

Harnessing the Efficiency of Nitrogen Carrier Gas with the Atmospheric Pressure Gas Chromatography (APGC) Source

Lauren Mullin and Adam Ladak
 Waters Corporation, Milford, MA, USA



GOAL

To highlight the ease of implementation and efficient performance of N_2 as a replacement carrier gas for helium (He) in GC separations interfaced with the atmospheric pressure gas chromatography (APGC) MS source.

BACKGROUND

Helium (He) is the most commonly used carrier gas in gas chromatography (GC) applications. However, the finite nature of reserves has resulted in periodic price increases and concern regarding availability.¹ Nitrogen (N_2) is a more affordable and readily available option that has historically been less utilized as a GC carrier gas. Reasons for this are that N_2 has lower diffusivity than He or hydrogen and often requires longer run times to achieve similar separations. In this technology brief we show GC coupled with an atmospheric pressure ionization mass spectrometry, which utilizes N_2 for both ionization and make-up flow. This allows a single gas source to be used for chromatographic separation as well as for ionization. Following automated method transfer calculations available within

Implementing nitrogen (N_2) as the carrier gas for GC experiments is a cost-effective approach for atmospheric pressure MS sources, while maintaining critical separations and chromatographic performance.

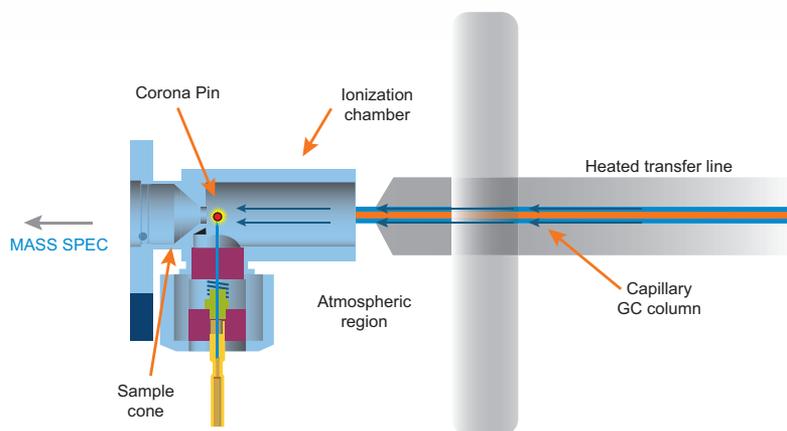


Figure 1. MS and GC atmospheric source interface. Nitrogen is supplied to the source from the heated transfer line, as well as cone and auxiliary gas supplies.

Waters® UNIFI® Software, efficient and comparable chromatography using N_2 carrier gas was achieved for pesticides, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and chlorinated dioxin/furans (PCDD/Fs). Unlike electron ionization, atmospheric pressure ionization remains robust during the introduction of N_2 . Also, a higher range of column flows can be used in the APGC source compared to tradition vacuum GC, and more flexibility with regards to method translation such that optimized carrier gas linear velocities could be achieved for N_2 .

THE SOLUTION

Experiments were performed on a Xevo® G2-XS QToF with APGC (Figure 1). Ionization was performed using atmospheric pressure chemical ionization, such that protonation (resulting in the [M+H]⁺ ion) or charge transfer (resulting in the M⁺⁺ ion) reactions occurred. The GC method for pesticides is described in Table 1a and 1b, and for the analysis of PBDEs, PCBs, and PCDD/Fs in Table 2a and 2b. Methods were revised using an automated calculator for method transfer to arrive at optimum values for N₂ as a carrier gas, resulting in comparable separations to those achieved using He. Figure 2 shows the calculator as available in Waters UNIFI Software for GC Instrument Control. When using the Speed Gain option of the calculator, the increase of the Outlet Flow rate (mL/min) and resulting Average Velocity (cm/s) resulted in a shortened method when N₂ carrier gas was used as compared to He.

