Using hydrogen as a carrier gas in gas chromatography mass spectrometry (GC-MS) applications – a case study for common contaminants

Nicholas A. Warner[1], Łukasz Rajski[1], Daniel Kutscher[1], Adam Ladak[2]
[1]Thermo Fisher Scientific, Bremen, Germany, D-28199; [2]Thermo Fisher Scientific, Hemel Hempsted, United Kingdom, HP2 7GE;

Abstract

Purpose: To demonstrate the performance of the new Thermo Scientifc™ HeSaver-H2Safer™ kit for the Thermo Scientific™ iConnect™ split-splitless (SSL) injection module for trace analysis of polyaromatic hydrocarbons (PAHs) and pesticides using H_2 as a carrier gas as a safe and sustainable solution for laboratory operations

Method summary: The performance of both single and triple quadrupole gas chromatography mass spectrometry (GC-MS) systems for routine analysis for polyaromatic hydrocarbons (PAHs) and pesticides was evaluated using a novel SSL injector design to decouple the pressurizing gas from the carrier gas flow (Figure 1.). Using nitrogen as a pressurizing gas and hydrogen as a carrier gas, performance was evaluated for PAHs and pesticides according US.EPA method 8270E[1,2] and DG Sante guidleines[3], respectively.

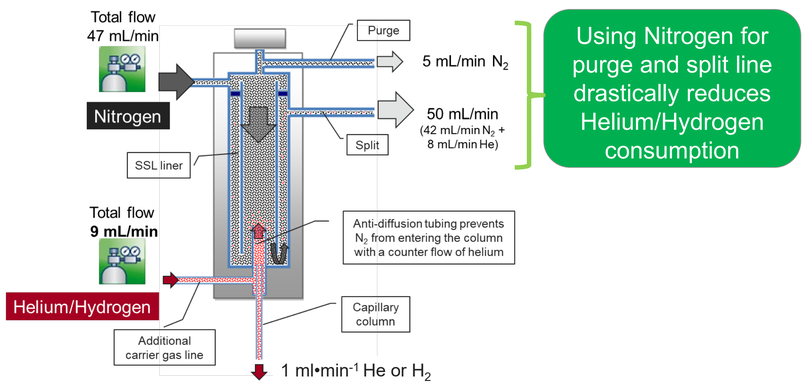


Figure 1. Schematic overview of HeSaver-H2Safer SSL injection module

Introduction

Laboratories are under constant pressure to deliver results that are compliant with regulations. Helium (He) is an ideal carrier gas in GC-MS operations due to its inert nature and fast pumping efficiency. However, the dwindling global gas supply of He has created challenges for laboratories to maintain operations from economic and productivity standpoints. To mitigate these challenges, laboratories have looked to switch their carrier gas to an a more abundant alternative such as Hydrogen (H_2). Although additional challenges arise in using H_2 such as:

- Safety hazard posed by high flammability of H_2 - sensors required in GC oven for gas supply / heating shutdown when leaks are detected
- Reactivity of H_2 in the hot SSL inlet might lead to analyte degradation
- Decreased sensitivity and higher LODs due to increased noise from lower pumping efficiency of H_2 – reducing analytical performance towards reaching regulatory requirements
- Re-optimization bd validation of methods when switching carrier gas from He to H_2

Despite these challenges, laboratories are still faced with gas supply uncertainty and rising costs. Thus, technical solutions are needed to mitigate these challenges without compromising instrument performance and data quality.

Materials and methods

Standard and sample preparation

PAH analysis in soil - A two-gram soil sample was extracted in a bi-phasic mixture of acetonitrile/ hexane (4 ml:4 ml) followed by centrifugation at 3000 rpm. 500 µL of the hexane layer was evaporated to dryness, spiked deuterated (d) internal standards of Napthalene (d8) and Phenantrene (d10) and reconstituted to 0.5 ml with dichloromethane (DCM). A spiked soil extract was also prepared in the same manner except with the addition of 50 µL of 100 pg•µL native PAH solution to produce a final concentration of 10 pg•µL^{-1} to assess method recovery. Calibration standards were prepared in DCM with a concentration range from 2 – 5000 pg•µL^{-1}

Pesticide analysis in baby food and honey – A 10-gram sample was extracted using the QuEChers method[4] In brief, acetonitrile was added to the sample material followed by the addition of magnesium sulphate, sodium chloride, trisodium citrate dihydrate, and disodium hydrogen citrate sesquihydrate (Thermo Scientific™ QuECheRS EN 15662 Method Extraction Kit). After mixing and centrifugation, a 5-mL aliquot of supernatant was mixed with magnesium sulfate and PSA sorbent, centrifuged again, and transferred to an amber GC vial and acidified with formic acid prior to analysis. A matrix matched calibration curve was prepared for both matrices in a concentration range of 0.005 – 0.500 mg•kg^{-1}.

