Utilizing cost effective helium saving technology for low level quantitation of Polychlorinated dibenzo-p-dioxins/furans using gas chromatograph mass spectrometry

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Abstract

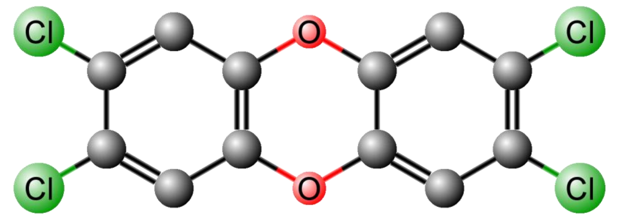
Purpose: To demonstrate high sensitivity and robustness of a cost-effective and sustainable Helium saving injector for the analysis of polychlorinated dibenzo-p-dioxins/furans (PCDD/PCDF).

Methods: Sample analysis was carried out on the Thermo Scientific™ TSQ™ 9610 GC-MS/MS equipped with the new Thermo Scientific™ iConnect™ HeSaver-H2Safer™ split/splitless (SSL) injector. A sample volume of 1.5 µL was injected for chromatographic separation using a TG-Dioxin (60 m × 0.25 mm, 0.25 µm) capillary GC column with previously described conditions.[1] The GC-MS/MS system was equipped with an advanced electron ionization (AEI) source to increase sensitivity for analyte detection. Quantification was performed using isotopic dilution in Thermo Scientific™ Chromeleon™ Chromatography Data System software using the Dioxin Analyzer workflow .

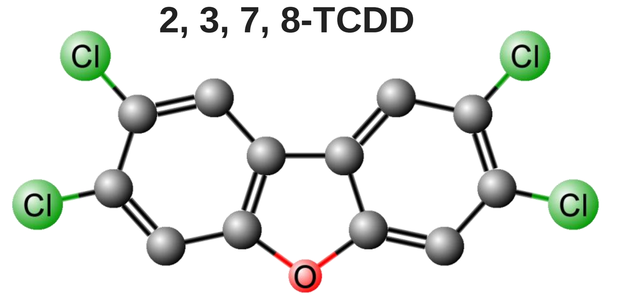
Results: The He saver demonstrated excellent robustness, precision, and sensitivity for PCDD/F analysis in soil extracts (analyzed with no prior clean-up) at fg levels while consuming 8 times less helium compared to the standard SSL injector

Introduction

Polychlorinated dibenzo-p-dioxins/furans (PCDDs / PCDFs) and their toxicity at trace levels continue to be a concern for regulatory agencies. With maximum allowable limits set at sub pg/g levels, sensitivity is of utmost importance for gas chromatography-triple quadrupole mass spectrometry (GC-MS/MS) as a confirmatory method for PCDDs / PCDFs analysis under EU regulations 644/2017 and 771/2017.



2, 3, 7, 8-TCDD



2, 3, 7, 8-TCDF

Helium is an ideal carrier gas in GC-MS instrumentation due to its high purity, inert nature, and overall performance. However, dwindling global supply has laboratories facing challenges in supply and increasing costs. Use of an alternative carrier gas, such as hydrogen, is a possible solution. However, its reduced pumping efficiency can detrimentally impact sensitivity of MS instrumentation several fold, posing challenges to meet regulatory requirements for tightly regulated substances, such as PCDDs / PCDFs.

