Environmental

Sustainable, safe, and reliable analysis of polyaromatic hydrocarbons by gas chromatography-mass spectrometry using hydrogen carrier gas with HeSaver-H_2Safer technology

Authors

Nicholas Warner[1], Adam Ladak[2], Daniela Cavagnino[3], Daniel Kutscher[1]

[1]Thermo Fisher Scientific, Bremen, DE

[2]Thermo Fisher Scientific, Hemel Hempstead, UK

[3]Thermo Fisher Scientific, Milan, IT

Keywords

PAH, carrier gas, hydrogen, polyaromatic hydrocarbon, EPA Method 8270E, HeSaver-H_2Safer technology, GC-MS, ISQ 7610 GC-MS

Introduction

Polyaromatic hydrocarbons (PAHs) are ubiquitous in the environment, originating from incomplete combustion of natural organic carbon (i.e., wood, coal, fossil fuels) or anthropogenic activities (i.e., vehicle emissions, waste incineration, industrial processes). Due to their inherent toxic properties and continued emission/exposure into the environment, the analysis of PAHs is often performed by analytical testing laboratories to adhere to environmental health requirements.

Laboratories are under high demand to continuously deliver data for regulatory purposes. However, the current crisis surrounding the helium gas supply is making laboratory operations unsustainable from both economic and throughput standpoints. Helium is the ideal carrier gas for gas chromatography-mass spectrometry (GC-MS) due to its inert nature and fast-pumping efficiency, making it the preferred option to maintain optimal performance of GC-MS instrumentation. Therefore, conservation of helium is ideal to help maintain supplies of this non-renewable gas. However, conservation of helium is of little help when laboratories cannot obtain supplies when needed, thus, alternative carrier gases must be used to keep laboratories operational. The Thermo Scientific™ HeSaver-H_2Safer™ carrier gas saving technology[1] offers a unique solution for laboratories to minimize carrier gas consumption during both standby and operation 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 for additional sensors to be installed. 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 optimize usage of gas generators.

In this note, the performance of the Thermo Scientific™ TRACE™ 1610 gas chromatograph equipped with the new HeSaver-H_2Safer SSL injector using hydrogen as a carrier gas is demonstrated for the analysis of PAHs with the Thermo Scientific™ ISQ™ 7610 GC-MS, according to U.S. EPA Method 8270E.[2] Analysis speed, chromatographic efficiency, and instrument detection and quantification limits were evaluated for the repetitive analysis of a raw (i.e., no sample clean-up) soil extract using previously established instrument parameters.[3] A 9-point calibration curve was constructed for all analytes with a concentration range spanning over three orders of magnitude for linear dynamic range assessment.

Results and discussion

One of the key benefits of using hydrogen as carrier gas is its optimal chromatographic efficiency obtained at higher flow rates compared to helium. Although this can provide faster analysis times without sacrificing separation efficiency between critical analytes, higher hydrogen flow can be detrimental to MS performance. Figure 1 shows the chromatographic performance towards PAH analysis for both hydrogen and helium using the same carrier flow and oven program conditions. Improvement of analysis speed by one minute (equivalent to a reduction in sample