Instrumental configuration

PAH Analysis - Sample analysis was performed on the Thermo Scientific™ ISQ™ 7610 GC-MS equipped with Thermo Scientific™ TRACE™ 1610 GC equipped with the HeSaver-H2Safer. Chromatographic separation was performed using a Thermo Scientific™TG-PAH capillary GC column (30 m × 0.25 mm, 0.10 µm) with hydrogen as a carrier gas at a constant flow rate of 1.5 mL•min^{-1} . Analysis was performed in single ion monitoring (SIM) acquisition mode. Injection, oven and mass analyzer conditions have been previously described[5].

Pesticide analysis - Sample analysis was performed on the Thermo Scientific™ TSQ™ 9610 mass spectrometer with the same GC and injector configuration as described for the PAH analysis. Chromatographic separation was preformed on a Thermo Scientific™ TG-5SilMS capillary GC column (20 m × 0.18 mm, 0.18 µm) using hydrogen as a carrier gas at a flow of 1.2 mL•min^{-1} The TSQ 9610 mass spectrometer was operated in timed-SRM mode with all transitions optimized with Thermo Scientific™ AutoSRM software to obtain the highest possible sensitivity. Optimized ion transitions for H_2 along with injector, oven and mass analyzer conditions have been previously described[4].

References

1. Warner N, Ladak A, Cavagnino D, Kutscher D. Thermo Fisher Scientific application note 002027: *Sustainable , safe and reliable analysis of PAH by gas chromatography-mass spectrometry using hydrogen carrier gas with HeSaver-H2 Safer technology.* ***2023***.
2. U.S. EPA Method 8270E: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 6, June **2018**.
3. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis In Food And Feed. SANTE 11312/**2021**.
4. Rajski Ł, Kutscher D, Ladak A. Thermo Fisher Scientific application note 002225: *Reducing running costs for GC-MS/MS analysis of pesticide residues using hydrogen carrier gas.* ***2023***.
5. Calaprice C Pike, B; Riccardino G, Ladak A, Silcock P. Thermo Fisher Scientific application note 000455: *Analysis of mulitple matrices with a single calibration curve for polycyclic aromatic hydrocarbons (PAHs) with the ISQ 7610 GC-MS system.* ***2021***.

Learn more at thermofisher.com/GC-MS

Results

PAH analysis

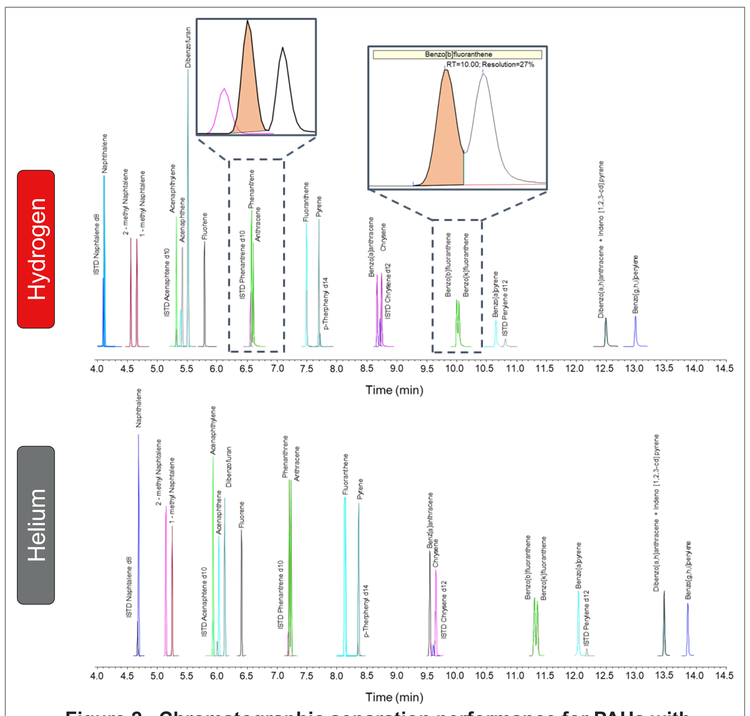


Figure 2 . Chromatographic separation performance for PAHs with hydrogen and helium as a carrier gas at 1.5 mL•min^{-1}

