Low Level Formaldehyde Detection with the Polyarc System

Application Note

Sub 1 mg/kg (ppm)

Author

Jonathan McIntyre
Activated Research Company
Eden Prairie, MN

Abstract

Method development for the analysis of formaldehyde has been historically tricky to derive in a simplistic and easily available way for all laboratories to perform. The detector of choice when using gas chromatography (GC) is the flame ionization detector (FID) because of its large linear dynamic range and robustness. Formaldehyde, however, has a low response in the FID due to its lack of C-H bonds. Incorporation of the Polyarc reactor into the GC/FID system allowed for sub-ppm detection of formaldehyde by converting it to methane prior to FID detection.

Introduction

Methanal, commonly known as formaldehyde, is one of the most common Volatile Organic Compounds (VOCs) that is present in numerous products including textiles, plywood, a multitude of resins, preservatives, tobacco products, and even in pharmaceutical drugs as an impurity. The Department of Health and Human Services (HHS) has recently listed high exposure to formaldehyde as carcinogenic.

Alternative methods for formaldehyde detection require either expensive liquid chromatography (LC) test time, or complicated GC configurations using either a photoionization detector to quantitate only formaldehyde, or multiple detectors to detect formaldehyde along with other common organics[1].

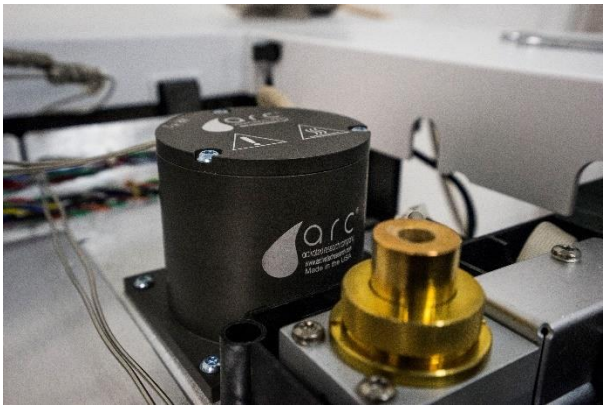


Figure 1. Polyarc System on an Agilent 7890 GC.

In this application note, a Polyarc is used with a GC/FID to and accurately detect formaldehyde down to the single mg/kg (ppm) level. Previously, an FID was not able to accurately detect formaldehyde due to the small amount of C-H bonds available for ionization in the flame. This is a known issue with heteroatom-containing organic compounds, which has historically been resolved with lengthy calibration and verification steps to estimate the FID response per unit of concentration for each compound. The Polyarc converts organic compounds to methane after chromatographic separation via a two-stage combustion-reduction reaction sequence. The result of having only C-H bonds and complete conversion to methane is universal carbon detection that provides a tenfold increase in the formaldehyde signal. Now, multiple calibrations or additional detectors are no longer necessary to quantitate exceptionally elusive compounds such as formaldehyde.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet (Agilent G3454-64000), capillary-optimized FID, 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 the Polyarc, which was then connect to the capillary-optimized FID.

Samples were prepared for GC analysis by serial dilutions of 37% wt. formaldehyde in methanol (RICCA, 37%) diluted in HPLC water (MSI, >99%) to create a solution of 1.18 mg/kg of formaldehyde in water with a methanol stabilizer. Additional samples of 100, 1,000, and 10,000 mg/kg were also made.

GC conditions

Front inlet	Split/splitless
Inlet temperature	250 °C
Inlet linter	Agilent 5190-2295
Carrier gas	He; 35.3 cm/sec constant flow
Septum purge flow	0.5 sccm
Oven	40 °C (hold 5 min) to 100 °C at 50 °C/min (hold 2 min)
Column	DB-WAX (30 m x 0.25 mm x 0.25 µm film)
Syringe	10 µL
Injection volume	1 µL

FID conditions

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

Polyarc® System conditions

Temperature Setpoint	293 °C
H_2 Flow Rate	35 sccm
Air Flow Rate	2.5 sccm

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 = Wt. % 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

