

Poster Reprint

ASMS 2022
Poster number TP151

A Novel EI Source Optimized for Use with Hydrogen Carrier Gas in GC/MS and GC/MS/MS

Anastasia Andrianova, Angela Smith Henry, Amanda
McQuay, and Bruce Quimby

Agilent Technologies, Little Falls Site, Wilmington, Delaware

Introduction

Recent concerns with the price and availability of helium have led laboratories to look for alternative carrier gases for their GC/MS and GC/MS/MS systems. For GC/MS, hydrogen is the best alternative to helium. Among the problems encountered when converting to hydrogen carrier gas is that hydrogen is a reactive gas and may cause chemical reactions in the EI source. This can lead to disturbed ion ratios in the mass spectrum, spectral infidelity, and in some cases peak tailing.

This poster presents a novel EI source developed to address the hydrogen-related source issues and provide improved performance with hydrogen carrier gas in GC/MS and GC/MS/MS analysis. Semi-volatile organic compounds (SVOCs) from US EPA Method 8270 are used to evaluate performance of the source with respect to peak shape, initial calibration (ICAL) and spectral fidelity when searched against NIST.

Experimental

HydroInert Source.

The new EI source optimized for use with hydrogen is dimensionally similar to the current Agilent Inert Extractor (Inert Plus) source but fabricated with a proprietary alternative material. The HydroInert source [1] is a direct replacement for the Inert Extractor and can be used in all 5977 Series MSDs originally equipped with the Inert Xtr, as well as all 7000B and later GC/TQ systems.

GC/MS Configuration.

Three identically configured systems were used. The instrument configuration is shown in Fig. 1. Each system consists of an Agilent 7890B GC with 7693 Autosampler and 5977A Inert Xtr MSD. The HydroInert source with a 9 mm extractor lens was installed. The column and method parameters are listed in Table 1.

The 0.18 mm id column chosen gives excellent resolution and is compatible with hydrogen's lower viscosity. The MMI is a temperature programmable inlet which in this work is ramped from 200 °C to 320 °C to minimize reactions of analytes with the H₂ carrier in the inlet. This is especially important when using DCM as the solvent, which at temperatures above ~230 °C can form HCl and cause problems in the inlet and column [2].

