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Faster Qualitative Analysis of Essential Oils Using GC/MS with Hydrogen Carrier Gas and a Hydrogen Optimized EI Source

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Introduction

Due to the price of helium (He), many laboratories are looking for alternative carrier gases for their gas chromatography/mass spectrometry (GC/MS) methods. This work describes the conversion of a GC/MS method for the identification of flavor and fragrance compounds in essential oils from helium to hydrogen (H_2). A single quadrupole GC/MS system was used with hydrogen carrier gas and an EI source optimized to provide spectral fidelity with hydrogen. To increase confidence in compound identifications, deconvoluted mass spectra and linear retention indices (RI) were searched against the NIST23 mass spectral library. A column and chromatographic conditions for hydrogen were chosen that reduce the analysis time by 2.5 times compared to the helium method and generates results comparable to helium.

Experimental

HydroInert Source

The HydroInert source is an EI source optimized for use with hydrogen carrier gas. Due to its inert nature, it minimizes undesirable in-source chemical reactions between the analytes and hydrogen. This results in improved library match scores (LMS) vs helium-based libraries and allows using the same target ions in GC/MS and MRM transitions in GC/MS/MS. This makes the transition of methods from helium to hydrogen much easier.

Considerations for GC/MS Method Conversion

The following should be considered when converting from helium to hydrogen.

- Review the document “The EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion Guide” [1] for detailed instructions for method conversion from He to H_2 carrier. This covers all aspects, including H_2 safety, you should consider.
- Use Agilent’s Method Translation calculator [2] to pick a column and parameters to obtain the same elution order as with the helium method. Since most helium methods use a 30 m x 0.25 mm id column, the 20 m x 0.18 mm version is a great place to start.
- The increased resolution afforded by hydrogen may allow the development of a faster method.

Results and Discussion

Translation of GC Method from Helium to Hydrogen

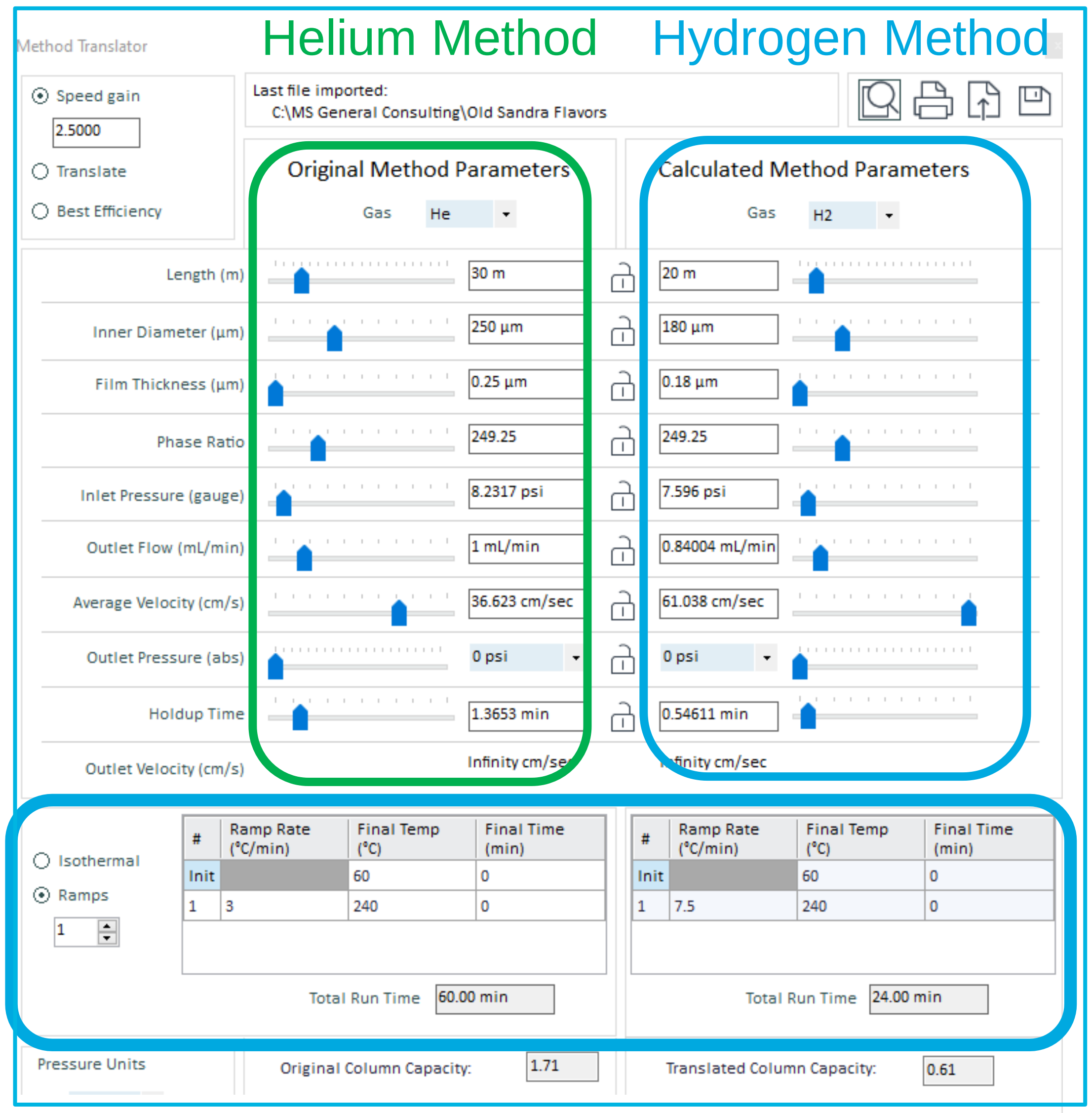
Figure 1 shows the Agilent Method Translation calculator used to design the H_2 method. The chromatographic parameters for He are entered in the left column and corresponding calculated H_2 parameters appear on the right. The calculator is designed to maintain the same elution order as with the original method. This is crucial with complex analyses and especially if retention indices (RI) are to be used. The chosen conditions allowed a 2.5 x speed increase, albeit with a predicted capacity 36% of the He method.

