Accurate Single Injection Quantification of Organochlorides Using the Polyarc® System

Application Note

Halogens

Authors

Tommy Saunders
Activated Research Company
7561 Corporate Way
Eden Prairie, MN 55344
tommy.saunders@activatedresearch.com

Abstract

The analysis of organochlorides in by GC/FID typically requires calibrations to determine the responses of each individual analyte before quantitative information can be obtained. In this application note, the analysis of samples containing organochlorides with the Polyarc system is demonstrated. Because the Polyarc converts all organic molecules to methane before detection in the FID, calibration is not required. Instead, the sum of the peak areas of all detected compounds are used to accurately determine the weight percent of every component in the mixture. The concentrations from samples 1, 2, and 3 were calculated using the Polyarc data and found to fall within the ranges of expected concentrations.

Introduction

Organochlorides are commonly used as industrial solvents in chemical processes, as reagents and precursors for other solvents, and are common impurities in chemical processes. Vinyl chloride is the most common organochlorides, with an annual production of about 13 billion kilograms. Vinyl chloride is chiefly used to produce polyvinyl chloride (PVC). Other applications of organochlorides include pesticides, insulators, and refrigerants.

This complexity of organochlorides makes obtaining quantitative data both time-consuming and challenging, as the FID response must first be calibrated for each individual compound. This is because the response of the FID for each VOC is variable, based on the number of heteroatoms (Cl, O, etc.) and its chemical structure. Additionally, there are safety concerns with storing standards, as many of the compounds, such as bis(2-chloroethyl) ether, are highly toxic and carcinogenic.

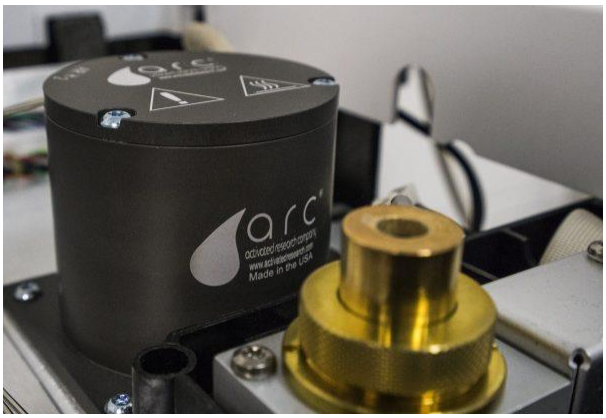

Figure 1. Polyarc System installed in the back detector position next to an FID on an Agilent 7890 GC.

In this application note, it is shown how the Polyarc System (Figure 1) can be used to save time by reducing calibrations for the GC/FID analysis of organochlorides. 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:

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

The response-per-carbon atom in the FID becomes equivalent for all carbon-containing molecules because the FID only sees methane. Thus, a single internal (or external) standard can be used to quantify all other components in the mixture, without the need to calibrate for each individual compound. The relative

amounts of detectable compounds can be determined without a standard simply from their relative areas.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet (Agilent G3454-64000), capillary-optimized FID, mass spectrometer (Agilent 5973), and Polyarc® reactor (ARC PA-RRC-A02) were 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 from a VICI DBS hydrogen generator (VICI DBS FT-NM 300 PLUS) 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 an Agilent 3-way CFT splitter (G3183-60500). The MS was connected to the splitter via a retention gap column (Agilent, 160-2635-5, 0.61 m, 0.1 mm ID). The inlet capillary to the Polyarc® was connected directly to the splitter. The splitter was controlled by an EPC (with restrictor frit removed) set to 4 psig.

GC conditions

Front inlet	Split/splitless
Inlet temperature	250 °C
Inlet linter	Agilent 18740-80190
Carrier gas	He; 40 cm/sec constant flow
Septum purge flow	3 sccm
Oven	40 °C (hold 4 min) to 250 °C at 15 °C/min (hold 25 min)
Column	ZB-5 (30 m × 0.25 mm × 1 µm film)
Syringe	10 µL
Injection volume	0.5 µL

FID conditions

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

Polyarc® System conditions

Setpoint	293 (450 °C actual temp.)
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

Three samples were analyzed with the Polyarc System using the experimental information shown above. They were directly injected into the system (see chromatograms in Figures 2-4). Peaks were identified using simultaneous data collection from a mass spectrometer (MS) (see Tables 1-3 for identification). The tables only include identified peaks. All FID-detectable peaks were quantified using the procedure outlined in the Analysis Procedure section but are not reported in this application note for brevity.

