Product spotlight | 001606

Polyaromatic hydrocarbon analysis by gas chromatography mass spectrometry using HeSaver-H_2Safer technology

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Introduction

Polyaromatic hydrocarbons (PAHs) are organic chemicals consisting of two or more benzene rings fused together in linear and/or cluster arrangements. These are naturally present in fossil fuel sources and produced through incomplete combustion of organic matter through both natural (e.g., forest fires) or anthropogenic activities (e.g., coal/oil/wood burning, vehicle emissions, waste incineration). Possessing a wide range of physical/chemical properties, over 100 different PAH compounds have been identified in environmental matrices, many being highly toxic with carcinogenic and endocrine disruption behavior. As toxic effects from PAHs can be induced at low levels of exposure, sensitive analysis techniques are needed to ensure environmental regulations and health protection is met.

Due to their semi-volatile nature, gas chromatography mass spectrometry (GC-MS) is the most common analysis technique used for PAH analysis. Helium is the most used carrier gas for gas chromatography due to its high chromatographic efficiency and inertness. However, with declines in global supply, GC laboratories are pressured to investigate mitigation options to ensure continuity in operation. Switching to alternative carrier gases, such as hydrogen or nitrogen, is one possible solution. However, MS vacuum and detection performance are reduced, highlighting the need for helium conservation to maintain current system performance. The Thermo Scientific™ HeSaver-H_2Safer™ carrier gas saving technology[1] offers an innovative and smart approach to dramatically reduce carrier gas consumption, even during GC operation. It consists of a modified Split Splitless (SSL) injector body connected to two gas lines: an inexpensive gas (e.g., nitrogen or argon) is used for inlet pressurization, analyte vaporization and transfer to the analytical column, while the selected carrier gas (e.g., helium or hydrogen) is used only to supply the chromatographic column for the separation process, with a limited maximum flow rate. When used with helium as carrier gas, the limited consumption allows mitigation of shortage issues while maintaining GC-MS performances without the need of instrument method re-optimization required when switching to a different carrier gas.

A Thermo Scientific™ TRACE™ 1610 gas chromatograph equipped with a Thermo Scientific™ iConnect™ SSL injector adapted for HeSaver-H_2Safer capability, was coupled to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer for the analysis of PAHs according to U.S. EPA Method 8270E.[2] Injection performance, linearity and instrument detection limits (IDLs) were evaluated against results obtained previously using a standard SSL injector.[3]

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Results and discussion

One of the key benefits of maintaining helium as carrier gas while reducing its consumption with the HeSaver-H_2Safer option, is that no method re-optimization is needed, allowing direct transfer of method parameters developed on the standard SSL to the HeSaver-H_2Safer inlet. Method parameters as previously established on a standard SSL for the analysis of PAHs in water and soil[3] were applied to assess the injection performance of the SSL in the HeSaver-H_2Safer mode. Peak area response variation across repeated injections (n = 9) of the lowest calibration standard (i.e., 2.5 ng•mL^{-1}) demonstrates consistent injection performance using the HeSaver-H_2Safer inlet in both split and splitless injection modes (Figure 1). Relative standard deviation in peak area response was <7.0% for split injection (split flow: 15 mL•min^{-1}) for all compounds (Figure 1, Table 1). At higher split flows (30 and 60 mL•min^{-1}), performance on injection repeatability was maintained with %RSD within injection performance criteria limits (%RSD <15%). Variation in peak response for splitless injection was also well within performance criteria (Figure 1), demonstrating excellent injection repeatability.

A 9-point calibration curve was constructed for each analyte with the calibration ranges listed in Table 1. Linear response was observed for all analytes (coefficient of determination (R^2) >0.997) spanning a concentration range over 4 orders of magnitude. Variation in average response factors (AvCF %RSD) and IDLs were comparable to values obtained previously using a standard SSL injector.[3] Peak shape was also maintained at the low concentrations (2.5 ng•mL^{-1}) using the HeSaver-H_2Safer SSL. An example of this can be seen in Figure 2, where a peak asymmetry value of 1.15 for fluoranthene was obtained after 200 sample injections, within acceptable limits (0.9 – 1.2) for analysis purposes (calculated according to European Pharmacopeia EP). These results highlight that it is possible to run samples with a reduced carrier gas consumption and maintain high performance in linearity, sensitivity, and peak shape.

