Modified FID for Determination of Formaldehyde in Consumer Products

Application Note

Sensitivity Comparison for GC/FID

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Abstract

Formaldehyde is a common, naturally occurring chemical found in foods and added to treated wood products commonly used in the construction of homes across the world. Formaldehyde has been known to be a carcinogen and health hazard to humans. The need and use of a simple and effective method for detection would be beneficial in the deterrent of high levels of formaldehyde exposure. The sampling and determination of formaldehyde levels in products can be difficult to analyze and measure with a typical Gas Chromatograph (GC) using a Flame Ionization Detector (FID). With the use of the Polyarc reactor in line with the FID, the determination of formaldehyde and formaldehyde byproducts can be detected and measured by FID. Using the Polyarc reactor technology, we will be able to test and measure formaldehyde levels in certain foods that are naturally occurring versus treated wood that is found in homes across the world by headspace.

Introduction

Formaldehyde is a hazardous compound commonly found in treated wood, caulk, hair products, and a variety of other substances (soil near burial grounds, glue, plywood, fiberboard insulation, car exhaust, etc.). OSHA established an exposure limit of 0.75 ppm on average over an 8-hour work day. Measuring compounds like formaldehyde and formic acid by gas chromatography is difficult due to the low response in the flame ionization detector. Historically, formaldehyde determination required the addition of a mass spectrometer (MS) or photo ionization detector (PID). There are also HPLC methods, but those require the use of post-column derivatization to detect the formaldehyde.

In this study, we investigate the use of the Polyarc® two-stage reactor in-line with a flame ionization detector to measure the presence of formic acid and formaldehyde. The first stage of the reactor oxidizes all the carbon-containing compounds into carbon dioxide. The second stage employs a proprietary catalyst in a hydrogen-rich environment to convert the carbon dioxide into methane, which is then easily detected by the FID. We investigate the use of this detection scheme to measure low levels of formaldehyde and formic acid in a variety of consumer products.

Experimental

An Agilent 7890A GC equipped with a capillary-optimized FID and an ARC Polyarc reactor (PA-RRC-A02) were used for the analysis. Helium (99.999%, Praxair) was used as the carrier and FID makeup gas. Air (ultra-zero grade, Praxair) and H_2 (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 sent directly to the inlet of the Polyarc reactor via a zero-dead volume union (PA-CPM-R46). The reactor effluent was connected directly to the FID. Figure 1 illustrates the configuration.

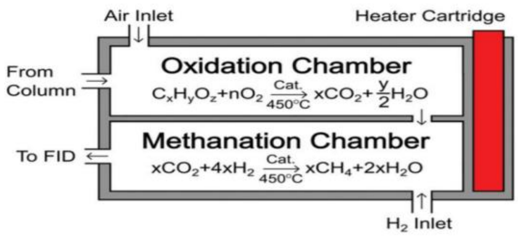

Figure 1. GC-Polyarc/FID configuration

Samples of consumer products were tested by headspace and liquid injections.

GC conditions

Front inlet	Split 10:1 (Headspace Injections) Split 50:1 (Liquid Injections)
Inlet temperature	250°C
Oven	60 °C (Isothermal)
Column	HP-5 (30 m × 0.25 mm × 0.25 µm)
Syringe	10 µL
Injection volume	0.5 mL (Headspace Injections) 1 µL (Liquid Injections)

FID conditions

Temperature	250 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	20 sccm (He)
Sampling rate	100 Hz

Polyarc reactor conditions

Setpoint	293 °C
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

Calibration curves of formaldehyde and formic acid were compared by liquid injections comparing the FID to the Polyarc. Figure 2 and 3 illustrates the calibration curves.

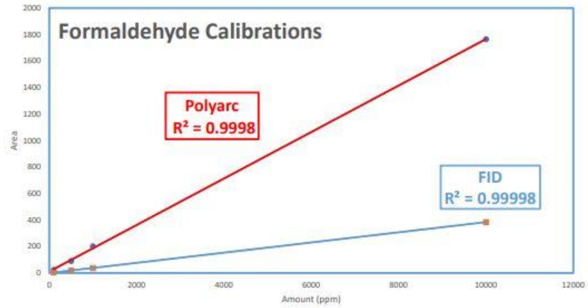

Figure 2. FID and Polyarc Formaldehyde Calibrations

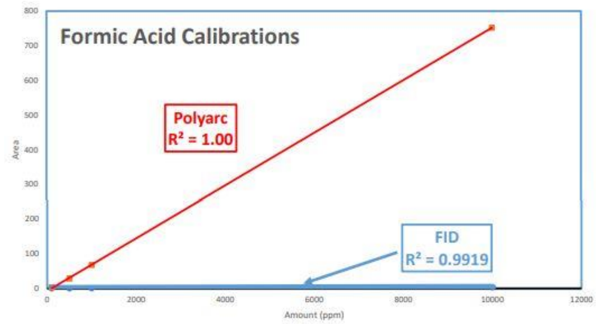

Figure 3. FID and Polyarc Formic Acid Calibrations

In figure 4 and 5, we demonstrate the sensitivity of the FID vs Polyarc-FID coupled together. We examined the sensitivity of formaldehyde using a 10,000 ppm standard. We found the Polyarc-FID is 1.5 times more sensitive for formaldehyde. In figure 4, the signal to noise ratio is shown to prove how more sensitive the Polyarc-FID is than FID.