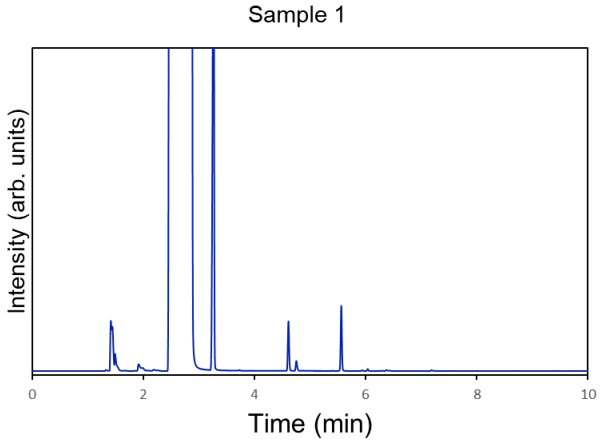

Figure 2. Chromatogram of a sample 1 using the Polyarc System.

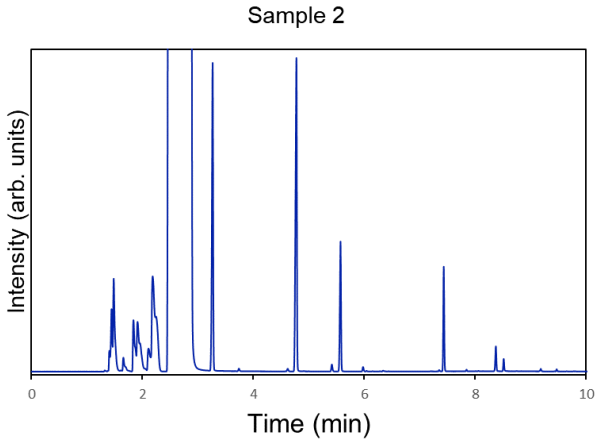

Figure 3. Chromatogram of a sample 2 using the Polyarc System.

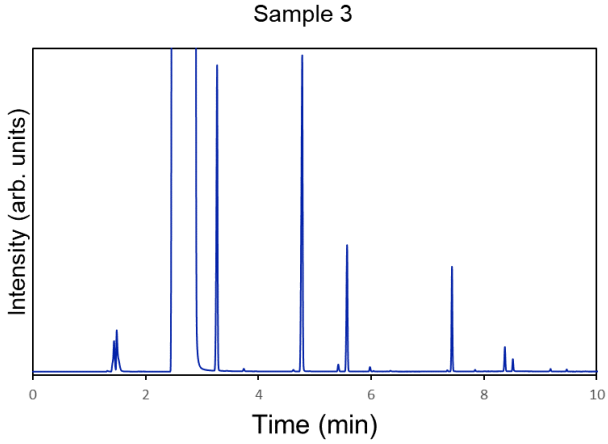

Figure 4. Chromatogram of a sample 3 using the Polyarc System.

Table 1. Quantitative analysis of sample 1 using the Polyarc system

Analyte	Mw (g/mol)	#C	Ret time (min)	Area	Conc. (ppm)	Expected Conc. (ppm)
Ethane, 1,2-dichloro-	98.96	2	2.85	1.79E+10	991128.4	
Trichloroethylene	129.91	2	3.262	84359550	6129.998	5500-7000
1,3-Butadiene, 1,4-dichloro-	121.97	4	4.611	6022185	205.4285	250-500
Ethane, 1,1,2-trichloro-	131.93	2	4.753	1314850	97.02939	0-150
Tetrachloroethylene	163.88	2	5.562	7634049	699.7846	500-750
1,3-Dichloro-2-butene	123.99	4	6.038	231655	8.033076	