- Improvements in PAH analysis speed with H_2 using same methodology without comprising separation efficiency
- Linear dynamic range from 2.0 – 5000 pg•µL^{-1} with calibration response variation < 15% with sensitivity comparable to results obtained with He as carrier gas[5]
- Acceptable recovery of spike concentrations (70 -102 %) in raw soil extract (no cleanup)

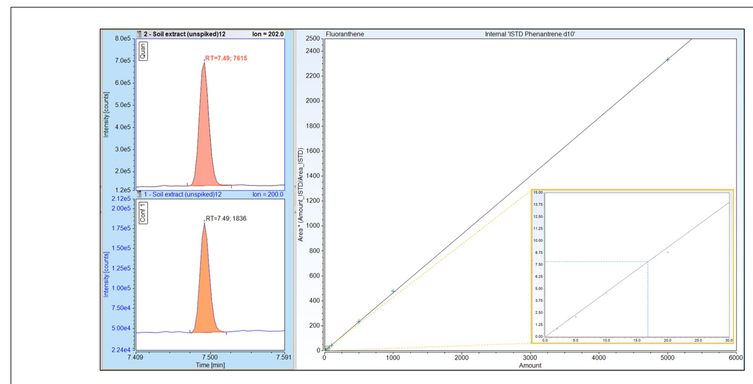


Figure 3 . Quantification and confirmation ions of fluoranthene in un-spiked soil extract with response vs concentration highlighted on calibration curve

Peak Name	Unspiked soil (pg•µL^{-1})	Spiked soil (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 ± 0.1[a]	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

Table 1 . PAH concentration in un-spiked and spiked soil extracts with spike recovery after 100 injections. Limits of detection (LOD) and quantification (LOQ) determined with repetitive analysis of lowest calibration standard.

Ion source after 100 injections of raw soil extract

Pesticide analysis

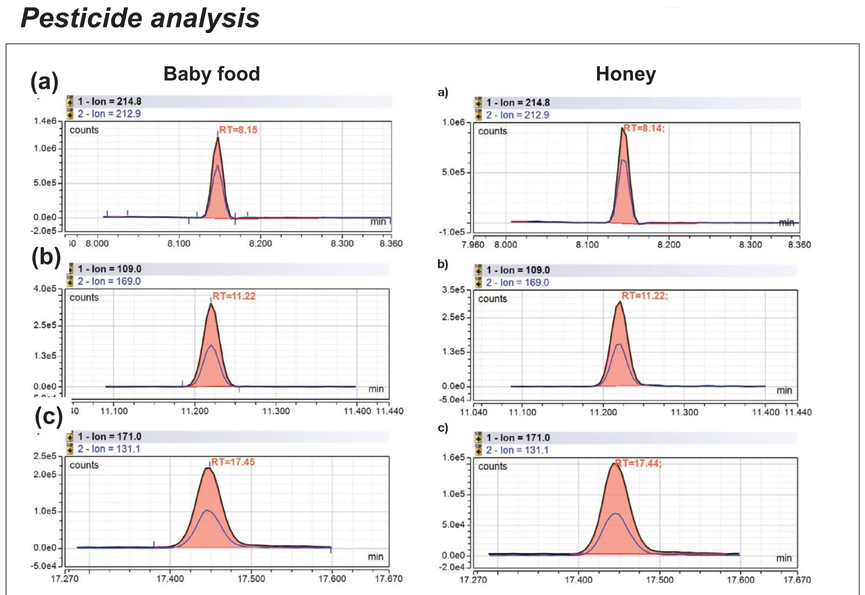


Figure 4. Sensitivity and peak shape obtained at 0.005 mg•kg^{-1} in baby food and honey for (a) pentachlorbenzene, (b) fenthion and (c) tebufenpyrad