RI Calibration and Component Identification

RI calibration was performed with a custom mixture of all the n-alkanes from n-C_5 to n-C_{40} (Agilent). Compounds were identified using MassHunter Unknowns Analysis where the deconvoluted spectra were searched against NIST23 with RI time filtering.

Instrument Parameters

GC: Agilent 8890, MSD: Agilent 5977C
Injection: Split, split ratio 25:1, 250 °C, 1 µL volume
MSD Transfer Line: 300 °C, Source 300 °C, Quad: 150 °C
Source: 3 mm Inert Extractor (He), 9 mm HydroInert (H_2)
Solvent Delay: 2.2 min (He), 0.88 min (H_2)
Scan: 40-400 m/z, TID ON, A/D samples 8 (He), 4 (H_2)
Sample Preparation: Essential oils diluted to 5% in ethanol



● Speed gain 2.5000
○ Translate
○ Best Efficiency

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	Original Method Parameters	Calculated Method Parameters
Gas	He	H2
Length (m)	30 m	20 m
Inner Diameter (µm)	250 µm	180 µm
Film Thickness (µm)	0.25 µm	0.18 µm
Phase Ratio	249.25	249.25
Inlet Pressure (gauge)	8.2317 psi	7.596 psi
Outlet Flow (mL/min)	1 mL/min	0.84004 mL/min
Average Velocity (cm/s)	36.623 cm/sec	61.038 cm/sec
Outlet Pressure (abs)	0 psi	0 psi
Holdup Time	1.3653 min	0.54611 min
Outlet Velocity (cm/s)	Infinity cm/sec	Infinity cm/sec

○ Isothermal
● Ramps 1

#	Ramp Rate (°C/min)	Final Temp (°C)	Final Time (min)
Init		60	0
1	3	240	0

Total Run Time 60.00 min

#	Ramp Rate (°C/min)	Final Temp (°C)	Final Time (min)
Init		60	0
1	7.5	240	0

Total Run Time 24.00 min

Pressure Units
Original Column Capacity: 1.71
Translated Column Capacity: 0.61

Figure 1. Method Translation from He to H_2.

Fig. 2 shows the Total Ion Chromatograms (TIC) for the Brazilian orange oil with He and the translated H_2 methods. The H_2 method is 2.5 times faster and retains the same elution order and chromatographic resolution, but with reduced capacity.