Experimental

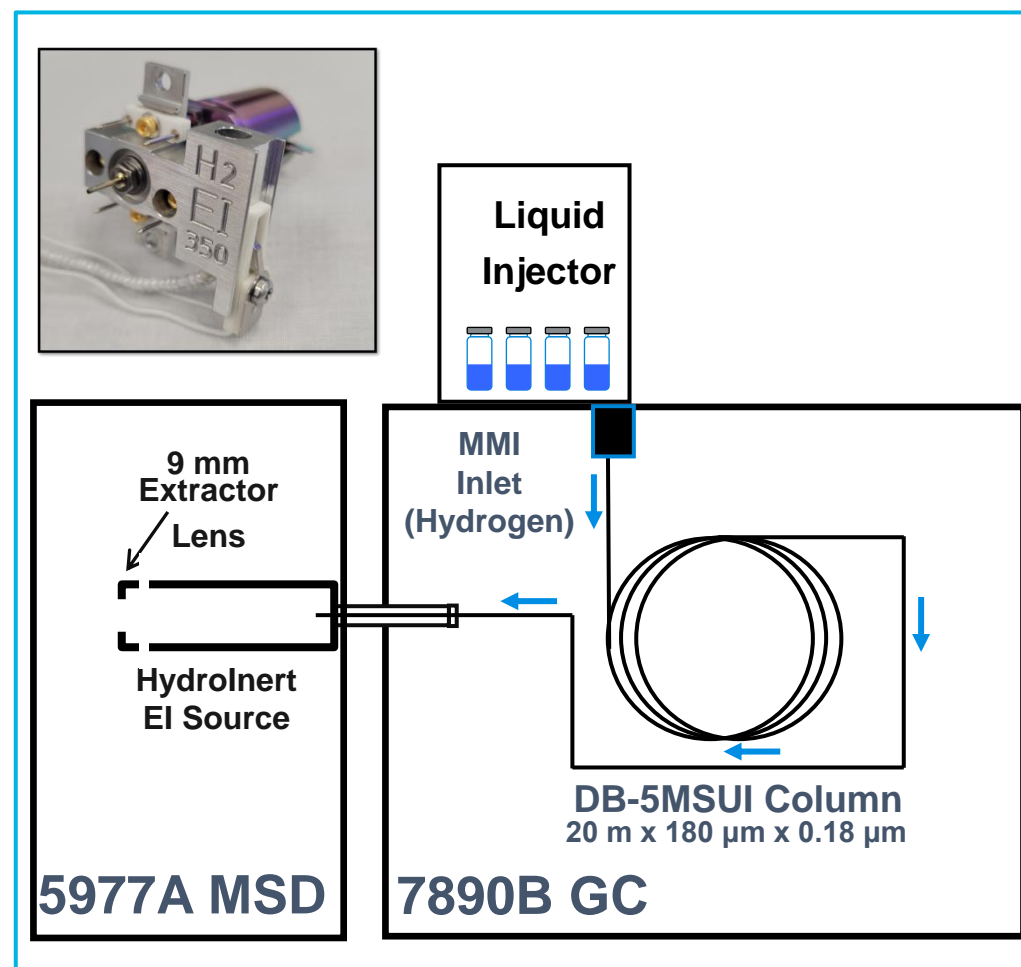


Fig.1 HydroInert Xtr Source (top) and system configuration (bottom).

GC conditions	
MMI Inlet Temperature Ramp	200 °C (0.2 min), 200 °C/min to 320 °C (0 min)
Inlet Liner	5190-2295 UI, low pressure drop
Carrier Gas	Hydrogen, 1.25 mL/min constant flow
Injection Mode	Split, Split Ratio 20:1
Carrier gas	Helium, constant flow 1.2 mL/min
Oven program	40 °C(0 min), 30 °C/min to 320 °C,(2 min)
GC Column	DB-5MSUI 20 m x 0.18 mm x 0.18 μm
MS conditions	
Solvent Delay	0.85 min
Tune	ETUNE, except where noted
EM gain	0.25
Scan Range	40-540 Da
Scan Speed	A/D Samples 2, TID on
Temperatures	
Source	300 °C
Transfer Line	320 °C
Quad	150 °C

Table 1. Experimental parameters.

Standards.

A total of 10 calibration levels ranging from 0.1 to 100 ppm were prepared in dichloromethane using a 77-compound mix and six internal standards (ISTDs) (AccuStandard). ISTD concentration was at the midpoint (4 ppm), and the method was retention time locked to acenaphthene-d10.