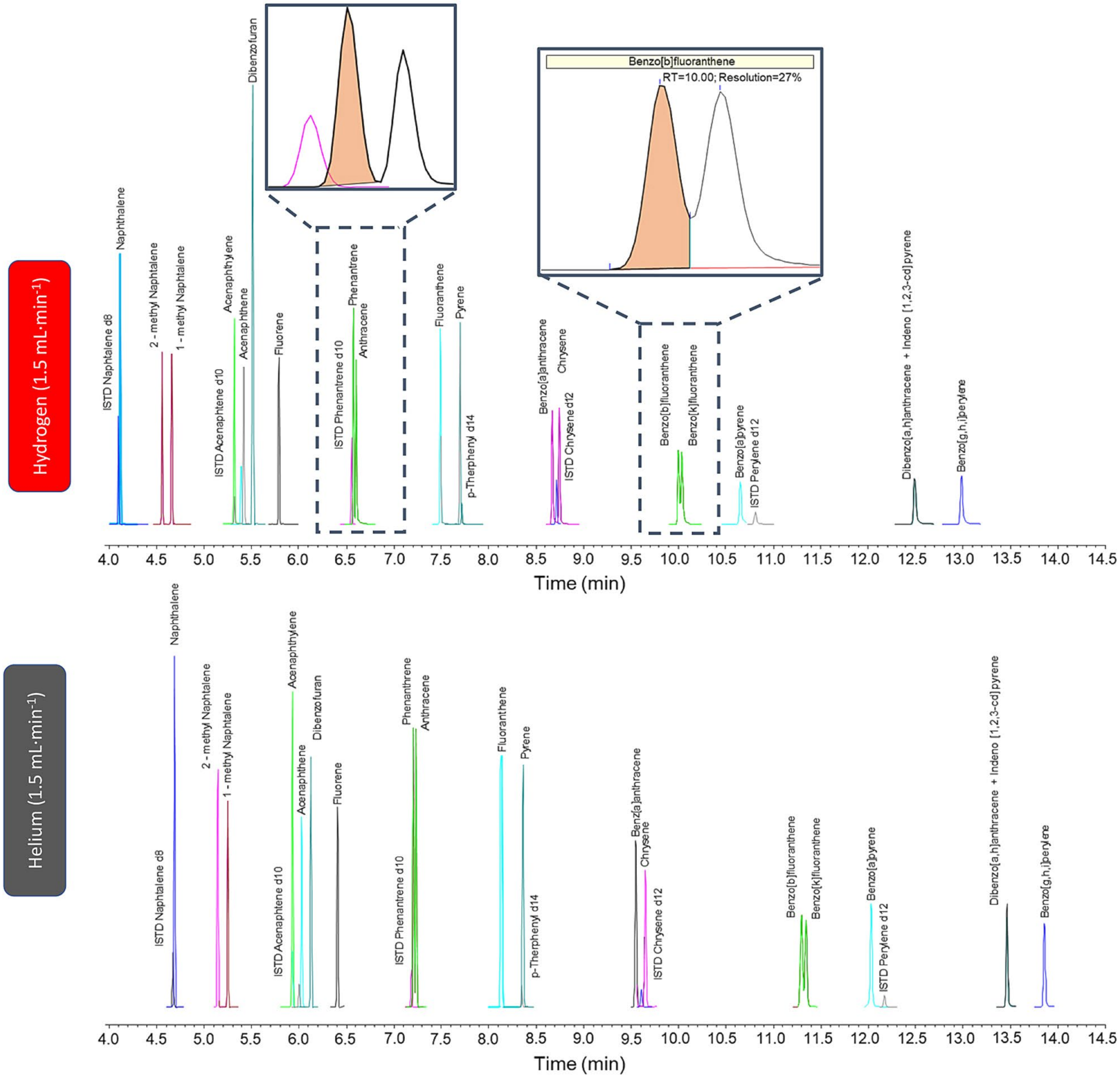


Figure 1. Chromatographic separation performance for PAH analysis using hydrogen (top) and helium (bottom) as a carrier gas at 1.5 mL·min^{-1}

turnover time of approximately 7%) was obtained with hydrogen, while separation between isobaric compounds was maintained. Separation between phenanthrene and anthracene is baseline resolved, while a resolution of 27% (ratio between valley height and height of the least high compound apex) was obtained between the isomers of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene without any re-optimization of method parameters for the HeSaver-H_2Safer SSL.

