important and calibration is cumbersome, expensive, and/or impossible. Furthermore, we find that the analysis of standard mixtures with the Polyarc® reactor allows for the detection of issues in the GC system including preferential inlet vaporization and leaks.

References

1. Scanlon, J. T., and Willis, D. E., *J. Chrom. Sci.*, 23 (1985) 333-340.

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.