Formaldehyde Analysis in Water using the Polyarc System

Application Note

Increased FID Response

Authors

Bruce Pierson, James Humpula
POET Research
4615 N Lewis Ave
Sioux Falls, South Dakota 57104

Abstract

Formaldehyde has a poor response when run by conventional GC-FID. However, when run on a GC-FID system equipped with a Polyarc® reactor, formaldehyde (HCHO) can be seen down to at least 100 mg/L in water. It was also found that to reduce apparent adsorption of HCHO onto the glass surface of the liner, it was necessary to exchange the default split/splitless liner for an Ultra Inert liner.

Introduction

Formaldehyde is one of many compounds monitored when investigating Hazardous Air Pollutants (HAPs). Unfortunately, gas chromatographic (GC) analysis of formaldehyde requires derivatization, which complicates real time monitoring using GC, or use of GC detectors, which can have limitations in sensitivity.

Previous work has shown that the Polyarc System (Figure 1) can be used to detect formaldehyde in aqueous solution without the need for derivatization.[1] The Polyarc is a catalytic microreactor that is an intermediate step after the column and before detection in the FID, in which all organic compounds are converted to methane through a two-step catalytic reaction:

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

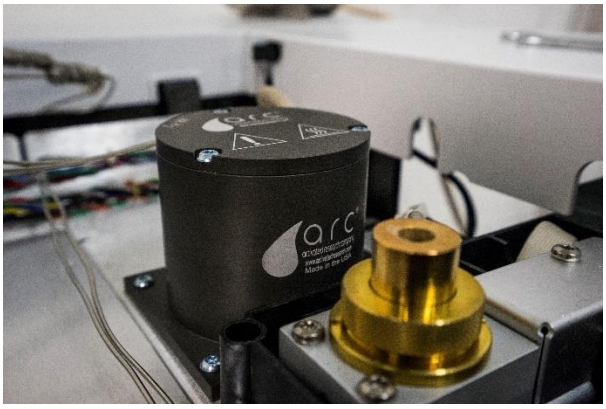

Figure 1. Polyarc System on an Agilent 7890 GC.

The response-per-carbon in the FID is equivalent for all molecules because the FID only ionizes methane.

While the catalytic reaction of the Polyarc allows the formaldehyde to be detected, interactions within the inlet and on the column can still affect the intensity and shape of the peak. These interactions can include adsorption and chemical interactions with the column's stationary phase. This application note describes the optimization of a method for analyzing formaldehyde using a GC system with a Polyarc reactor. During optimization, it was discovered that formaldehyde can adsorb to the inlet liner; an ultra-inert liner was found to resolve this issue.

Experimental

A stock solution of 37% w/w formaldehyde in water/ methanol was diluted to ~10,000 mg/L HCHO with deionized water. This solution was then diluted with deionized water to make ~1,000 and ~100 mg/L HCHO solutions. These 3 solutions were used to evaluate the response and the linearity of the system. As a note, concentrated formaldehyde solution generally contains methanol to inhibit polymerization,

as was the case with the stock formaldehyde used in these experiments.

These solutions were run on an Agilent 7890 GC-FID system equipped with a Polyarc catalytic reactor (PA-SUB-42D). After a set of initial runs with a default split/splitless liner, an Ultra Inert liner (Agilent) was installed for the final run.

GC conditions

Inlet temperature	250 °C
Inlet liner	Agilent Ultra Inert (5190-2293)
Carrier gas	Hydrogen
Column Flow	2 mL/min
Oven	40 °C, hold 7 min
Column	DB Wax 30 m x 320 µm x 0.5 µm
Syringe inj. volume	1 µL

FID conditions

Temperature	350 °C
H_2	1.5 mL/min
Air	400 mL/min
Makeup (N_2)	25 mL/min

Polyarc System conditions

Temperature	450 °C
H_2	40 mL/min
Air	7.5 mL/min

Analysis Procedure

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

However, in this set of experiments, no quantitation was attempted, as the primary objective was to evaluate whether HCHO could be run with adequate peak shape and sensitivity.

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

Results and Discussion

Initially, the standard injections were made on the GC using a previously installed split/splitless liner (Agilent 5183-4647). Due to the poor peak shapes seen for formaldehyde, injection temperatures were evaluated over a range of 150 °C to 350 °C (Figure 2).

