

Application News

No. SCA_280_100

Gas Chromatography Mass Spectrometry

Hydrogen as carrier gas for the high sensitive analysis of PCBs, PAHs, and VOCs

▪ Introduction

Helium is the most frequently used carrier gas in GCMS analysis. Due to its inertness it allows high sensitivity analysis combined with very good chromatographic separation. As the worldwide production of Helium is decreasing while the demand is permanently growing, Helium prices have doubled in the last 12 months. As the gap between supply and demand is expected to persist for longer times, further price increases are likely.

Hydrogen is known to be a very interesting alternative as carrier gas for GCMS. Especially, chromatographic separation can be improved by use of hydrogen. Unfortunately, hydrogen is not an inert gas. It is able to react with analytes and claimed to increase the background noise.

This application note shows the use of hydrogen as carrier gas for typical compound classes like PCBs, PAHs and VOCs. Main focus is drawn on the influence of hydrogen carrier gas on the instrument sensitivity. The QP2020 NX high performance turbo molecular pump (TMP) enables twinline setup, which allows easy vent free exchange between different applications.

▪ Standard preparation

60 VOCs (Stock solution: Restek Volatiles MegaMix 30603) have been diluted in 10 ml water in 20 ml headspace vials to give calibration levels between 0.05 ppb and 10 ppb.

6 typical indicator PCBs and 16 EPA PAHs have been diluted to give calibration levels between 0.5 and 200 ppb. PCB 209 was used as internal standard for PCBs analysis, deuterated Acenaphthene-D10, Chrysene-D12, and Benzo(a)pyrene-D12 for PAH analysis.



▪ Sample measurement

Samples were analyzed using a Shimadzu GCMS-QP2020 NX equipped with HS-20 and AOC-20i/s for sample injection. Hydrogen was used as carrier gas. For comparison reason also Helium was applied as carrier gas for PAH and PCB measurements.

HS-20 was used for the headspace analysis of VOC samples, while AOC-20i/s was used for the liquid injection of the PAH/PCB samples. A twinline, two-column setup was used so that the instrument can switch between headspace and liquid injections without any user intervention. This configuration maximizes system efficiency and flexibility whilst minimizing downtime.

▪ Measurement of VOC samples

Method details

Full separation of VOC samples was done on a SH-RTX-624Sil MS column (20m, 0.18mm, 1 μ m) in less than 7 minutes. Table 1 summarizes used parameters for VOC separation.

HS-20 parameter	
Incubation Temp.	70 °C
Incubation Time	10 min
Sample Lines	150 °C
Press. Pressure	60 kPa (Nitrogen)
Press. Time	1 min
Load Time	0.5 min
Injection Time	1 min
GC parameter	
Injection Mode	Split
Split ratio	40:1
Column	SH-Rxi-624Sil MS, 20 m, 0.18 mm, 1 µm (227-36075-01)
Lin. Velocity	66 cm/s (hydrogen)
GC Oven Method	40 °C, hold 0.3 min, 50 °C/min to 80 °C, 25 °C/min to 240 °C, hold 1 min
Transfer Line Temp.	250 °C
MS parameter	
Ion Source Temp.	250 °C
Emission Curr.	150 µA (high sensitivity)
Det. Volt.	1.5 kV
Ionization Mode	EI, 70 eV
Loop Time	0.15 s
Acq. Mode	Timed SIM

Tab.1: Parameters for VOC method

Sensitivity

Method sensitivity was evaluated by determination of signal to noise ratio (S/N) at the lowest calibration level using a root mean square approach. All 60 compounds were detectable (S/N >3:1) at 100 ng/L. 55 compounds were even detectable at 50 ng/L. Figure 1 shows some peak profiles of difficult compounds at 100 ng/L. Table 2 summarizes all S/N ratios at 100 ng/L.

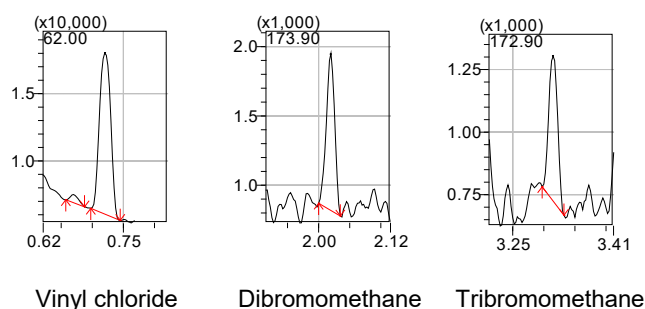


Fig. 1: Vinyl chloride, Dibromomethane, and Tribromomethane at 100 ng/L using hydrogen as carrier gas

Calibration

Linear regression of acquired data in the calibration in the range from 0.1 µg/L to 10 µg/L revealed excellent R²-values. Table 2 summarizes all R²-values.