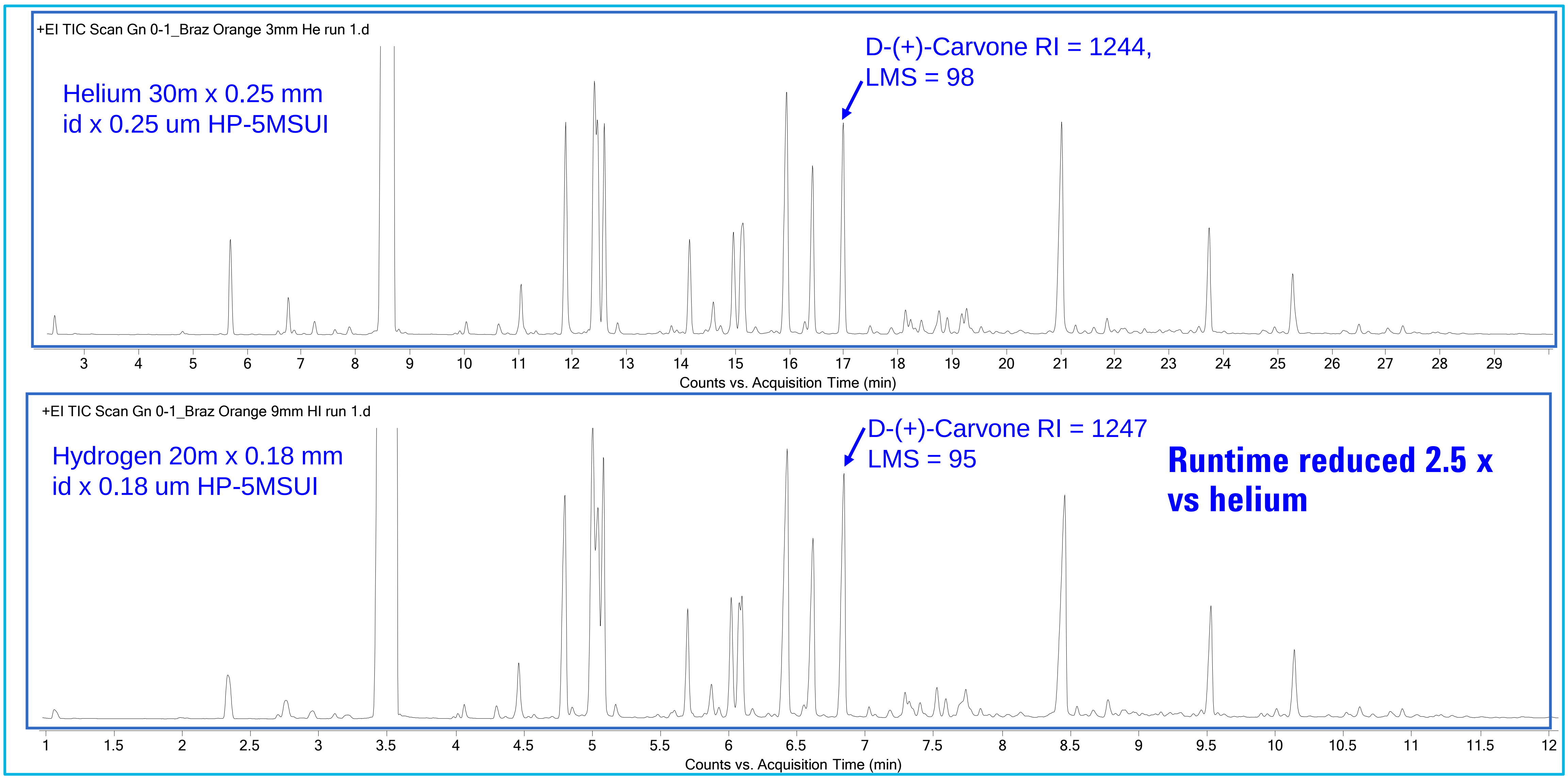

Figure 2. TIC chromatograms of Brazilian orange oil with helium (top) and the translated hydrogen method (bottom).

Spectral Fidelity With H_2

One of the problems with converting to H_2 carrier is the possibility of in-source hydrogenation reactions, which can result in spectral changes and poorer library match scores (LMS). The HydroInert source was developed to minimize these reactions.

As an example, Fig 3 shows the carvone oxide spectrum obtained with the H_2 method using the HydroInert source (top) and the conventional source (bottom). The NIST23 library reference spectrum for carvone oxide is inverted for comparison. The spectrum with HydroInert matches the NIST23 library reference spectrum with an LMS of 95.8. For comparison, the He method had an LMS of 95.5. With the standard 3 mm inert extractor and H_2, the spectrum exhibits changes due to in-source reactions and has a poorer LMS of 85. If the 9 mm inert extractor is used with H_2 instead of the 3 mm, spectral changes are still evident, but the LMS is improved to 91.2. As seen in Table 1, LMS scores with H_2 and HydroInert show excellent agreement with the He values. The exceptions are due to either lower response for small peaks with H_2 or overlapping peaks causing spectral interferences.

Measured RI Values With He and H_2

As seen Table 1 in the column listing the difference between the RI measured with helium and that with hydrogen (labeled RI He-RI H_2), the agreement of the RIs measured with both methods is excellent. The only exception is the earliest peak.