Table 2. Quantitative analysis of sample 2 using the Polyarc system

Analyte	Mw (g/mol)	#C	Ret time (min)	Area	Conc. (ppm)	Expected Conc. (ppm)
Ethane, 1,2-dichloro-	98.96	2	2.867	1.88E+10	985880	
Trichloroethylene	129.91	2	3.266	35523098	2443.5	1000-4000
1,3-Butadiene, 1,4-dichloro-	121.97	4	4.619	342989	11.075	0-150
Ethane, 1,1,2-trichloro-	131.93	2	4.774	41339967	2887.8	1000-4000
Butane, 1,2-dichloro-	126	4	5.416	788733	26.310	0-150
Tetrachloroethylene	163.88	2	5.571	14295843	1240.5	1000-1300
Butane, 1,4-dichloro-	126	4	5.978	465088	15.514	0-150
Ethane, 1,1,2,2-tetrachloro-	165.89	2	7.432	9571221	840.72	750-1000
Ethane, pentachloro-	199.85	2	8.37	2488448	263.32	100-350
Bis(2-chloroethyl) ether	142	4	8.512	1134214	42.640	0-150
1-Butene, 1,4-dichloro-	123.99	4	9.181	277721	9.1166	
Ethane, hexachloro-	233.81	2	9.646	22149	2.7421	0-150

Table 3. Quantitative analysis of sample 3 using the Polyarc System

Analyte	Mw (g/mol)	#C	Ret time (min)	Area	Conc. (ppm)	Expected Conc. (ppm)
Ethane, 1,2-dichloro-	98.96	2	2.878	1.88E+10	991480	
Trichloroethylene	129.91	2	3.268	35236695	2440.5	1000-3000
*1,3-Butadiene, 1,4-dichloro-	121.97	4	4.621	212121	6.8970	250-500
Ethane, 1,1,2-trichloro-	131.93	2	4.778	41001707	2884.0	2000-5000
*Butane, 1,2-dichloro-	126	4	5.417	769616	25.850	0-150
Tetrachloroethylene	163.88	2	5.573	14175261	1238.5	1000-1300
*Butane, 1,3-dichloro-	126	4	5.979	465244	15.626	0-150
Ethane, 1,1,2,2-tetrachloro-	165.89	2	7.433	9386266	830.16	750-1000
Ethane, pentachloro-	199.85	2	8.371	2421453	258.01	100-300
Bis(2-chloroethyl) ether	142	4	8.512	1097558	41.546	0-150
*2-Butene, 1,4-dichloro-, (E)-	123.99	4	9.18	260667	8.6158	

Analysis Procedure

The area-per-mol of carbon is equivalent for all carbon-containing analytes because every molecule is completely converted to methane. This property allows for the determination of the concentration of any analyte using no internal or external standard. Tetrachloroethylene was chosen arbitrarily as the reference standard for calculating the RMRF terms, though any compound can be used. For unknowns, an average of the known RMRF values were applied to the calculations. The concentrations of all analytes were then calculated using the following equations:

$$C_A = \frac{(Area_A \cdot RMRF_A)}{\sum_{i=1}^{n}(Area_i \cdot RMRF_i)} * 100 \quad (1)^*$$

$$RMRF_A = \left(\frac{Mw_A}{Mw_S}\right)\left(\frac{\#C_S}{\#C_A}\right) \quad (2)^*$$

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.

Conclusions

The Polyarc System is a useful tool for the analysis of organochlorides because of the complexity associated with these samples and difficulties associated with calibration standards. Traditional methods for quantification of analytes in a complex mixture includes time-consuming calibrations of each individual components. With the Polyarc System, this process is greatly simplified because every molecule gives a uniform (equimolar) response in the FID. In addition to saving time and money, the Polyarc allows for safer laboratory environments because of the decreased need to store hazardous chemical standards for calibration. Further work will continue to explore the wide range of organochlorides for which this method is applicable.

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

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Please visit our website for details and additional technical literature.

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