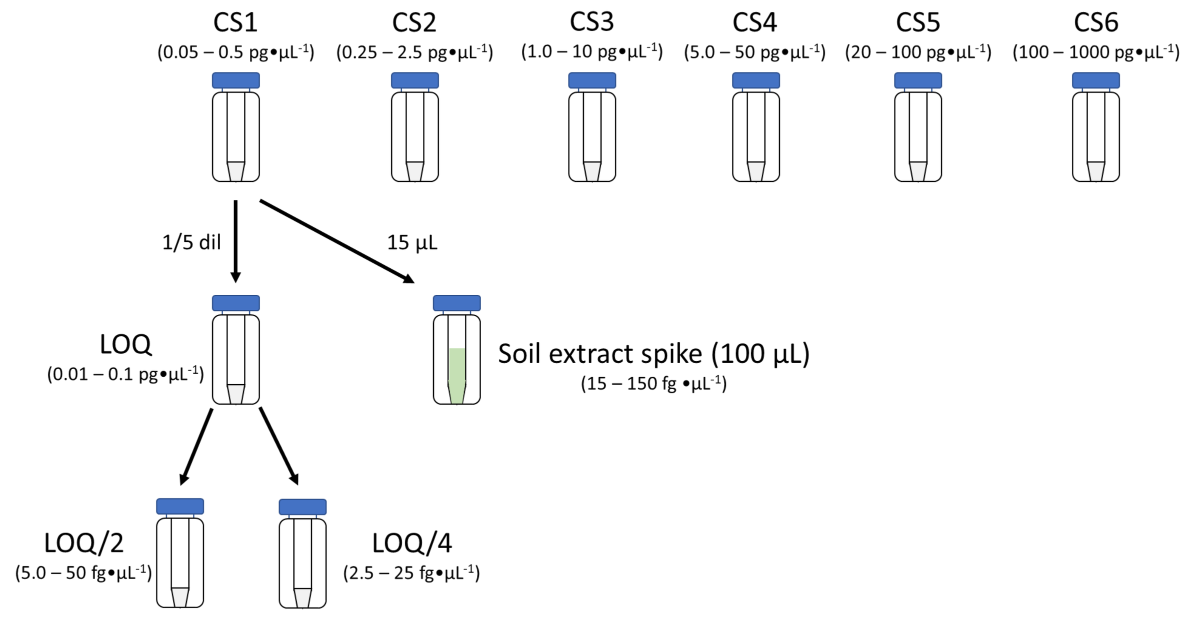
To maintain the current performance of GC-MS systems, technological solutions are needed to minimize helium consumption without compromising analytical results. In this study, the performance of the new Helium saver injection module was evaluated for trace analysis of PCDDs / PCDFs.

Materials and methods

Standard preparation

Isotopically labelled calibration standards (EPA-1613) were purchased from Wellington Laboratories (Canada). Each standard was diluted by a factor of 2 to construct a 6-level calibration curve (Figure 1.). The lowest calibration standard was diluted by a factor of 10 to produce a limit of quantification (LOQ) check standard (0.01 – 0.1 pg•µL⁻¹). LOQ and sensitivity check standards (LOQ/2 and LOQ/4) were prepared through dilution of the lowest calibration standard (Figure 1).