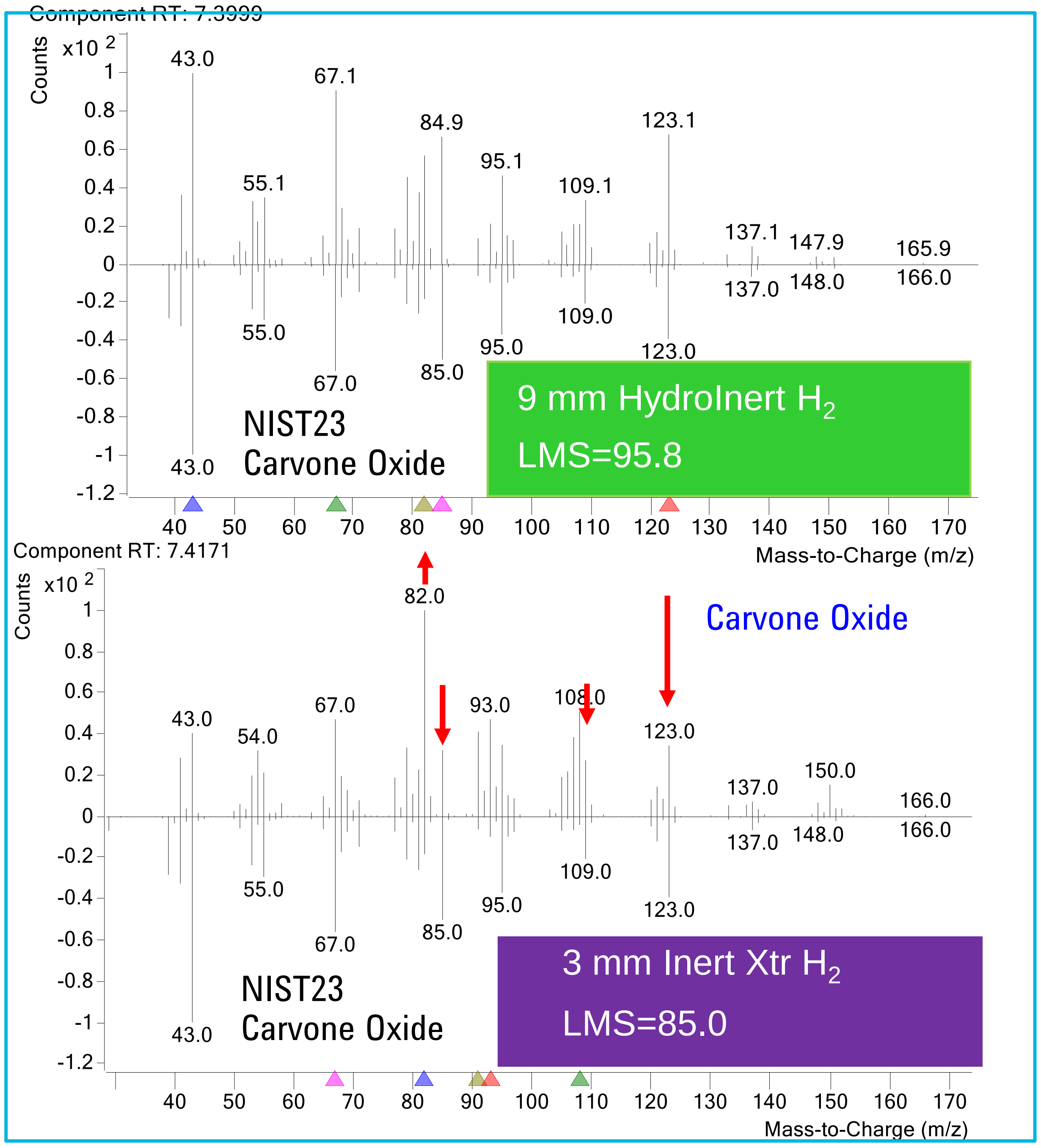

Figure 3. Deconvoluted spectra of carvone oxide with H_2 carrier gas and with HydroInert source (top) and standard inert extractor (bottom).

Table 1. Partial results for Brazilian orange oil comparing RI and LMS scores with the He and H_2 methods.