Compound	S/N	R ²	Compound	S/N	R ²	Compound	S/N	R ²
Dichlorodifluoromethane	72	0.9998	1,2-Dichloropropane	17	0.9998	1,1,2,2-Tetrachloroethan	4	0.9999
Chloromethane	10	0.9999	Dibromomethane	10	0.9999	1,2,3-Trichloropropane	5	0.9996
Vinyl chloride	11	0.9999	Bromodichloromethane	10	0.9999	Bromobenzene	17	0.9998
Bromomethane	12	0.9994	cis-1,3-Dichloropropene	24	0.9999	n-Propylbenzene	77	0.9999
Chloroethane	8	0.9991	Toluene	86	0.9998	2-Chlorotoluene	60	0.9999
Trichlorofluoromethane	52	0.9999	trans-1,3-Dichloropropene	15	0.9999	1,3,5-Trimethylbenzene	114	0.9999
1,1-Dichloroethene	39	0.9999	1,1,2-Trichloroethane	17	0.9998	4-Chlorotoluene	52	0.9999
Methylene chloride	14	0.9999	Tetrachloroethene	46	0.9999	tert-Butylbenzene	114	0.9999
trans-1,2-Dichloroethene	32	0.9999	1,3-Dichloropropane	13	0.9999	1,2,4-Trimethylbenzene	101	0.9999
1,1-Dichloroethane	80	0.9999	Dibromochloromethane	4	0.9998	sec-Butylbenzen	67	0.9999
cis-1,2-Dichlorethen	19	0.9999	1,2-Dibromoethane	6	0.9999	4-Isopropyltoluene	243	0.9999
2,2-Dichloropropane	15	0.9994	Chlorobenzene	161	0.9998	1,3- Dichlorobenzene	99	0.9999
Bromochloromethane	8	0.9999	1,1,1,2-Tetrachloroethane	12	0.9998	1,4-Dichlorobenzene	93	0.9998
Trichloromethane	33	0.9999	Ethylbenzene	89	0.9999	n-Butylbenzene	130	0.9999
1,1,1-Trichloroethane	20	0.9999	p+m-Xylene	185	0.9999	1,2-Dichlorobenzene	92	0.9998
1,1-Dichloropropene	35	0.9999	p+m-Xylene	185	0.9999	1,2-Dibromo-3-chloropropane	6	0.9994
Tetrachloromethane	15	0.9999	o-Xylene	43	0.9999	1,2,4-Trichlorobenzene	51	0.9999
Benzene	45	0.9999	Styrene	83	0.9999	Hexachloro-1,3-butadiene	124	0.9999
1,2-Dichlorethan	13	0.9999	Tribromomethane	6	0.9995	Naphthalene	26	0.9997
Trichloroethene	62	0.9995	Isopropylbenzene	132	0.9999	1,2,3-trichlorobenzene	63	0.9998

Tab.2: S/N at 100 ng/L and R²-values for 60 VOC compounds

▪ **Measurement of PAH and PCB samples**

Separation of PAH and PCB samples was done on a fast SH-RXI-XLB column.

Two methods have been developed for hydrogen. Method 1 fully separates all 16 PAHs. Method 2 reduces GC run time by a factor of 2, but does not separate Dibenz(a,h)anthracene and Indeno(1,2,3-cd)pyrene.

Method 1 details (full separation)

Table 3 summarizes used parameters for full PAH and PCB separation.

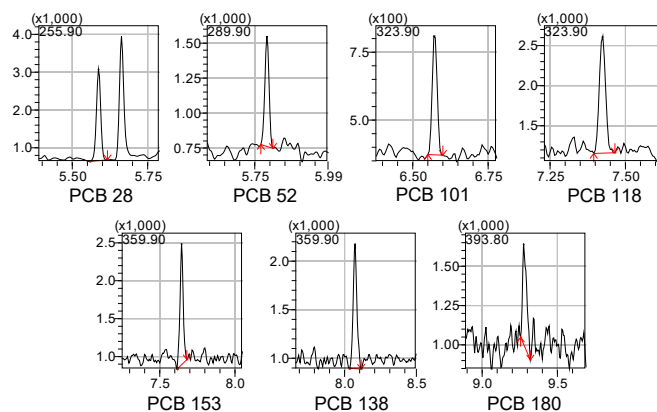


Fig. 2: PCBs at lowest level (0.5 µg/L)