Figure 1. Overview of standard and sample preparation



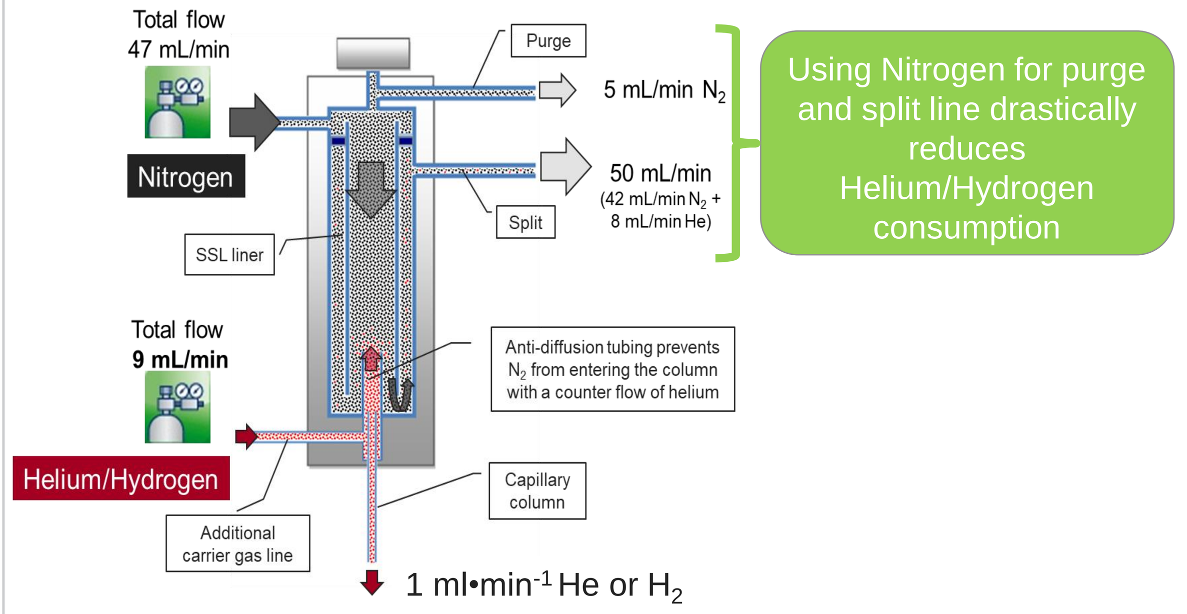
Sample preparation

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. 100 µL of the hexane layer was evaporated to dryness and spiked with 15 µL of the lowest calibration standard and reconstituted in 100 µL nonane (Figure 1).

Robustness and sensitivity evaluation

The spiked soil extract was injected repeatedly in two separate analyses over a 5-day period with calibration and LOQ/sensitivity check standards to assess instrument precision and sensitivity robustness over the entire duration of the analysis.

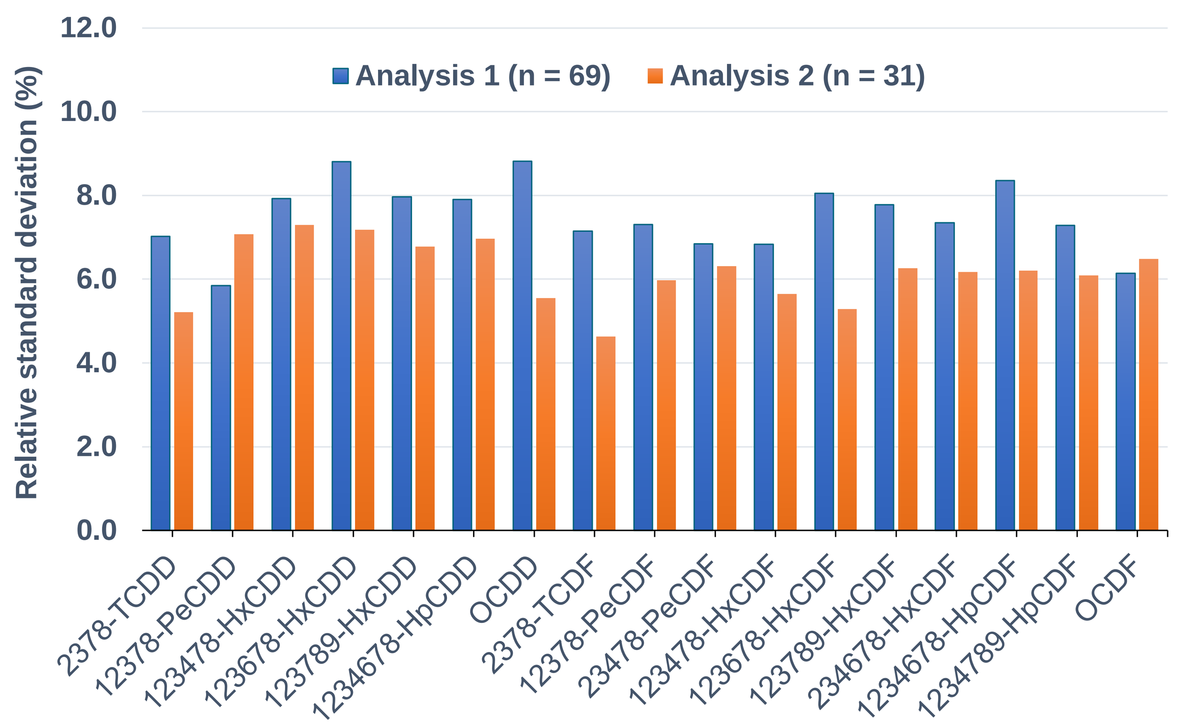
Figure 2. Schematic overview of HeSaver-H2Safer SSL injection module