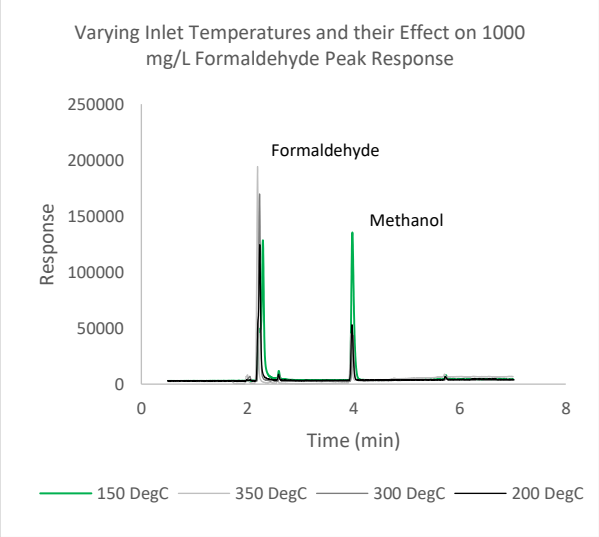

Figure 2. Varying inlet temperatures and their effect on the response of the peak of 1000 mg/L of formaldehyde. At 150 C, formaldehyde exhibited poor peak shape and a change in retention time (outlined in green).

At 150 °C, formaldehyde exhibited poor peak shape and a change in retention time. From 200 °C to 350 °C the peak shape seemed to improve with increasing temperature, but the baseline noise also got worse. It was also suspected that the HCHO may be adsorbing onto the liner based on the response ratio between the HCHO peak and the methanol peak. These issues seemed to have been resolved by switching to an Ultra Inert liner (Agilent 5190-2293) at an injection temperature of 250 °C. The HCHO responses for the 3 solutions were also linear (R^2 = 0.9968) over the 100-fold (~100 to 10,000 mg/L) range evaluated (Figure 3).

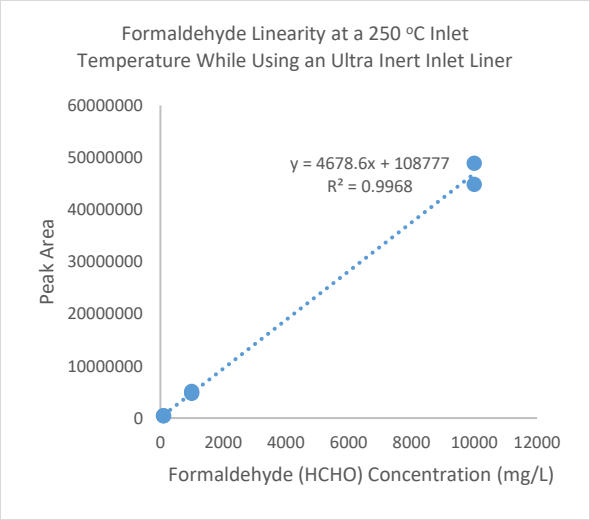

Figure 3. Linearity of formaldehyde (HCHO) from 100 mg/L to 10,000 mg/L with a 250 °C inlet and an ultra inert inlet liner.

A chromatogram of the 100 mg/L solution injected on the system after switching to the Ultra Inert liner is shown in Figure 4.

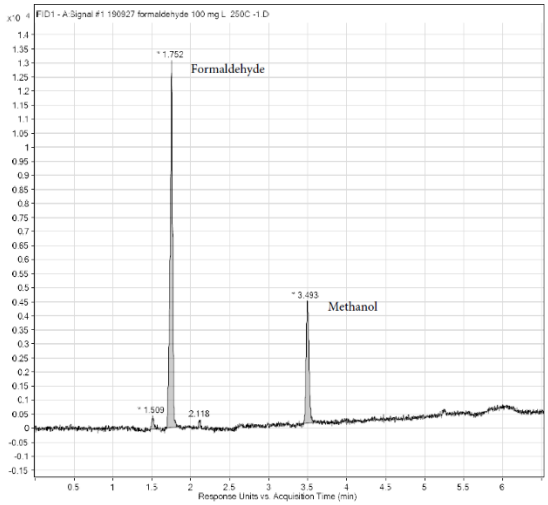

Figure 4. 100 mg/L HCHO injection on Ultra Inert liner.

Conclusions

A set of formaldehyde in water solutions ranging from 100 to 10,000 mg/L were successfully detected on the GC system equipped with the Polyarc reactor. After replacing the inlet liner, the peak responses and peak shape indicate that the system could likely be used for the intended application of determining formaldehyde and other compounds in an aqueous process stream.

References

1. Beach, C., Dauenhauer, P., Spanjers, C. and Jones, A. *Accurate Quantifiaction of CO, CO2, Formamide, Formaldehyde, and Formic Acid using the Polyarc® Reactor*. Application Note. March 2017; PA-APP-1623.

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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