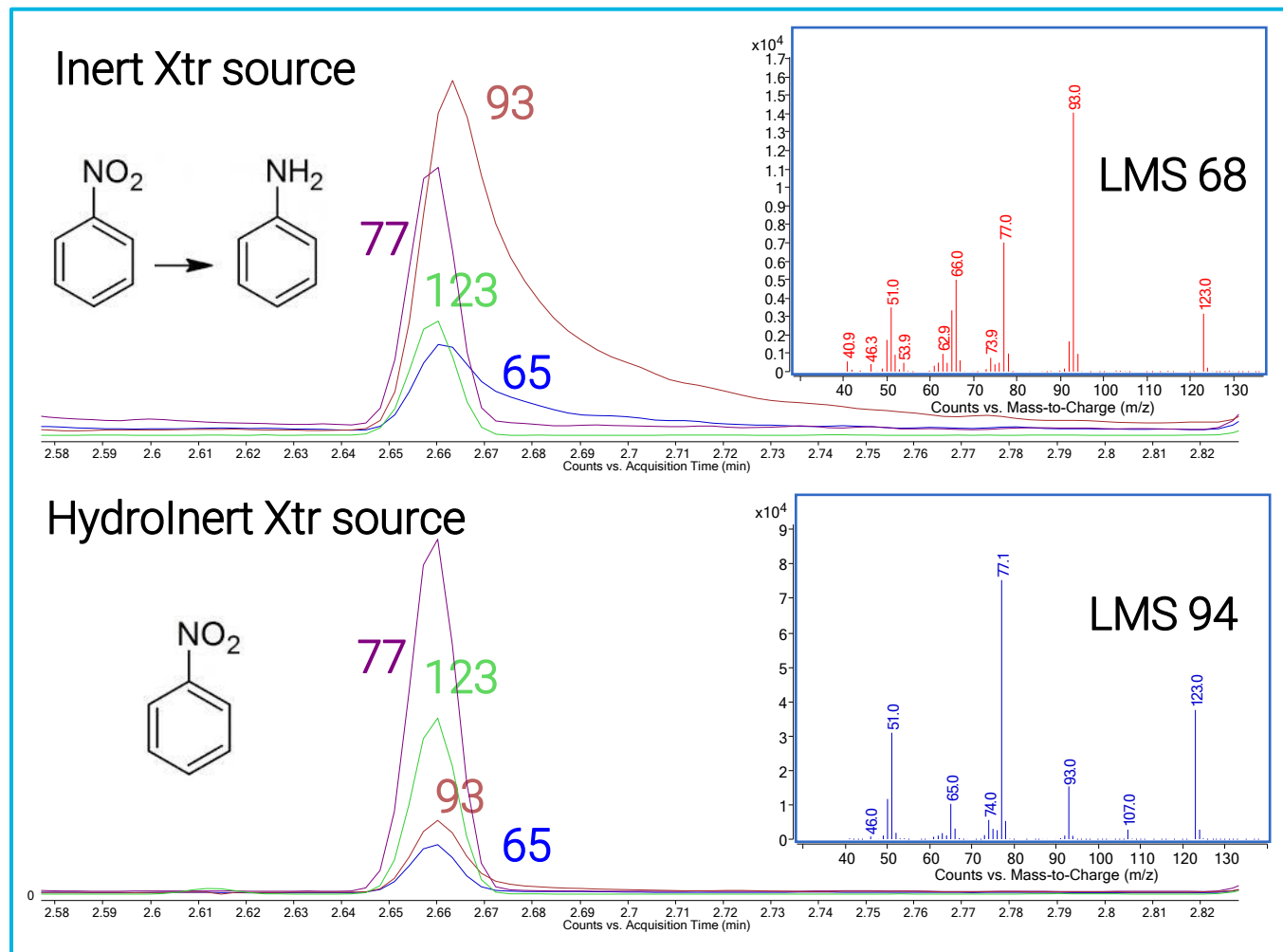


Fig.2 Nitrobenzene peak (50 ppm) EICs and Spectra with Inert Xtr 9 mm(top) and Hydrolnert Xtr 9 mm (bottom).

Reduced Hydrogenation of Nitrobenzene.

In the presence of H₂ and hot metal, like that in a typical source, nitrobenzene is readily hydrogenated to aniline. Figure 2 shows the problem. The Inert Xtr with a 9 mm lens (top) reduces the problem, but still produces spectra that are a poor NIST match for nitrobenzene and are often misidentified as aniline. The tailing of the 93 and 65 EICs shows this is a surface reaction.

The EICs and spectra acquired with the Hydrolnert 9 mm source show dramatic improvement.

Improved Peak Shape.

Figure 3 compares the TICs for the 50 ppm SVOCs standard with the two sources. The chromatograms exhibit significantly improved peak shape and chromatographic resolution with the Hydrolnert source, especially for the late eluting PAHs.

