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Environmental

Environmental analysis of polychlorinated biphenyls (PCBs) at reduced running costs using hydrogen as carrier gas

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Keywords

Polychlorinated biphenyls, PCBs, HeSaver-H_2Safer, GC-MS/MS, H_2 carrier gas, U.S. EPA 1668

Goal

The aim of this application note is to compare the performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer coupled to the Thermo Scientific™ TRACE™ 1610 GC with hydrogen versus helium as the carrier gas for the determination of polychlorinated biphenyls. For guidance on the analytical performance of the proposed method, acceptance criteria as per U.S. EPA Method 1668 were considered.

Introduction

Polychlorinated biphenyls (PCBs) are a group of industrial organic chemicals consisting of carbon, hydrogen, and chlorine atoms. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, hydraulic equipment, plasticizers, plastics, rubber products, and dyes. The production of these compounds has been banned in the United States since 1977[1] because of their persistence in the environment and their tendency to enter the food chain and bioaccumulate in living organisms due to their lipophilicity.

There are currently 209 known PCBs congeners that can be divided into two groups according to their structural and toxicological characteristics:

- Non-dioxin-like PCBs (non-DL-PCBs), which represent the majority of the PCB congeners, are characterized by a lower degree of toxicity.
- Dioxin-like PCBs (DL-PCBs) include the 12 most toxic congeners (non-ortho PCBs 77, 81, 126, 169 and mono-ortho PCBs 105, 114, 118, 123, 156, 157, 167, 189), which have structures and toxicities similar to dioxins.

DL-PCBs are classified as persistent organic pollutants (POPs), and they have been regulated under the Stockholm Convention for POPs since 2001.[2] Following the Clean Water Act (CWA) in 1972, the United States Environmental Protection Agency (U.S. EPA) developed an analytical method, U.S. EPA Method 1668 and following revisions[3] that can be applied for the determination of PCBs in wastewater, surface waters, soil, sediments, biosolids, and tissue matrices using gas chromatography coupled to high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).[3] However, recent advances in gas chromatography-triple quadrupole mass spectrometry allow for high sensitivity and selectivity, leading to the consideration of GC-MS/MS as a reliable tool for PCBs analysis.

This application note reproduces the experiments described in a previously published application note,[4] where polychlorinated biphenyls were analyzed using helium carrier gas. Here, helium was replaced by hydrogen. Additionally, the Thermo Scientific™ HeSaver-H_2Safer™ carrier gas saving technology was applied. HeSaver-H_2Safer technology offers a unique solution for laboratories to minimize carrier gas consumption during both standby and operational modes. When helium is used as carrier gas, the consumption can be drastically reduced without any changes to the analytical method or deterioration of performance. However, the Split-Splitless (SSL) injector modified to work in the HeSaver-H_2Safer mode can be used also in conjunction with hydrogen as a carrier gas, where the limited and fixed carrier gas flow allows for safe usage without the need to install additional sensors. At the same time, the hydrogen gas consumption is equally reduced and will lead to further cost savings, allowing laboratories to run their instrumentation longer on a single gas tank or using gas generators.

Experimental

The analytical method used for this study is described in a previous application note,[4] however, minor modifications to the method were made and are summarized in Table 1. The use of hydrogen as carrier gas often leads to shorter retention times, if the analytical conditions, such as column, carrier gas flow rate, and oven program, remain unchanged. The retention times obtained using hydrogen as carrier gas can be found in Appendix 1.

Table 1. GC-MS parameters modified in comparison to AN000561

SSL parameters	
Inlet module and mode	SSL, HeSaver-H_2Safer, Splitless
Split flow (mL/min)	50 (Nitrogen)
Carrier gas, flow (mL/min)	H_2; 1.2
Pressurizing gas	Nitrogen
Oven	
Column	Thermo Scientific™ TRACE™ TR-PCB 8 MS; 50 m, 0.25 mm, 0.25 µm (P/N 26AJ148P)
TSQ 9610 mass spectrometer parameters	
Transfer line temperature (°C)	330
Ion source type and temperature (°C)	AEI, 350
Emission current (µA)	10

Results and discussion

Separation

Maintaining chromatographic resolution is critical when analyzing PCBs. In the analyzed set of PCBs, the pentachlorobiphenyls, commonly referred to as PCB-123 and PCB-118, were monitored. These two compounds have similar retention times and identical transitions. Therefore, a good chromatographic method is necessary to avoid interference. With the TRACE TR-PCB 8 MS column, baseline separation of these two congeners was achieved (Figure 1) with no modification or amends to the chromatographic method.