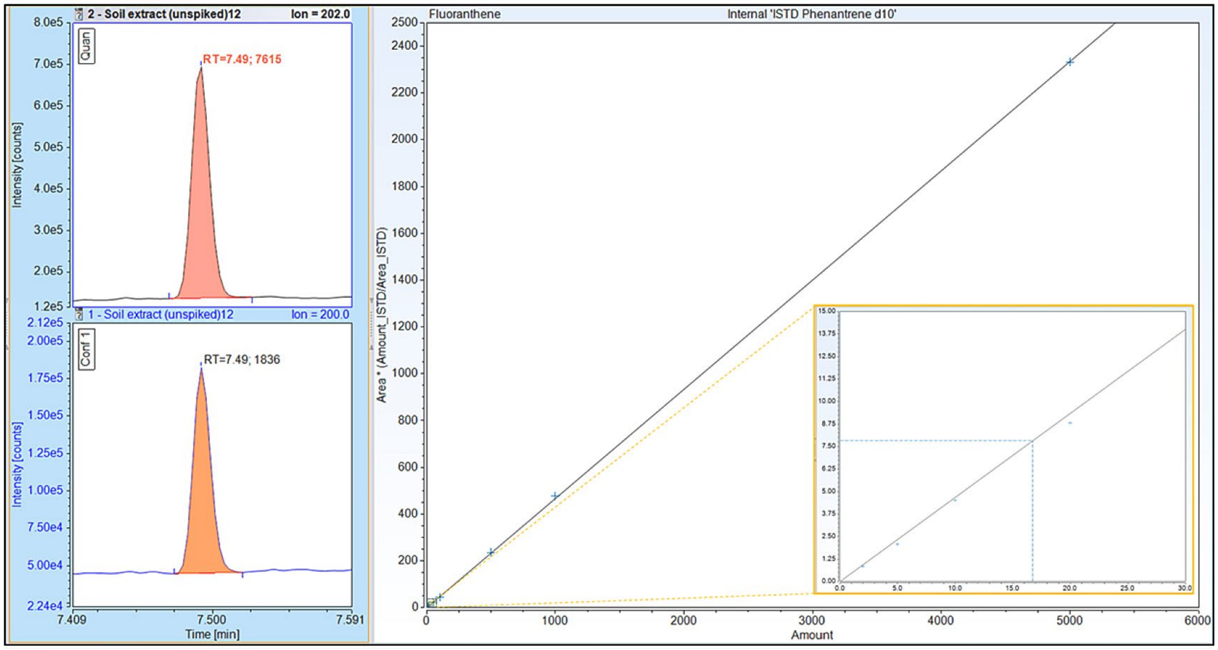
A 9-point calibration curve was constructed for each analyte with the calibration ranges listed in Table 1. Using a linear calibration model fit, excellent correlation (coefficient of determination $R^2 > 0.99$) was obtained for all analytes, spanning a calibration range of more than three orders of magnitude between 2.0 to 5,000 pg·µL^{-1}. Variation in the calibration response factors was well below 15%, thus, demonstrating the compatibility between the HeSaver-H_2Safer SSL with hydrogen as a carrier gas and high linear dynamic range of the Thermo Scientific™ XLXR™ (extended lifetime extended range) detector of the ISQ 7610 GC-MS.

One of the main challenges for analytical laboratories using hydrogen as carrier gas in a GC-MS system is the low pumping efficiency and possible breakdown of targeted analytes through hydrogenation reactions. Both traits negatively impact sensitivity which can hinder laboratories' abilities to meet detection requirements. To assess the detection capabilities, the analytical response variation through repetitive analysis (n = 10) of the lowest calibration standard (2.0 pg·µL^{-1}) was used to calculate limits of detection (LOD, 3× standard deviation response) and quantification (LOQ, 10x standard deviation response) (Figure 2). Detection and quantification limits ranged from 0.1 to 0.7 pg·µL^{-1} and from 0.4 to 2.3 pg·µL^{-1}, respectively and are comparable to method detection limits obtained in soil (0.5–7.6 pg·µL^{-1}) using helium as a carrier gas[3]. Although comparable sensitivity was observed between helium and hydrogen for PAH analysis, reactivity towards hydrogen will be analyte dependent and should be evaluated by users prior to considering changing carrier gas.

To assess the performance of the HeSaver-H_2Safer SSL using hydrogen towards a sample matrix, a two-gram aliquot of a soil sample was extracted in a biphasic mixture of acetonitrile and hexane with collection of the hexane layer without further clean-up. The soil extract was analyzed in its original form and spiked with 10 pg·µL^{-1} of a PAH standard. Internal standard was added to both extracts and subsequent analyses of over 100 injections were carried out to assess precision and method recovery. All PAHs were detected in the unspiked soil extract (except for acenaphthylene), although several compounds (i.e., naphthalene, 2-methyl napthalene, 1-methyl napthalene, fluorene, dibenzo[*a,h*]anthracene) were found to deviate outside the ion confirmation ratio limit (±20%). However, elevated concentrations were detected for several PAHs including pyrene and fluoranthene, confirming previous non-target screening results of the soil extract using the Thermo Scientific™ Orbitrap Exploris™ GC 240 mass spectrometer.[4] Despite the soil extract undergoing no sample clean-up, recovery of spike concentration was within acceptable ranges (70–102%).

