HARNESSING THE EFFICIENCY OF N_2 CARRIER GAS WITH AN ATMOSPHERIC PRESSURE MASS SPECTROMETER SOURCE

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INTRODUCTION

Helium (He) is the most commonly used carrier gas in gas chromatography applications; however recent global shortages have resulted in increasing costs[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 include lower diffusivity than He or hydrogen and often longer run times to achieve similar separations. Here we show GC coupled with an atmospheric pressure ionization mass spectrometry, which utilizes N_2 for both ionization and make-up flow. This approach allows a single gas source to be used for chromatographic separation as well as ionization. Following automated method transfer calculations available within the software, efficient and comparable chromatography using N_2 carrier gas were achieved for pesticides, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and chlorinated dioxin/furans (PCDD/Fs). Unlike traditional electron ionization, atmospheric pressure ionization is resilient to the introduction of N_2. Also, higher gas load allowance into the atmospheric pressure source afforded flexibility with regards to method translation such that appropriate velocities could be achieved for N_2 carrier gas.

MATERIALS AND METHOD

Experiments were performed an a Xevo XS QTof MS system interfaced with an atmospheric pressure gas chromatography (APGC) inlet (Figure 1). Ionization was performed using chemical ionization, such that protonation (resulting in the $[M+H]^+$ ion) or charge transfer (resulting in the $M\bullet^+$ ion) reactions occurred. The GC (Agilent 7890B) method for pesticides is described in Table 1, and for the analysis of PBDEs, PCBs and PCDD/Fs in Table 2. Methods were revised using automated software (shown in Results and Discussion) method transfer for optimum conditions using N_2 as a carrier gas.

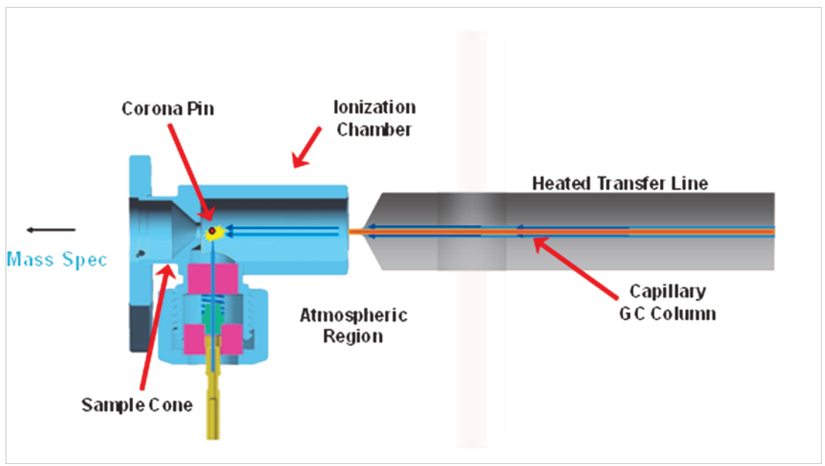

Figure 1: MS and GC atmospheric source interface. Nitrogen is supplied to the source from the heated transfer line, as well as cone and auxillary gas supplies.

Table 1: GC method for pesticide analysis.

Parameter	Value
Column	DB 5MS 30m x 0.25 mm 0.25µm (J&W)
Carrier gas	**Helium or Nitrogen**
Injection mode	Splitless
Liner	Gooseneck Splitless, Deactivated (Restek)
Column pneumatics	Constant flow
Column flow (mL/min)	**1.2 or 1.3105**
Injector temperature (° C)	280

Temperature (° C)	Temperature Ramp(° C/min)	Hold time (min)
40		**1.00 or 0.92**
320	**27 or 29.4853**	**2.63 or 2.41**

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

Parameter	Value
Column	Rxi 5Sil 60m x 0.25 mm 0.25µm (Restek)
Carrier gas	**Helium or Nitrogen**
Injection mode	Splitless
Liner	Gooseneck Splitless, Deactivated (Restek)
Column pneumatics	Constant flow
Column flow (mL/min)	**1.0 or 1.0866**
Injector temperature (° C)	280