Instrumental detection limits

One of the main concerns when changing the carrier gas from helium to hydrogen is a potential sensitivity drop. The instrumental detection limits (IDLs) were determined for the individual congeners by diluting the CS0.2 standard four times, so that a final concentration of 0.05 ng/mL was achieved. This solution was repeatedly injected (n=10). IDLs were calculated considering the one-tailed Student's *t*-test values for the corresponding n-1 degrees of freedom at 99% confidence, the injected on-column (OC) concentration, and the absolute peak area %RSD (<15%) for each analyte. Figure 2 shows that the IDLs obtained with hydrogen were nearly identical to those with helium. All compounds had an IDL under 20 fg except PCB-209.

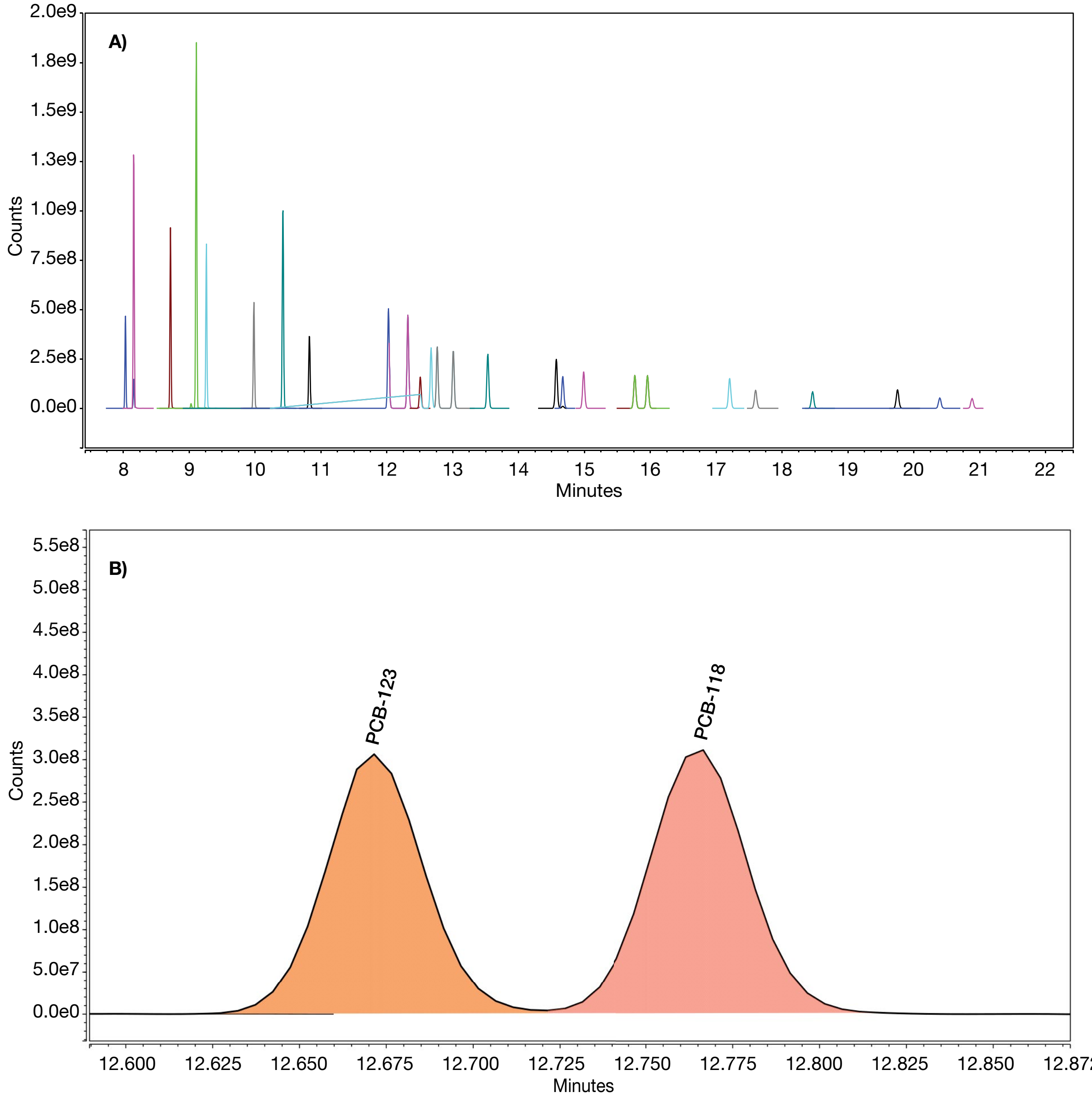

Figure 1. Quantifying peaks of all analyzed PCBs (A) and separation of the critical pair of PCB congeners 123/118 (B)

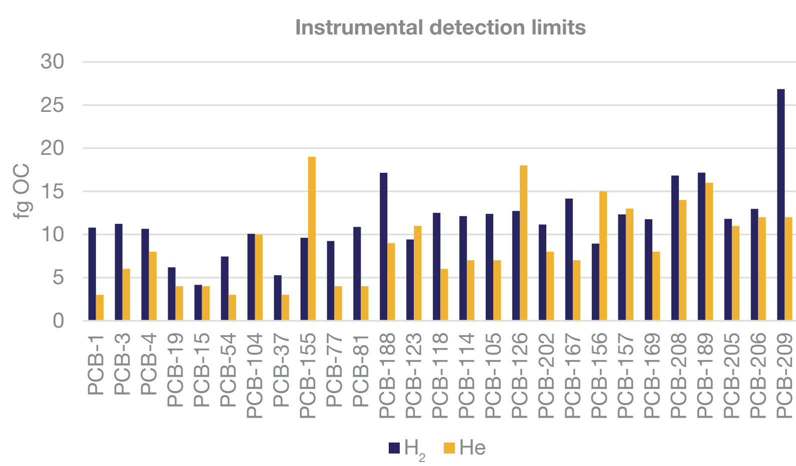

Figure 2. Instrumental detection limits expressed as the mass of PCB injected on column