1a

Parameter	Value
Column	DB 5MS 30 m x 0.25 mm, 0.25 µm (J&W)
Carrier gas	Helium or Nitrogen
Injection mode	Splitless
Inlet liner	Single taper splitless, deactivated (Restek)
Column pneumatics	Constant flow
Column flow (mL/min)	1.2 or 1.31
Inlet temperature (°C)	280

1b

Temperature	Temperature ramp (°C/min)	Hold time (min)
40		1.00 or 0.92
320	27 or 29.49	2.63 or 2.41

Table 1a and 1b. GC method for pesticide analysis.

2a

Parameter	Value
Column	Rxi 5Sil 60 m x 0.25 mm, 0.25 µm (Restek)
Carrier gas	Helium or Nitrogen
Injection mode	Splitless
Inlet liner	Single taper splitless, deactivated (Restek)
Column pneumatics	Constant flow
Column flow (mL/min)	1.0 or 1.09
Inlet temperature (°C)	280

2b

Temperature	Temperature ramp (°C/min)	Hold time (min)
120		2.00 or 1.84
200	35 or 38.05	0.00
215	5 or 5.43	18.00 or 16.57
235	5 or 5.43	7.00 or 6.44
290	5 or 5.43	5.00 or 4.60
325	7 or 7.93	2.30 or 2.12

Table 2a and 2b. GC method for PBDEs, PCBs, and PCDD/Fs analysis.

For the PBDEs, PCBs, and PCDD/Fs method, the separation of the closely eluting hexachlorodibenzo-p-furan (HxCDF) congeners 1,2,3,4,7,8- and 1,2,3,6,7,8-HxCDF is shown in Figure 3. A 25% valley is retained for the co-eluting 1,2,3,4,7,8- and 1,2,3,6,7,8-HxCDF congeners using both N₂ and He separations, as specified in the EPA 1613 analytical guidance.² In addition to both analytical assays retaining critical separations when using N₂ carrier gas, a faster run time was achieved. The reduced lifetime of the GC filaments traditionally caused during electron ionization when using N₂ carrier gas is eliminated by the use of an atmospheric pressure chemical ionization MS source. Thus far no negative implications from the use of N₂ as a carrier gas have been observed or are expected.

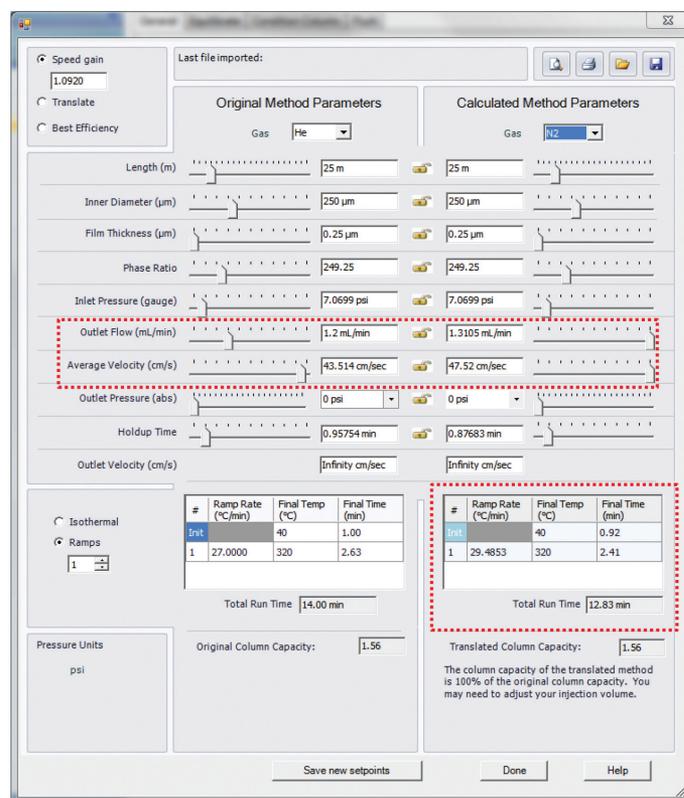


Figure 2. Method converter within UNIFI instrument control updates parameters based on the physical properties of N₂ carrier gas.