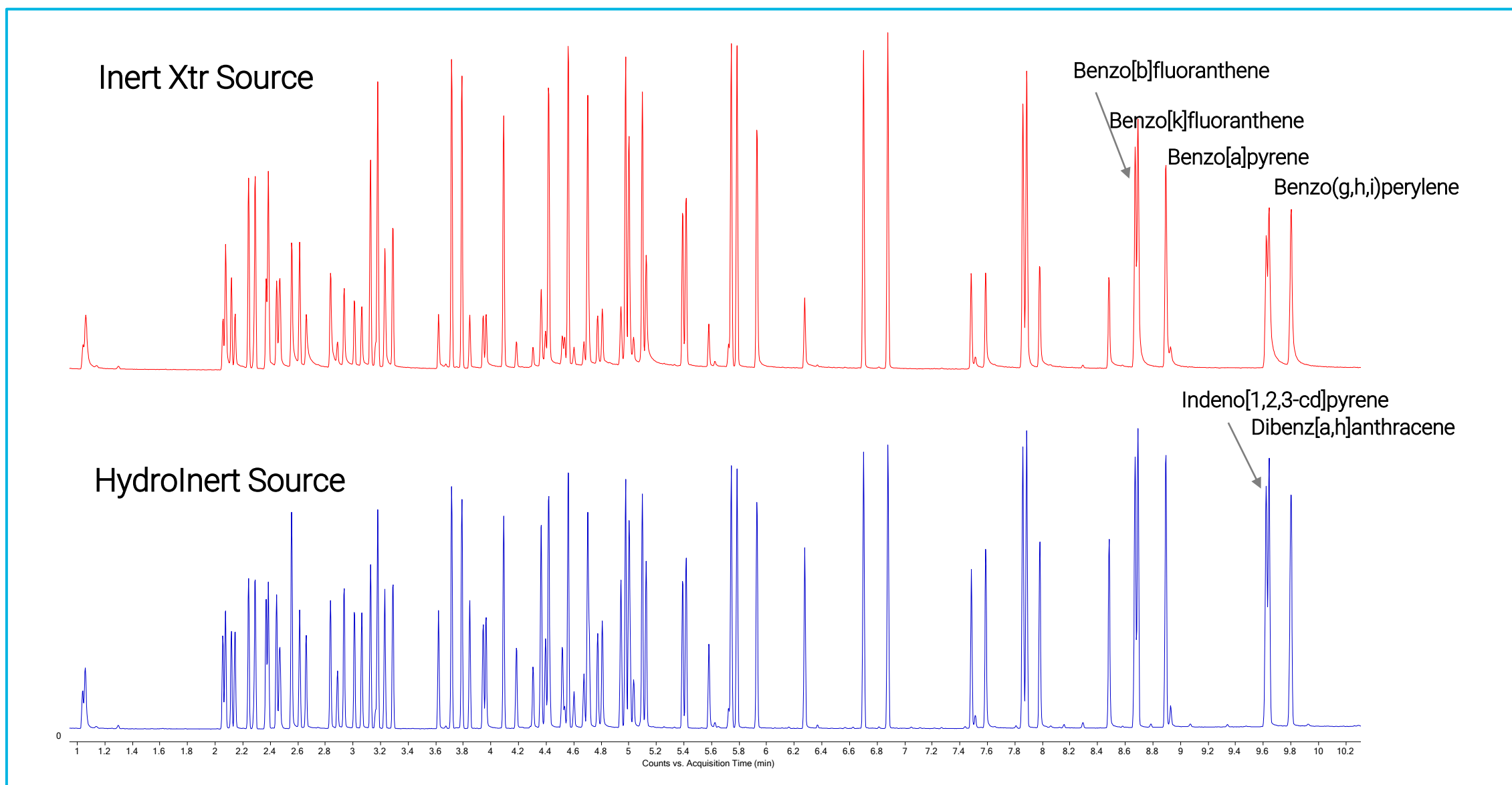


Fig.3 SVOCs calibration standard (50 ppm) TICs with Inert Xtr 9 mm(top) and Hydrolnert Xtr 9 mm (bottom).

Results and Discussion

Tune Type	System	# compounds met Average RF RSD < 20 criteria (out of 68 RC)	# compounds linear fit passing $R^2 > 0.99$ and accuracy 30% criteria	# compounds with quadratic fit and met $R^2 > 0.99$ and accuracy criteria	# compounds that had to be manually revised	Average RF RSD
Etune	A	53	2	13	9	12.80
Etune	B	53	5	10	8	11.93
Etune	C	57	1	10	14	13.18
Etune	C	55	5	8	8	11.75
Atune	C	57	2	9	7	11.70
Etune	A	58	3	7	15	11.25
Atune	A	59	3	6	8	9.85
Etune	A	42	6	20	25	18.57
Atune	A	43	0	25	26	17.72

Table 2. Comparison of 8270 initial calibration results with Hydrolnert Xtr 9 mm (blue box) and Inert Xtr 9 mm (red box).

Spectral Match Quality When Searched Against NIST 20.

The spectra from the scan files of the 50 ppm standard in Fig. 3 were deconvoluted and the spectra searched against NIST 20 using MassHunter Unknowns Analysis. Spectral matches with the Inert Xtr 9 mm for the 72 compounds ranged from 68 to 100, with 8 compounds having LMS values less than 90. With the Hydrolnert source, LMS values ranged from 83 to 99, with 6 compounds having LMS values less than 90. The average of LMS values for the Inert was 94.6 and for the Hydrolnert was 96.1. Both sources did well, but the Hydrolnert had better results for compounds with, for example, nitro groups.

Conclusions

Evaluation of the Hydrolnert source with the diverse set of compounds in US EPA 8270 has demonstrated:

- Significantly reduced in-source hydrogenation of compounds like nitrobenzene.
- Noticeably improved peak shapes, especially for the later eluting PAHs.
- Much better linearity as measured by the ICAL criteria of US EPA 8270.
- Excellent spectral fidelity with high library match scores vs NIST 20.

Note that helium is a better carrier gas for GC/MS(/MS), but if circumstances warrant conversion to hydrogen, the Hydrolnert source offers many advantages.

References

¹ Agilent Inert Plus Hydrolnert GC-MS System: Applying H₂ Carrier Gas to Real World GC-MS Analyses (Technical Overview) 5994-4889EN.

² Personal communication, Fred Feyerherm 11-20-2018.

Improved 8270 (ICAL) Performance.

Table 2 lists the 8270 ICAL results obtained on 3 identically configured systems with the Hydrolnert 9 mm and the Inert Xtr 9 mm sources in both ETUNE and ATUNE modes. Ten concentration levels ranging from 0.1 to 100 ppm were used and acquired in SIM mode. The quality of an ICAL is judged by:

- Maximizing the number of compounds that meet the average RF RSD criteria of <20%.
- Minimizing the number of compounds that require a linear fit, passing $R^2 > 0.99$ and the 30% accuracy criteria.
- Minimizing the number of compounds that require a quadratic fit, passing $R^2 > 0.99$ and the 30% accuracy criteria.
- Minimizing the number of compounds that require being manually revised.
- Minimizing the average response factor RSDs.

As can be seen in Table 2, the Hydrolnert source produces much better results than the Inert Xtr when using hydrogen carrier gas.