Ion ratio

The correct ion ratio is very important for the unambiguous identification of the analytes. However, at low concentration levels it can deviate from the expected value and subsequently generate a false negative result. The reproducibility of the ion ratio was thus investigated across a wide concentration range. Figure 3A presents the ion ratio values of PCB-114 as an example, whereas Figure 3B depicts a deviation of the average ratio of 10 injections at 0.05 ppb. The reference values for the data in Figure 3B were the average ion ratios from the calibration curve.

Linearity

All investigated PCBs showed excellent linearity. All analytes achieved a coefficient of determination equal to or higher than 0.9998 (Figure 4A), and the relative standard deviation of the average response factor did not exceed 3% (Figure 4B).

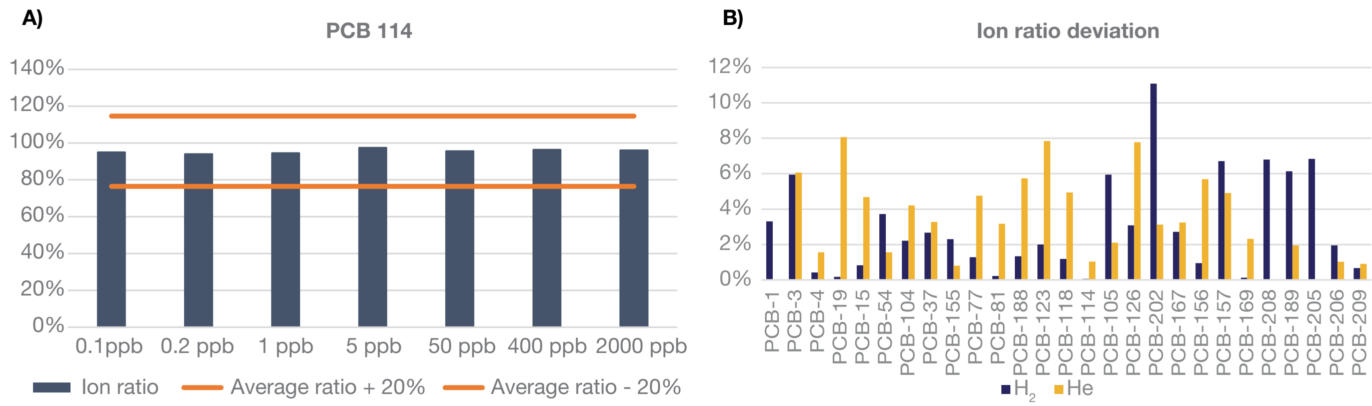

Figure 3. Ion ratio of PCB 114 at various concentration levels (A) and ion ratio deviation of all analytes at 0.05 ppb (B)