Temperature (° C)	Temperature Ramp(° C/min)	Hold time (min)
120		**2.00 or 1.84**
200	**35 or 38.0309**	**0.00**
215	**5 or 5.4330**	**18.00 or 16.57**
235	**5 or 5.4330**	**7.00 or 6.44**
290	**5 or 5.4330**	**5.00 or 4.60**
325	**7.3 or 7.9322**	**2.30 or 2.12**

RESULTS AND DISCUSSION

Comparable separations using N_2 carrier gas were achieved following method calculations contained within the software (UNIFI, Waters Corporation). Figure 2 shows the calculator, and the increase of the Outlet Flow rate (mL/min.) and resulting Average Velocity (cm/s) resulted in a shortened method (12.83 min.) when N_2 carrier gas was used as compared to He (14.00 min.). In the case of pesticides, a shorter run time was attained (Figure 2) whilst maintaining separation of analytes as seen. 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. 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 N_2 and He separations, as specified in the EPA 1613 analytical guidance[2]. In addition to both analytical assays retaining critical separations when using N_2 carrier gas, but a faster run time for both analyses in achieved. Damage traditionally caused to the GC filaments when using N_2 carrier gas is eliminated by the use of an atmospheric chemical ionization MS source, and thus far no negative implications from the use of N_2 as a carrier gas are apparent or expected.

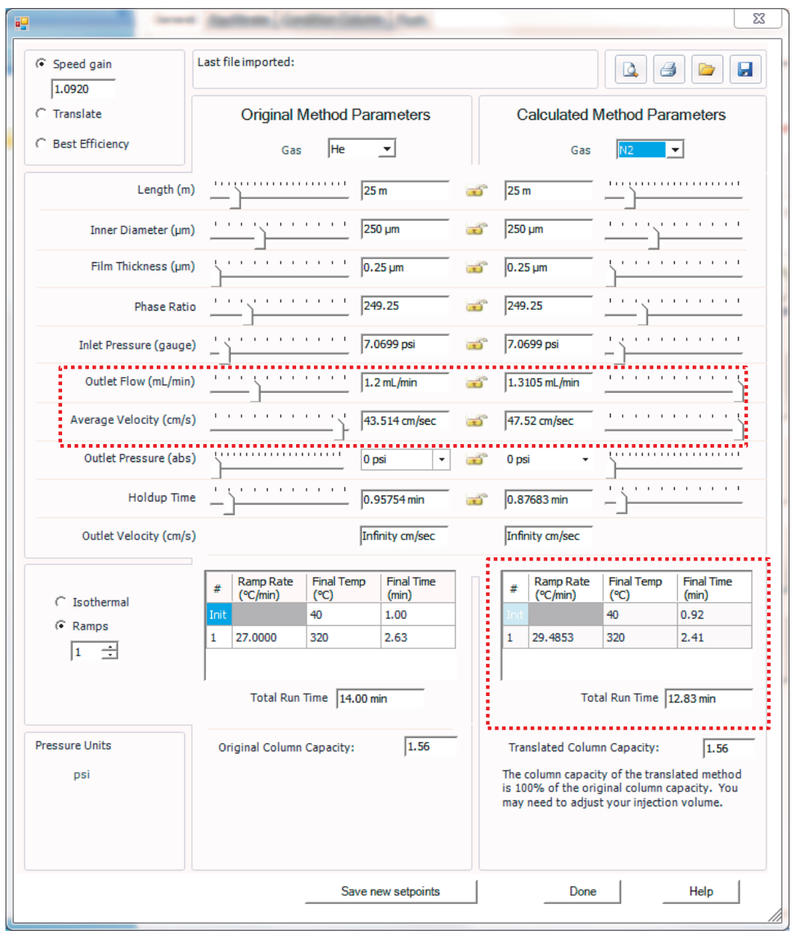

Figure 2: Method converter within UNIFI software updates parameters based on the physical properties of N_2 carrier gas.