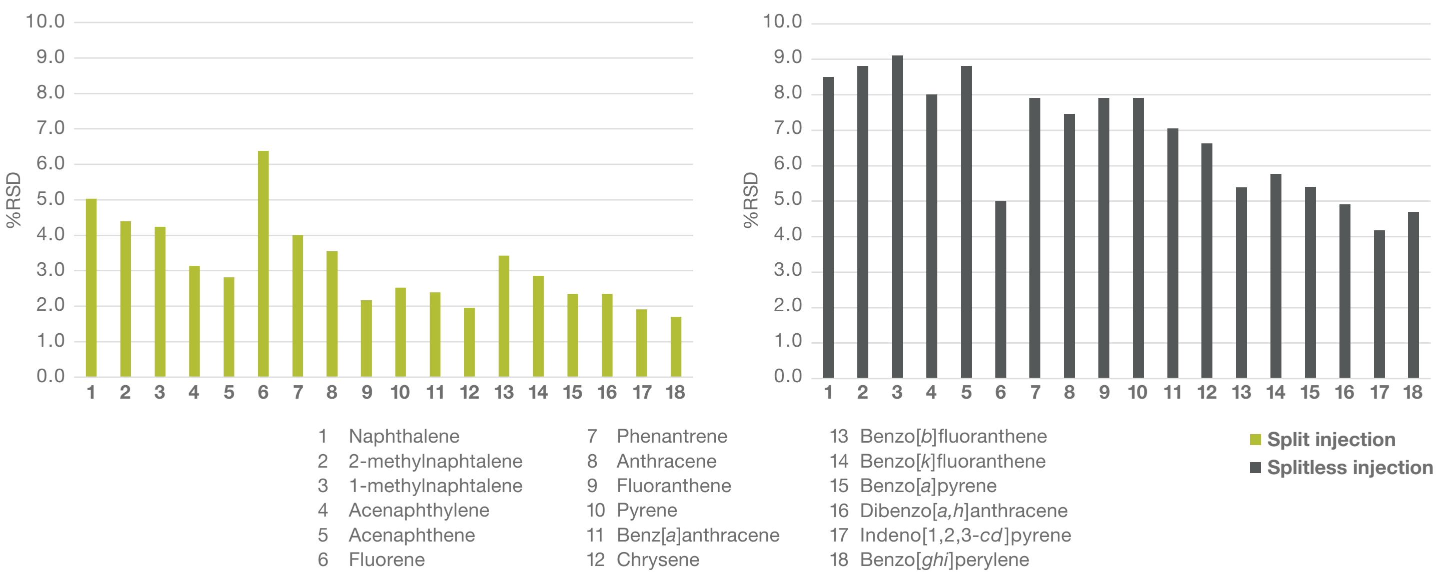

Figure 1. Relative standard deviation (%RSD) in peak area response of a 2.5 ng·mL^{-1} standard using the SSL in the HeSaver mode in split (split flow: 15 mL·min^{-1}) and splitless mode

Table 1. Retention time, calibration range, coefficient of determination (R^2), variation in average response factors (AvCF %RSD), IDLs and absolute peak area %RSDs at the lowest calibration point obtained using the HeSaver-H_2Safer technology

Compound	RT (min)	Cal range (ng/mL)	AvCF %RSD	Coefficient of determination (R^2)	Calculated IDL (ng/mL)	Peak area %RSD (lowest cal point, n = 9)
Naphthalene	4.71	1.25 – 5,000	10.2	0.998	0.23	5.0
2-Methylnaphthalene	5.16	1.25 – 5,000	9.3	0.998	0.22	4.4
1-Methylnaphthalene	5.26	1.25 – 5,000	10.2	0.998	0.24	4.2
Acenaphthylene	5.94	1.0 – 10,000	9.6	0.998	0.62	3.1
Acenaphthene	6.03	1.25 – 5,000	11.4	0.997	0.30	2.8
Fluorene	6.41	2.5 – 1,000	7.1	0.998	0.57	6.4