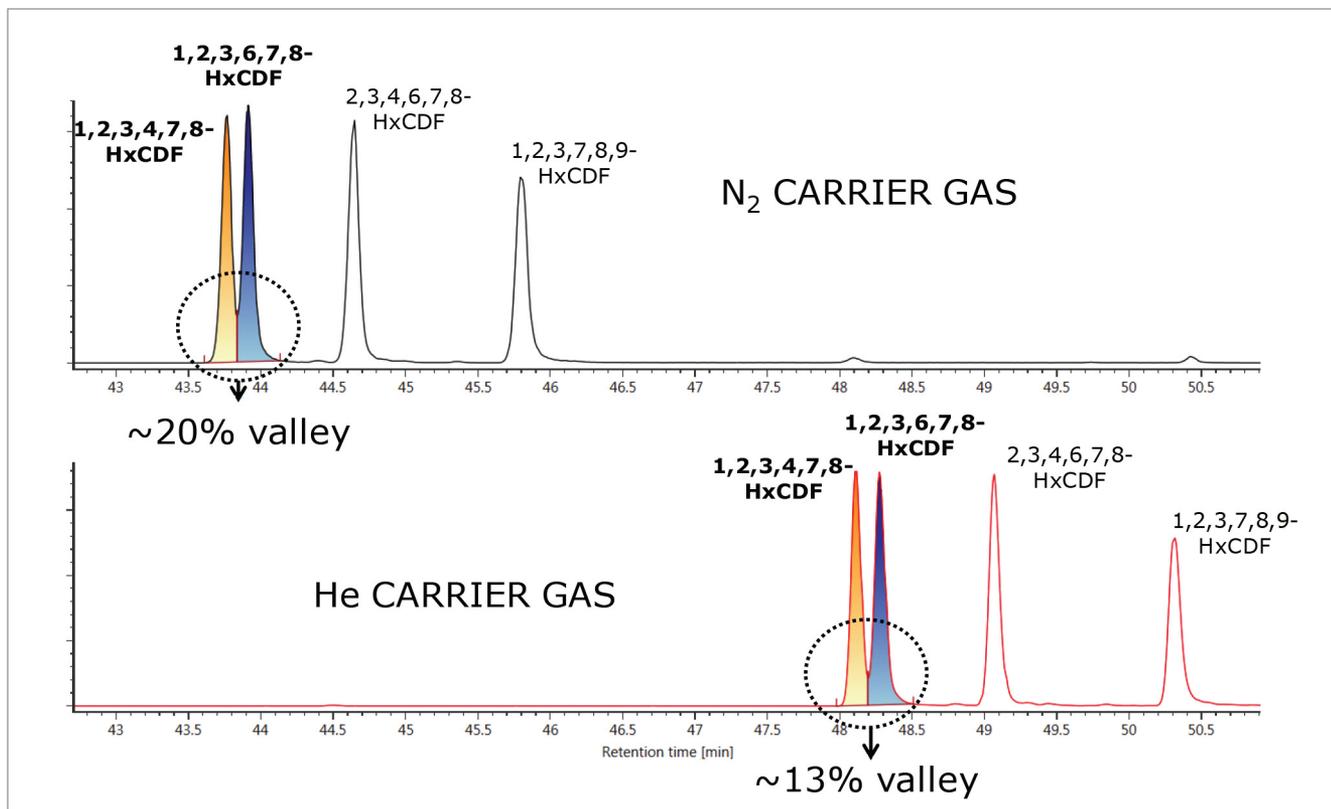


Figure 3. HxCDFs separation contrasting N_2 and He carrier gases, where both gases ensure the method requirement of 25% valley separation is achieved for the congeners specified.

SUMMARY

Nitrogen can be used as a single gas source for both GC carrier and MS source gas flows using the APGC source, and presents a viable replacement option to Helium carrier gas. N_2 optimized GC temperature program methods require less time without sacrificing critical separations for the pesticides and POPs analyses studied.

References

1. Harvey C. "The world is running dangerously low on helium. This discovery reinflates our supply." *The Washington Post*, June 26, 2016. Accessed Dec. 28, 2016.
2. U.S. E.P.A Method 1613 Rev. B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (1994).

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Waters Corporation
 34 Maple Street
 Milford, MA 01757 U.S.A.
 T: 1 508 478 2000
 F: 1 508 872 1990
 www.waters.com