Results

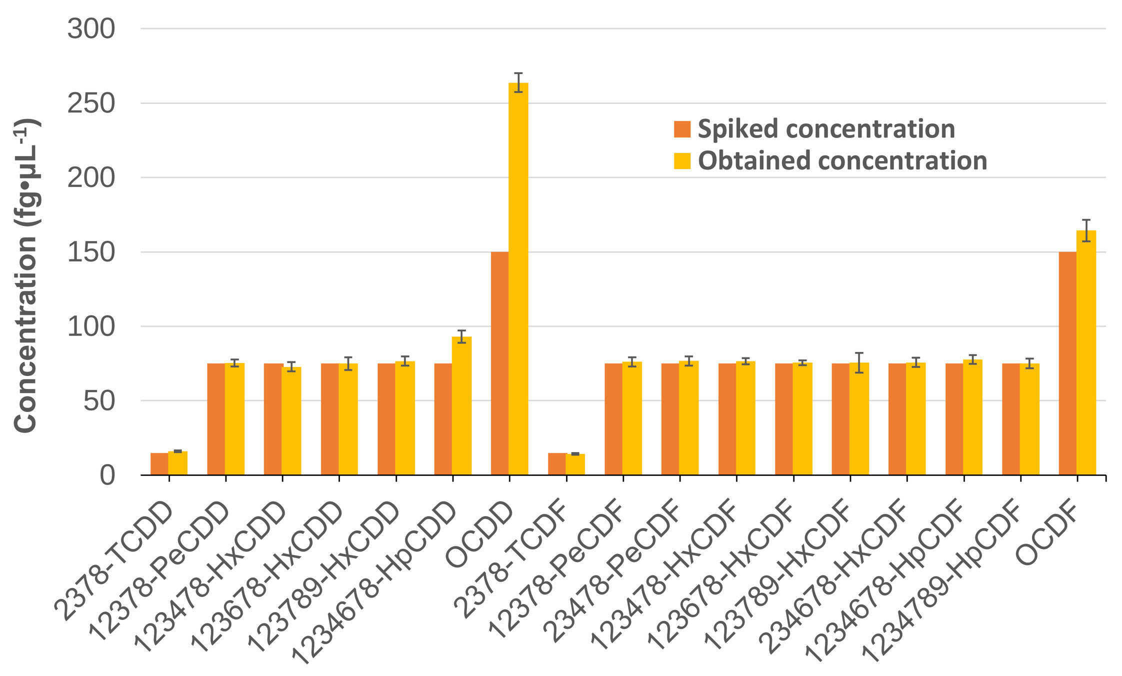
Robust injection performance

Figure 3. Relative standard deviation (%) in peak area obtained for repeated injection of a soil extract spiked with PCDD/F (15 – 150 fg •µL⁻¹) in two separate analyses. Number of injections (n) provided for separate analyses.