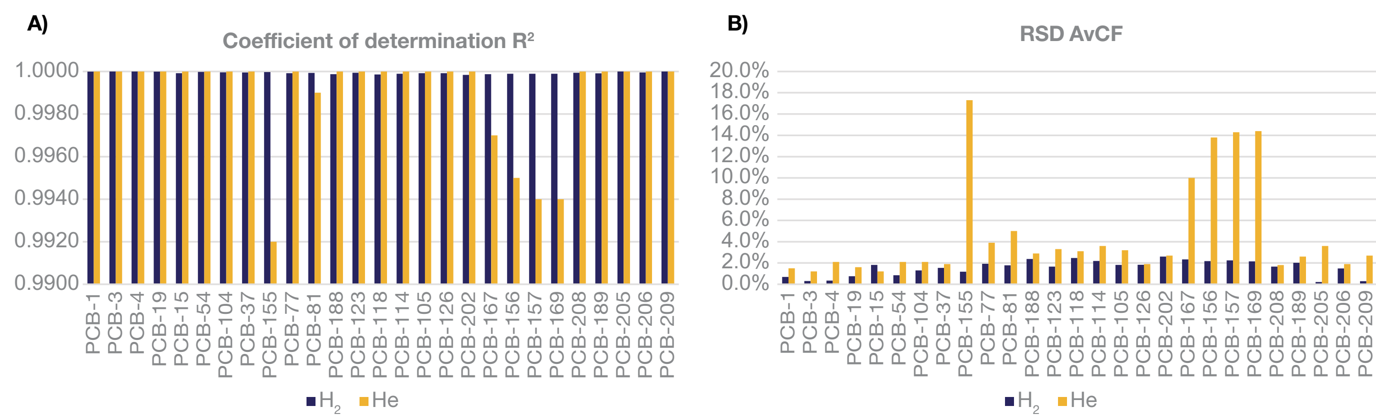

Figure 4. Evaluation of the linearity in the range 0.1–2000 ppb: coefficient of determination (A) and relative standard deviation of the average response factor (B)

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Summary

The HeSaver-H_2Safer inlet allows laboratories full flexibility to select the carrier gas of choice between helium and hydrogen, while achieving a significant reduction of the consumption. With a simple upgrade to the standard Thermo Scientific™ iConnect SSL injector, the HeSaver-H_2Safer inlet allows for the use of an inert and inexpensive gas for inlet pressurization, whereas the main carrier gas flow is limited to the column flow only.

- The use of hydrogen as carrier gas has been demonstrated as an alternative to helium for the analysis of PCBs, reducing the overall cost of running the laboratory.
- The use of the HeSaver-H_2Safer inlet reduces the amount of hydrogen going into the gas chromatography system such that safe operation is assured anytime, and no hydrogen sensor is needed inside the GC oven.
- Hydrogen did not affect the linearity range; all compounds showed a linear response from 0.1 to 2000 ppb, with avarage R^2 >0.999.
- The TSQ 9610 triple quadrupole mass spectrometer provided excellent IDLs with hydrogen carrier gas, comparable to those obtained with helium.
- The variation of ion ratios was less than 12% for all PCBs at 0.05 ppb.

References

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Appendix 1. List of PCBs retention times

Compound	Retention time [min]	Compound	Retention time [min]	Compound	Retention time [min]
PCB-1	7.61	PCB-77	12.04	PCB-167	15.02
PCB-3	8.04	PCB-81	12.34	PCB-156	15.79
PCB-4	8.16	PCB-188	12.53	PCB-157	15.99
PCB-19	8.72	PCB-123	12.69	PCB-169	17.24
PCB-15	9.11	PCB-118	12.79	PCB-208	17.64
PCB-54	9.27	PCB-114	13.03	PCB-189	18.50
PCB-104	9.99	PCB-105	13.56	PCB-205	19.79
PCB-37	10.43	PCB-126	14.60	PCB-206	20.44
PCB-155	10.84	PCB-202	14.70	PCB-209	20.93

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