Table 1. Retention time, calibration type, coefficient of determination (R^2), variation in response factors (%RSD), and response slope of calibration curve for targeted PAHs

Compound	Retention time (min)	Calibration type	Rel. Std. Dev. (%)	Coeff.of determination	Slope
Naphthalene	4.12	Linear	1.6	0.9999	0.49
2-methyl Naphtalene	4.56	Linear	0.6	0.9999	0.31
1-methyl Naphtalene	4.66	Linear	1.0	0.9999	0.31
Acenaphthylene	5.32	Linear	1.6	0.9999	0.68
Acenaphthene	5.42	Linear	2.1	0.9999	0.55
Dibenzofuran	5.52	Linear	1.7	0.9999	1.51
Fluorene	5.79	Linear	1.3	0.9999	0.56
Phenantrene	6.58	Linear	0.8	0.9999	0.49
Anthracene	6.61	Linear	1.5	0.9999	0.36
Fluoranthene	7.49	Linear	1.1	0.9999	0.47
Pyrene	7.70	Linear	0.7	0.9999	0.75
Benz[*a*]anthracene	8.67	Linear	4.2	0.9996	0.50
Chrysene	8.74	Linear	1.8	0.9999	0.51
Benzo[*b*]fluoranthene	10.00	Linear	5.6	0.9994	0.85
Benzo[*k*]fluoranthene	10.04	Linear	6.9	0.9991	0.94
Benzo[*a*]pyrene	10.65	Linear	10.3	0.998	0.60
Indeno[1,2,3-*cd*] pyrene	12.49	Linear	5.2	0.9995	0.41
Dibenzo[*a,h*]anthracene	12.50	Linear	8.7	0.9986	0.67
Benzo[*ghi*]perylene	12.98	Linear	5.3	0.9994	0.78



Compound	Unspiked soil (pg·µL^{-1})	Spiked soil extract (pg·µL^{-1})	Spike recovery (%)	LOD (pg·µL^{-1})	LOQ (pg·µL^{-1})
Naphthalene	0.6 ± 0.1[a]	10.8 ± 0.1	102 ± 1.4	0.5	1.7
2 - methyl Naphtalene	1.2 ± 0.1[a]	10.4 ± 0.2[a]	92 ± 2.2	0.3	0.9
1 - methyl Naphtalene	0.7 ± 0.1[a]	9.6 ± 0.3	89 ± 3.2	0.3	1.0
Acenaphthylene	< LOD	9.0 ± 0.5	90 ± 5.0	0.3	1.1
Acenaphthene	1.7 ± 0.3[b]	11.6 ± 0.5	99 ± 5.8	0.7	2.3
Dibenzofuran	0.2 ± 0.1	8.8 ± 0.2	86 ± 2.2	0.1	0.4
Fluorene	2.0 ± 0.2[a]	11.1 ± 0.2	91 ± 2.8	0.3	1.0
Phenantrene	6.1 ± 0.2	14.6 ± 0.6	85 ± 6.3	0.5	1.6
Anthracene	0.5 ± 0.1	7.6 ± 0.4	71 ± 4.1	0.4	1.4
Fluoranthene	17.0 ± 1.1	25.5 ± 1.2	85 ± 16	0.3	0.9
Pyrene	16.2 ± 1.0	24.8 ± 1.8	86 ± 20	0.3	1.0
Benz[*a*]anthracene	8.0 ± 0.6	15.5 ± 0.7	75 ± 9.2	0.3	1.1
Chrysene	12.2 ± 1.0	20.7 ± 1.2	85 ± 16	0.3	1.0
Benzo[*b*]fluoranthene	14.4 ± 0.9	21.8 ± 3.0	74 ± 31	0.2	0.7
Benzo[*k*]fluoranthene	5.8 ± 0.4	14.7 ± 0.7	89 ± 8.1	0.2	0.7
Benzo[*a*]pyrene	10.2 ± 0.4	18.1 ± 0.4	79 ± 5.6	0.3	1.1
Indeno[1,2,3-*cd*] pyrene	5.9 ± 0.7	12.9 ± 2.7	70 ± 2.9	0.3	1.1
Dibenzo[*a,h*]anthracene	1.5 ± 0.1a	9.3 ± 1.0	78 ± 10	0.2	0.7
Benzo[*ghi*]perylene	9.0 ± 1.0	18.1 ± 2.4	91 ± 26	0.3	1.1

[a] Outside ion confirmation ratio (± 20%)

[b] Below limit of qauntification (LOQ)

Figure 2. Quantification and confirmation ions of fluoranthene in unspiked soil extract with response vs concentration highlighted on calibration curve. The table shows the PAH concentrations (pg·µL^{-1}) in unspiked and spiked soil extracts, recovery of spiked concentration, and limit of detection (LOD) and quantification (LOQ) for targeted PAH analytes.