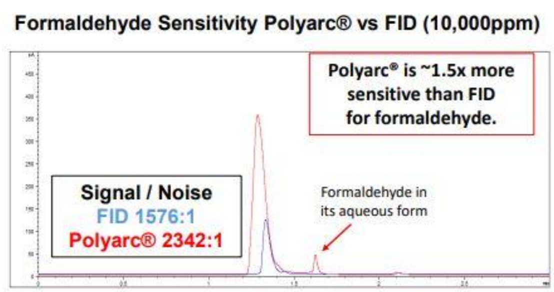

Figure 4. Formaldehyde sensitivity Polyarc vs FID

We examined the sensitivity of formic acid using a 10,000 ppm standard. We found the Polyarc-FID is 270 times more sensitive for formic acid. In figure 5, the signal to noise ratio is shown to prove how more sensitive the Polyarc-FID is than FID.

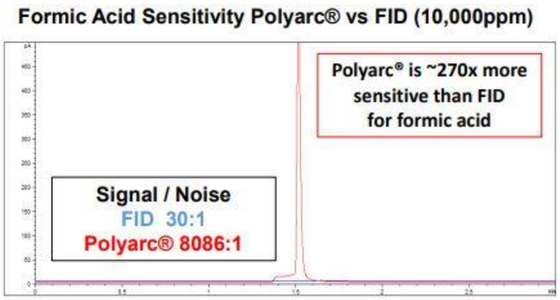

Figure 5. Formic Acid sensitivity Polyarc vs FID

With the sensitivity comparison of the FID vs Polyarc-FID, a comparison of consumer products was analyzed to identify and quantify the amount of formaldehyde and formic acid contained in the products. Known consumer products such as silicon caulk and hair relaxer solutions were analyzed by the Polyarc-FID. Both of these products were tested by headspace analysis. Figures 6 and 7 illustrate the use of the Polyarc-FID for analysis.

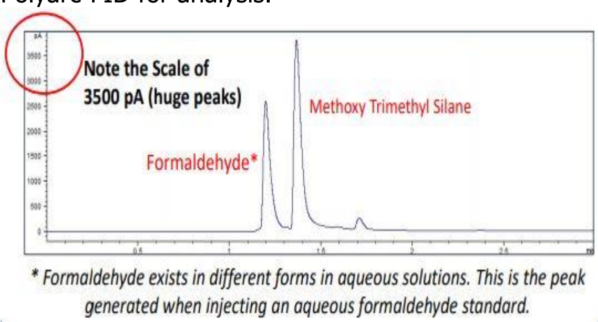

Figure 6. Silicon Caulk analysis by Polyarc-FID.

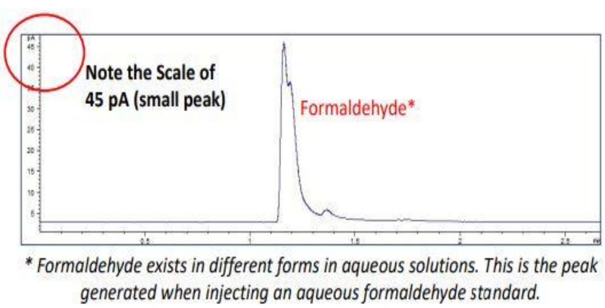

Figure 7. Hair Relaxer analysis by Polyarc-FID

Conclusions

The Polyarc was determined to be an effective tool for analyzing formaldehyde and formic acid. Compared to an FID, the Polyarc had a 1.5-fold increase in sensitivity for formaldehyde and a 270-fold increase in sensitivity for formic acid. Historically, formaldehyde has been difficult to analyze by GC since formaldehyde lacks enough C-H bonds to produce a significant signal from an FID. To mitigate that problem, the Polyarc first oxidizes all of the incoming hydrocarbons into carbon dioxide and water by adding oxygen (air), heat, and a catalyst. The subsequent CO_2 is then hydrogenated to methane with hydrogen, heat, and a propriety catalyst. The net result is that every carbon is converted to methane, thereby maximizing each compound's response in the FID. This is especially important for carbon-containing compounds with little to no C-H bonds and should work well for compounds such as CO, CO_2, CS_2, formaldehyde, formic acid, methanol, etc. It should also be noted that installation of the Polyarc system was very straightforward, and the operation is simple and robust.

Acknowledgements

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Contact Us

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

Please visit ARC's website for details and additional technical literature.

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