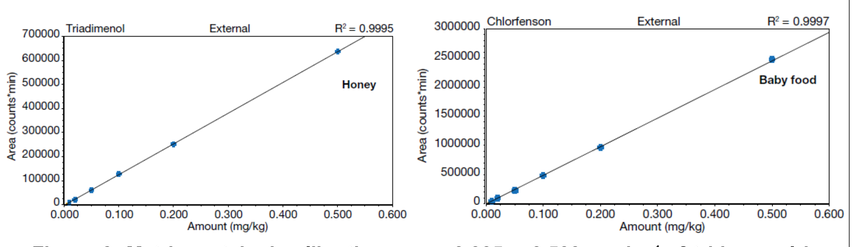


Figure 6. Matrix matched calibration curve 0.005 – 0.500 mg•kg^{-1} of tridemenol in honey and chlorfenson in baby food using hydrogen as a carrier gas

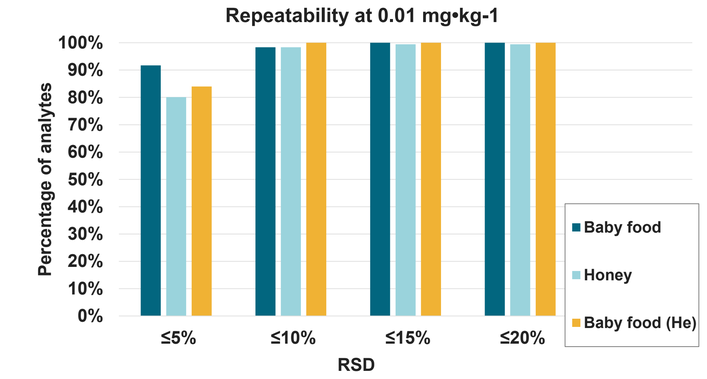


Figure 5. Repeatability (n = 5) of 181 pesticides in baby food and honey at 0.01 and 0.05 mg•kg^{-1} in baby food and honey using hydrogen compared to repeatability in baby food using helium

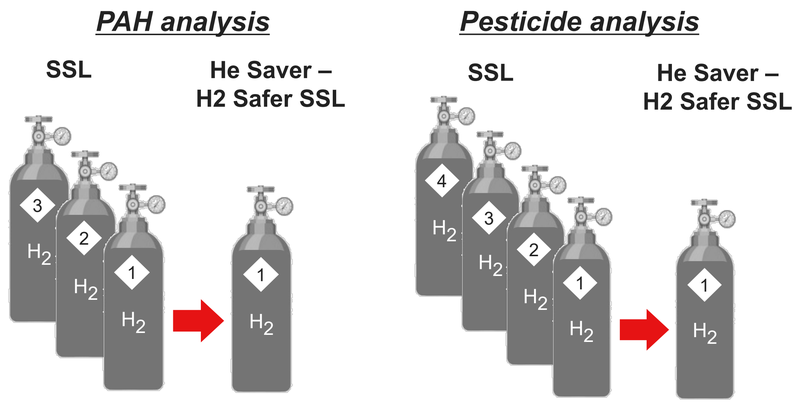
- At 0.01 mg•kg^{-1}, 98% of 181 pesticides showed RSD ≤ 10 % in repeatability experiments and well within the DG Sante criteria (RSD ≤ 20 %)
- Linear response observed from 0.005 – 0.500 mg•kg^{-1} in matrixed match calibration curves for baby food and honey for ≥ 97% of pesticides investigated
- Comparable sensitivity achieved with H_2 compared to He when SRM transitions optimized based on different fragmentation behavior

Conclusions

- Improvements in analysis speed achieved for both PAH and pesticide analysis without compromise to separation efficiency when using hydrogen as a carrier gas
- Comparable sensitivity achieved with H_2 compared to He for PAH and pesticide analysis with linear response ranging from 2 to over 3 orders of magnitude for pesticides and PAHs, respectively
- HeSaver-H2Safer SSL provides both safe and sustainable operation by eliminating the need for H_2 sensors by minimizing carrier gas flow, while greatly reducing gas consumption and laboratory costs.

Safety together with gas savings

Flow of H_2 carrier gas within the HeSaver-H2 Safer SSL is limited with no risk of hazardous concentrations being reached. In addition, users benefit from gas savings where consumption of carrier gas is reduced by a factor of 3 to 4 compared to the standard SSL for PAH and pesticide analysis, respectively.



Trademarks/licensing