Table 1 (continued). Retention time, calibration range, coefficient of determination (R^2), variation in average response factors (AvCF %RSD), IDLs and absolute peak area %RSDs at the lowest calibration point obtained using the HeSaver-H_2Safer technology

Compound	RT (min)	Cal range (ng/mL)	AvCF %RSD	Coefficient of determination (R^2)	Calculated IDL (ng/mL)	Peak area %RSD (lowest cal point, n = 9)
Phenanthrene	7.21	1.25 – 500	8.5	0.997	0.36	4.0
Anthracene	7.24	1.25 – 500	9	0.997	0.52	3.6
Fluoranthene	8.13	1.25 – 500	6.3	0.998	0.55	2.2
Pyrene	8.35	1.25 – 500	7.2	0.998	0.35	2.5
Benz[*a*]anthracene	9.54	1.25 – 500	3.8	0.999	0.41	2.4
Chrysene	9.64	1.25 – 500	8.6	0.997	0.64	2.0
Benzo[*b*]fluoranthene	11.27	2.5 – 500	5.8	0.998	0.53	3.4
Benzo[*k*]fluoranthene	11.32	2.5 – 500	4.7	0.999	0.39	2.9
Benzo[*a*]pyrene	12.01	2.5 – 500	4.9	0.999	0.62	2.3
Dibenzo[*a,h*]anthracene	13.44	2.5 – 1,000	5.8	0.999	0.84	2.3
Indeno[1,2,3-*cd*]pyrene	13.44	2.5 – 500	5.2	0.999	0.42	1.9
Benzo[*ghi*]perylene	13.82	2.5 – 1,000	4.5	0.999	0.40	1.7

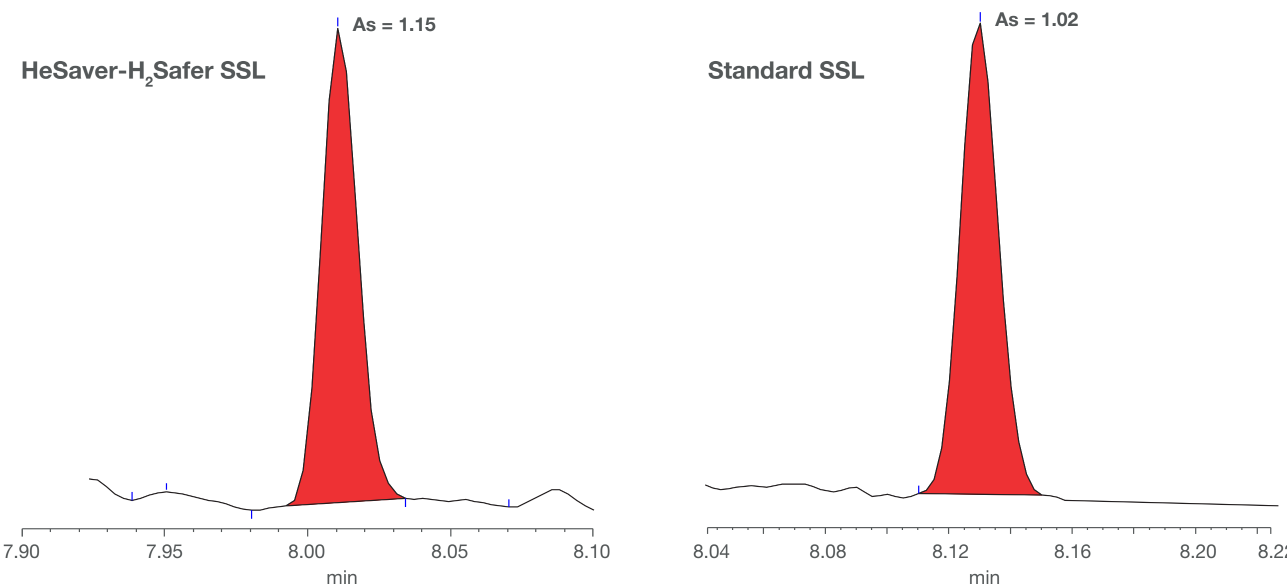

Figure 2. Chromatographic peak shape obtained at 2.5 ng·mL^{-1} standard for fluoranthene with the HeSaver-H_2Safer and Standard SSL. Peak asymmetry is within acceptable limits for analysis purposes (0.9 – 1.2). Separation performed on the TG-PAH GC column (30 × 0.25 mm × 0.10 um, PN 26055-0470).