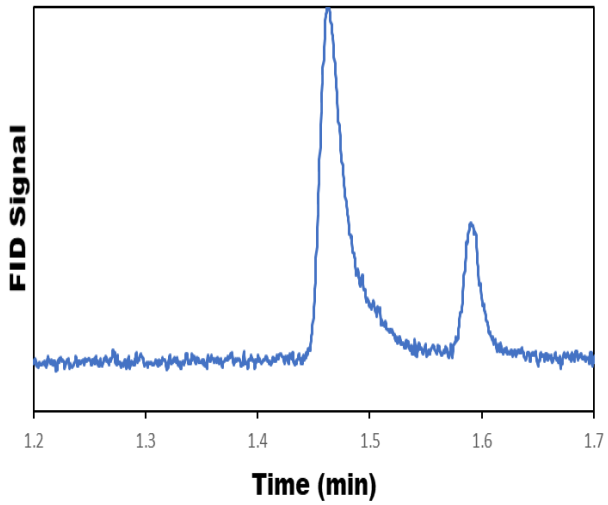
*See "Quantification with the Polyarc.pdf" at https://www.activatedresearch.com/documents/ for more information.

Results and Discussion

A GC method was optimized for the analysis of low levels of formaldehyde. Utilizing an injection volume of one uL and an inert DB-WAX phase column proved to have the correct inertness to deliver the challenging analyte to the Polyarc with proper chromatographic separation. Multiple injections from 1.18 mg/kg formaldehyde up to 10,000 mg/kg were performed and the averaged results are tabulated below, with the chromatograms shown in Figure 2.

Formaldehyde PPM (mg/kg)	Average Area	RSD %
1.2	25690	4%
91	1971389	10%
987	20895356	8%
10391	194170171	2%

Table 1. List of average peak areas per injection concentration.



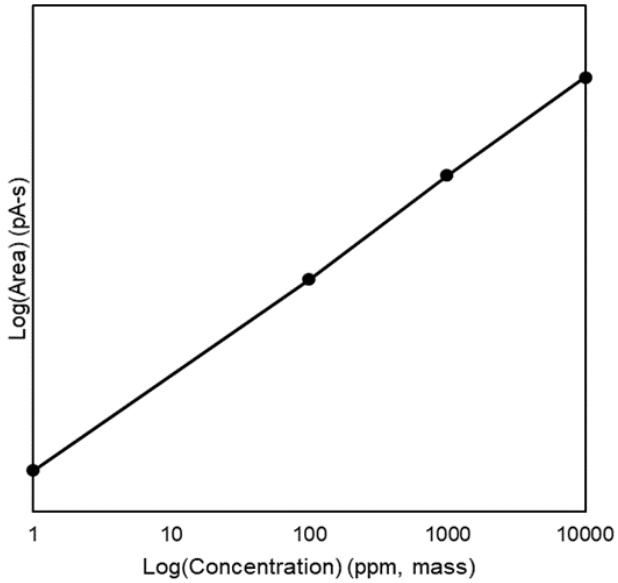


Figure 2. Polyarc/FID chromatogram for the analysis of 1.18 mg/kg formaldehyde in HPLC water with a methanol stabilizer using the Polyarc system. (Methanol retention time 1.48; formaldehyde retention time 1.59 minutes)

Figure 3. Linearity of formaldehyde via Polyarc system. Linear range of over four orders of magnitude.

The signal to noise (S/N) ratio, defined as three times the peak height divided by the noise, for the 1.18 mg/kg formaldehyde was determined via Agilent's Chemstation software to be S/N= 6.7. When defining the minimum detection limit at S/N= 3, the theoretical detection limit is approximately 0.53 mg/kg of formaldehyde. Figure 3 shows the integrated detector response of the Polyarc/FID as a function of the amount of carbon injected in the form of formaldehyde. The figure also shows linearity over four orders of magnitude.

Conclusions

The Polyarc system is capable of detecting sub-ppm levels of formaldehyde by converting to methane before detection via FID. The lower linear detection range of formaldehyde was experimentally verified from 1000 mg/kg to 1 mg/kg. The theoretical minimum detection limit was extrapolated from experimental data as 0.53 mg/kg.

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.

Printed in the USA
March 19, 2020
PA-APP-2029

References

[1]Luong, J., Sieben, L., Fairhurst, M. and De Zeeuw, J. (1996), Determination of low levels of formaldehyde and acetaldehyde by gas chromatography/flame ionization detection with a nickel catalyst. J. High Resol. Chromatogr., 19: 591-594. doi:10.1002/jhrc.1240191013