			Helium				Hydrogen with Hydroinert						
Compound Name	CAS	Lib RI	RT	RI	Delta RI	LMS	RT	RI	Delta RI	LMS	RI He-RI H_2	LMS He-LMS H_2	
Ethane, 1,1-diethoxy-	105-57-7	726	2.445	723	3	98	1.061	732	-6	96	-9	2	
Nonane	111-84-2	900	4.807	900	0	95	1.983	900	0	91	0	4	
(1R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	7785-70-8	932	5.688	933	-1	99	2.332	933	-1	97	0	2	
1-Heptanol	111-70-6	970	6.566	966	4	98	2.699	968	2	95	-2	2	
Bicyclo[3.1.0]hexane, 4-methylene-1-(1-methylethyl)-	3387-41-5	974	6.757	973	1	98	2.759	974	0	98	-1	0	
.beta.-Myrcene	123-35-3	991	7.240	991	0	97	2.953	992	-1	95	-1	2	
Octanal	124-13-0	1003	7.616	1004	-1	98	3.116	1006	-3	97	-2	1	
3-Carene	13466-78-9	1011	7.883	1011	0	98	3.211	1012	-1	89	-1	9	
D-Limonene	5989-27-5	1031	8.682	1034	-3	99	3.562	1037	-6	99	-3	0	
1-Methylbicyclo[2.2.1]heptan-exo-2-ol	766-25-6	1039	8.796	1037	2	76	3.593	1039	0	74	-2	2	
trans-Sabinene hydrate	17699-16-0	1070	9.837	1066	4	74	3.985	1067	3	77	-1	-3	
1-Octanol	111-87-5	1070	9.919	1068	2	98	4.016	1070	0	97	-2	1	
cis-Linalool oxide	5989-33-3	1074	10.039	1072	2	94	4.063	1073	1	94	-1	0	
trans-Linalool oxide (furanoid)	34995-77-2	1086	10.630	1088	-2	95	4.297	1089	-3	94	-1	0	
Benzene, 1-methyl-4-(1-methylethenyl)-	1195-32-0	1090	10.665	1089	1	91	4.306	1090	0	92	-1	-1	
Epoxymyrcene,6,7-	29414-55-9	1090	10.804	1093	-3	73	4.365	1094	-4	79	-1	-6	
Linalool	78-70-6	1099	11.051	1100	-1	97	4.462	1101	-2	95	-1	1	
Nonanal	124-19-6	1104	11.232	1104	0	96	4.533	1105	-1	86	-1	10	LR
cis-Pinen-3-ol	1010292-85-2	1108	11.324	1107	1	81	4.574	1108	0	73	-1	8	
2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethenyl)-, trans-	7212-40-0	1123	11.872	1120	3	95	4.799	1122	1	96	-2	-1	
5-Undecene, 4-methyl-	143185-91-5	1132	12.217	1129	3	74	4.925	1130	2	71	-1	4	
7-Oxabicyclo[4.1.0]heptane, 1-methyl-4-(1-methylethenyl)-	1195-92-2	1133	12.401	1133	0	86	5.003	1134	-1	90	-1	-4	
cis-p-Mentha-2,8-dien-1-ol	3886-78-0	1133	12.462	1135	-2	79	5.042	1137	-4	89	-2	-10	
(+)-(E)-Limonene oxide	6909-30-4	1139	12.586	1138	1	97	5.082	1139	0	98	-1	-1	

(LR indicates a small peak with low response when using H_2)

Conclusions

The data presented here shows that H_2 can successfully be used as a carrier gas for flavor and fragrance analyses with the proper conversion steps.

- The choice of the 20 m x 0.18 mm id x 0.18 µm film HP-5MSUI column allowed a 2.5 times faster analysis with equivalent chromatographic resolution.
- The Method Translation calculator provided chromatographic conditions that maintained the same elution order as with the He method, resulting in excellent agreement of the RI values measured with both methods.
- The use of MassHunter Unknowns Analysis software to deconvolute spectra and search them with RI filtering against the NIST23 library significantly simplified identification of the flavor components.
- The HydroInert EI source minimized in-source reactions with H_2, resulting in higher LMS values.

For further details on this work, please see reference 3. Reference 4 provides more information on flavor components that can react with H_2 in the source, and which benefit from the use of HydroInert.

Note that if He is available at an acceptable price, it is the preferred carrier for GC/MS and should be used. However, as shown in this work, H_2 can be used if appropriate method adjustments are made to accommodate its use.

Figure 4. The HydroInert source for hydrogen carrier gas on GC/MS.

References

[1]Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion. User Guide. 5994-2312EN, 2022.

[2]Agilent GC Calculators and Method Translation Software. Tools available for download from: https://www.agilent.com/en/support/gas-chromatography/gccalculators

[3]Qualitative Analysis of Essential Oils Using GC/MS with Hydrogen Carrier Gas and the Agilent HydroInert Source, Agilent, 5994-7058EN, 2024.

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