Reduced helium consumption and cost savings

The HeSaver-H_2Safer technology offers significant gas savings not only when the GC is idle, but during operation. This technology can extend helium/hydrogen cylinder lifetime from months to years, depending on instrument method parameters, usage, and the number of GCs supported by a given gas cylinder. The Thermo Scientific™ Helium Saver Calculator tool[4] offers an easy-to-use and intuitive interface to estimate helium consumption and cost impact on individual laboratories activities. GC parameters regarding column dimensions, carrier gas and split flow settings, as well as helium and nitrogen costs are adjustable to reflect a given laboratory's methodology and regional gas cost, to provide estimates on helium cylinder lifetime and cost savings (Figure 3A). The usage of the HeSaver-H_2Safer technology for the analysis of PAHs according to the U.S. EPA Method 8270E[2] would allow the helium cylinder to last three times longer in comparison to the usage of a standard SSL injector (Figure 3B).

A

Column length (m)*	30	Column flow (sccm)*	1.5
Column ID (mm)*	0.25	Total time per sample (mins)	15.2
Film thickness (µm)*	0.1	Cost of helium cylinder (UHP 5.0)	350
Split flow setting (sccm)*	15	Cost of nitrogen cylinder (UHP 5.0)	50

B

	Helium usage featuring Helium Saver Technology	Standard helium usage
He volume used per sample:	0.12 Liters	0.37 Liters
N_2 volume ued per sample:	0.25 Liters	0
Estimated lifetime of helium cylinder (if using 24/7/365):	1.7618 Years	0.5712 Years
Estimated lifetime of helium cylinder (if using 8 hrs x 5 days/wk for 365):	7.2411 Years	2.3874 Years
Annual cost savings (if using 24/7/365):	$354.73	$0.00
Lifetime cost savings (assuming 14 years of GC-MS instrument life time):	$4,966.17	$0.00

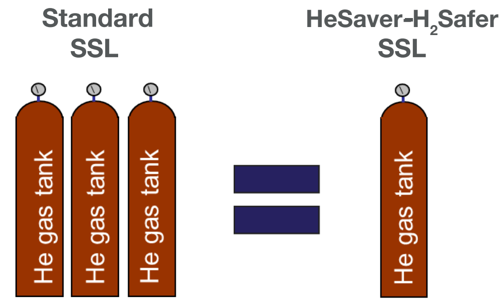

Figure 3. (A) Column dimensions, gas flow settings, and gas cylinder costs (region dependent) for U.S. EPA Method 8270E and (B) estimated helium consumption, cylinder gas lifetime and cost savings comparison between the HeSaver-H_2Safer and standard SSL injector

Summary

The HeSaver-H_2Safer technology offers a simple upgrade to the standard iConnect SSL injector with the advantage of reduced helium gas consumption, without compromising GC-MS performance. This has been demonstrated in this work for the analysis of PAHs in environmental samples.

- The transition from the injection phase using an inexpensive pressurizing gas to the separation process using the best carrier gas (e.g., helium) is extremely fast (within a few milliseconds), ensuring a rapid gas replacement into the column and thus maintaining chromatographic and MS performance compared to using a standard SSL injector.
- Existing validated methods can be maintained without modifications, providing consistent analytical performance in terms of injection repeatability, analyte transfer, linearity, sensitivity and robustness.
- HeSaver-H_2Safer technology provides additional advantages surrounding inlet maintenance where column flow can be maintained while opening the injector. Additionally, the pressurizing gas flushing the injector is for the majority of the time, discharged only through the split line, protecting the column from possible introduction of contaminants.
- The Helium Saver Calculator tool[4] allows for easy and immediate estimation of helium cylinder lifetime and cost savings when using the Helium Saver technology.

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