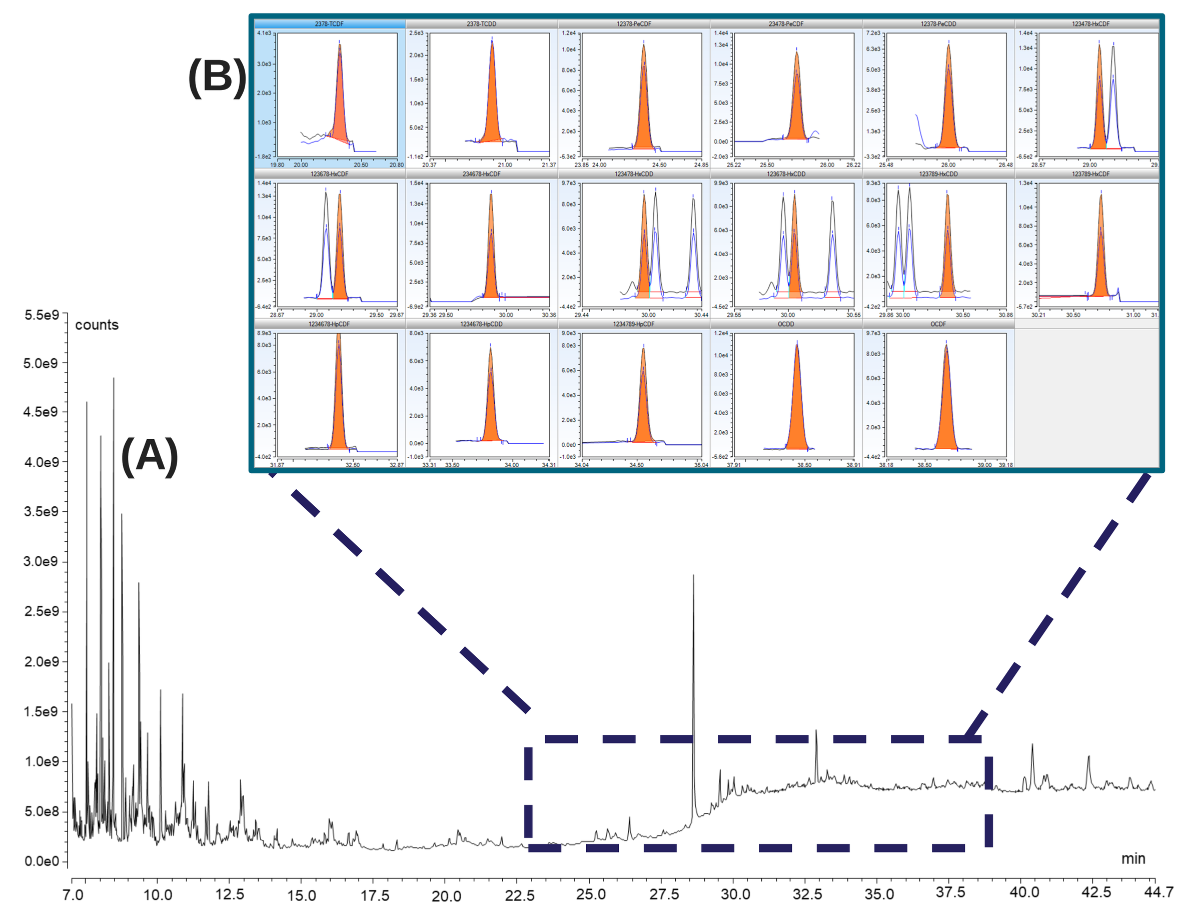
Accurate quantitation with precision

Figure 4. Spike and obtained concentration of soil extract for Dioxin analysis



Variation in obtained PCDD/F concentration across all soil extract injections ≤ ± 7.2 fg. Good agreement was achieved between spiked and obtained concentration with exception to 1234678-HpCDD, OCDD and OCDF due to native concentrations present in sample

Figure 5. Full scan (50 – 500 m/z) total ion chromatogram (A) and extraction SRM (B) for PCDD/F in spiked soil extract (TCDD/F: 15 fg, PeCDD/F: 75 fg, HxCDD/F: 75 fg, HpCDD/F: 75 fg and OCDD/F: 150 fg)



Helium Savings

The iConnect HeSaver-H2Safer SSL consumes 8 times less helium per sample compared to standard SSL with over a $ 1,000 annual cost savings with for continuous Dioxin analysis 24/7 for 365 days