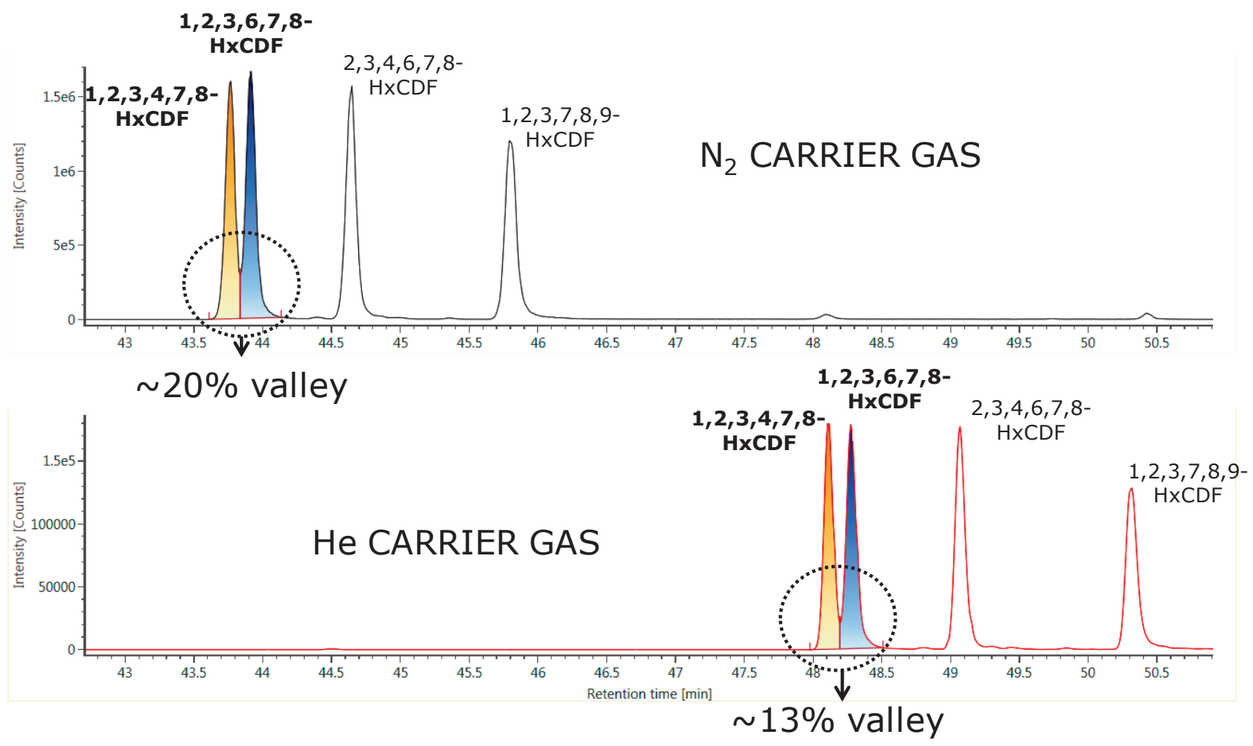

Figure 3: HxCDFs separation contrasting N_2 and He carrier gases.

CONCLUSIONS

- **N_2 can be used a single gas source for both GC carrier and MS source gas flows using the APGC source**
- **Updated GC ramp methods to are less time without sacrificing critical separations for pesticides and POPs when using N_2 carrier gas**
- **N_2 presents a viable replacement option to He for GC applications when coupled to an atmospheric pressure MS source**

REFERENCES

1. Plummer, Brad. "Congress Turns Its Attention To... America'S Helium Crisis". *Washington Post* 2012. Web. 24 June 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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