Reduced carrier gas consumption for economical and for safe operation

The HeSaver-H_2Safer SSL provides significant carrier gas savings not only when the GC is idle but also during operation. Using the Thermo Scientific™ Helium Saver Calculator tool[5], laboratories can assess their carrier gas consumption based on their own method parameters and settings. Using the method parameters of U.S. EPA, Method 8270E[2] for PAH analysis, hydrogen consumption is reduced by a third compared to a standard SSL injector, helping to reduce additional cost for gas cylinder replacement. The use of the HeSaver-H_2Safer SSL with hydrogen as carrier gas eliminates safety risks associated with the use of hydrogen. Use of an inert gas (i.e., nitrogen or argon) to pressurize the injector and split the sample avoids the discharge of high flows of hydrogen in the ambient air through the split and purge lines. Also, the limited maximum flow rate of hydrogen eliminates the need for an additional sensor on the GC, as levels of hydrogen remain below safety concern limits even in case of column breakage in the oven. In addition, the constant flow of hydrogen delivered with the HeSaver-H_2Safer SSL allows an optimized usage of hydrogen generators as renewable gas supply, offering a safe and sustainable alternative for laboratories without access to helium as a carrier gas option.

Summary

The HeSaver-H_2Safer technology offers carrier gas conservation technology not only for helium, but for hydrogen as well. This offers both a sustainable and economical solution for laboratories that cannot acquire reliable supplies of helium. The consistent analytical performance of using hydrogen as carrier gas with a GC-MS system has been demonstrated in this work for the analysis of PAHs in environmental samples.

- Improvements in analysis speed with use of hydrogen carrier gas without loss in separation efficiency between key isobaric compounds.
- Large linear dynamic range from 2.0 to 5,000 $\text{pg}\cdot\mu\text{L}^{-1}$ for a wide analysis range of PAHs in environmental samples.
- Comparable detection limits for targeted PAHs achieved using hydrogen as a carrier gas compared to helium, providing laboratories uncompromised performance while reducing gas consumption by a third compared to the standard SSL injector.
- Unique HeSaver-H_2Safer technology for SSL injector minimizes carrier gas consumption required for analysis and significantly reduces safety risks associated with the use of hydrogen as a carrier gas.

References

1. Scollo, G.; Parry, I.; Cavagnino, D. Thermo Fisher Scientific Technical Note 001218: Addressing gas conservation challenges when using helium or hydrogen as GC carrier gas, 2022. https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-001218-gc-hesaver-h2safer-trace1600-tn001218-na-en.pdf
2. U.S. EPA Method 8270E: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 6, June 2018. https://www.epa.gov/sites/default/files/2020-10/documents/method_8270e_update_vi_06-2018_0.pdf
3. Calaprice, C.; Pike, B.; Riccardino, G.; Ladak, A.; Silcock, P. Thermo Fisher Scientific Application Note 000455: Analysis of multiple matrices with a single calibration curve for polycyclic aromatic hydrocarbons (PAHs) with the ISQ 7610 GC-MS system following EPA Method 8270, 2021. https://appslab.thermofisher.com/App/4636/analysis-multiple-matrices-with-a-single-calibration-curve-for-polycyclic-aromatic-hydrocarbons-pahs-with-isq-7610-gcms-system-following-epa-method-8270e
4. Rajski, Ł.; Waner, N.; Kutscher, D.; Roberts, D. Thermo Fisher Scientific Application Note 001605: Differential analysis of soil using the Orbitrap Exploris GC mass spectrometer and Compound Discoverer software, 2022. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-001605-gc-orbitrap-ms-enviro-omics-soil-extracts-an001605-na-en.pdf
5. Thermo Fisher Scientific Helium Saver Calculator. https://www.thermofisher.com/it/en/home/industrial/chromatography/chromatography-learning-center/chromatography-consumables-resources/chromatography-tools-calculators/helium-saver-calculator.html

Learn more at **thermofisher.com/helium-saver**