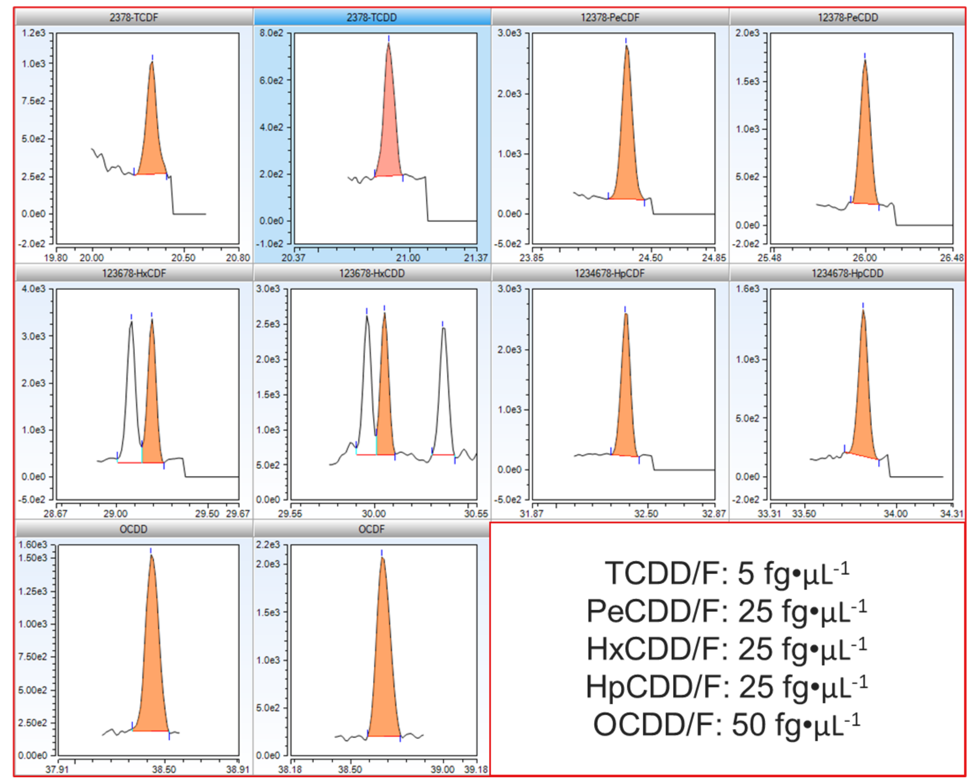
Table 1. Column and injection parameters with helium and nitrogen cylinder cost

Column length (m)*	60	Column flow (sccm)*	1.2
Column ID (mm)*	0.25	Total time per sample (mins)	44.7
Film thickness (µm)*	0.25	Cost of helium cylinder (UHP 5.0)	375
Split flow setting (sccm)*	120	Cost of nitrogen cylinder (UHP 5.0)	80

Table 2. Estimated helium lifetime and costs for Dioxin analysis for HeSaver-H2Safer and standard SSL injector

	Helium usage featuring Helium Saver Technology	Standard helium usage
He volume used per sample:	0.33 Liters	2.50 Liters
N_2 volume ued per sample:	2.17 Liters	0
Estimated lifetime of helium cylinder (if using 24/7/365):	1.8727 Years	0.2479 Years
Estimated lifetime of helium cylinder (if using 8 hrs x 5 days/wk for 365):	7.6847 Years	1.0411 Years
Annual cost savings (if using 24/7/365):	$1,021.25	$0.00
Lifetime cost savings (assuming 14 years of GC-MS instrument life time):	$14,297.48	$0.00

Figure 6. LOQ/2 check solution response



	LOQ (fg•µL⁻¹)
TCDD/F	5.0 / 5.7
PeCDD/F	29 / 21
HxCDD/F	20 / 25
HpCDD/F	48 / 24
OCDD/F	58 / 40

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Conclusions

The TSQ 9610 GC-MS/MS system showed excellent results for dioxin analysis:

- The iConnect HeSaver-H2Safer SSL showed stable injection repeatability over long injection sequences in complex sample matrix
- Precise quantification achievable at fg levels
- Despite lower injection volume, sensitivity requirements achievable showing no uncompromised performance of mass spectrometer with the iConnect HeSaver-H2Saver.

References

1. Law R, Schaechtele A, Gujar A, Xing J, Cojocariu C.. (2019). *Thermo Scientific. Application note 10703.*
2. Scollo G, Parry I, Cavagnino D, . (2022) . *Thermo Scientific Technical note 001218.*

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