GC parameter	
Injector	SPL -2030
Injection Volume	1 µL
Liner	Topaz 3.5 mm ID Single Taper Inlet Liner w/ Wool (980-19747)
Injector Temp.	300 °C
Injection Mode	Splitless
Splitless Time	1 min
High Press. Inj.	400 kPa (1 min)
Column	SH-Rxi-XLB, 20 m, 0.18 mm, 0.18 µm (227-36309-01)
Lin. Velocity	95 cm/s (hydrogen)
GC Oven Method	80 °C, hold 1 min, 30 °C/min to 220 °C, 5 °C/min to 265 °C, hold 2.5 min 30 °C/min to 310 °C, hold 1 min
Transfer Line	300 °C
MS parameter	
Ion Source	280 °C
Emission Curr.	150 µA (high sensitivity)
Det. Volt.	1.4 kV (1-6min), 1.6 kV (>6min)
Ionization Mode	EI, 70 eV
Loop Time	0.2 s (1-6min), 0.3 s (>6min)
Acq. Mode	Timed SIM

Tab.3: Parameters for full separation method

Sensitivity

Method sensitivity was evaluated by determination of signal to noise ratio (S/N) at the lowest calibration level using a root mean square approach. Figures 2 & 3 show the peak shapes of each quantifier at the lowest concentration level.

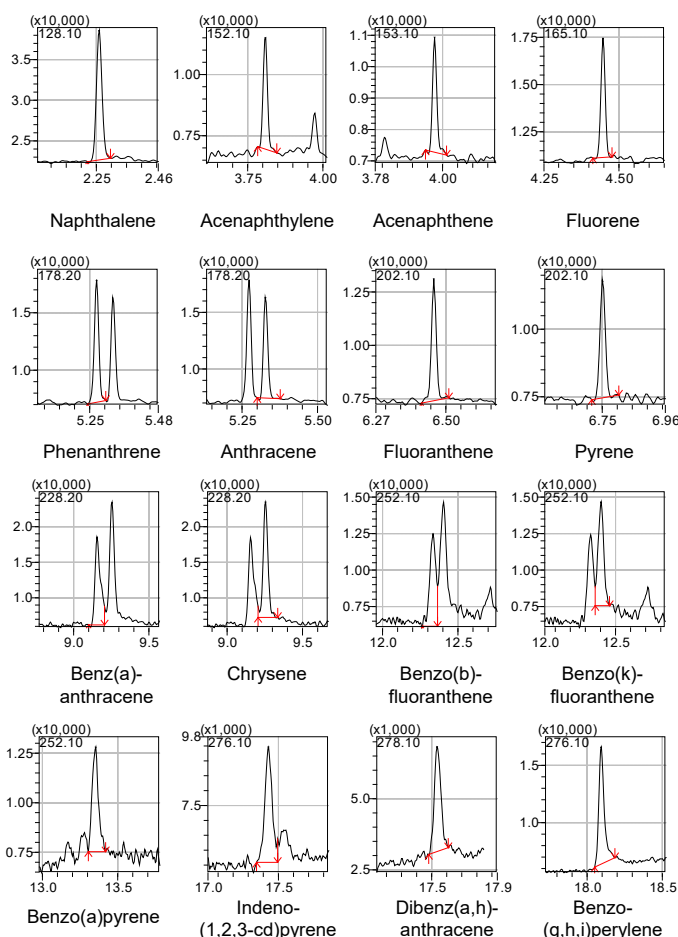


Fig. 3: PAHs at lowest level (0.5 µg/L)

Table 4 summarizes S/N values. No smoothing was applied to enable better comparability with Helium results.

Compound	S/N	Compound	S/N
Naphthalene	72	Benz(a)-anthracene	44
Acenaphthylene	20	Chrysene	58
Acenaphthene	18	Benzo(b)-fluoranthene	27
Fluorene	39	Benzo(k)-fluoranthene	32
Phenanthrene	58	Benzo(a)-pyrene	18
Anthracene	49	Dibenz(a,h)-anthracene	33
Fluoranthene	41	Indeno(1,2,3-cd)-pyrene	26
Pyrene	32	Benzo(g,h,i)-perylene	69
PCB 28	54	PCB 138	34
PCB 52	13	PCB 153	27
PCB 101	17	PCB 180	7
PCB 118	50		

Tab. 4: S/N at lowest level (0.5 µg/L)

Calibration data

Linear regression of acquired data in the calibration range from 0.5 µg/L to 200 µg/L revealed excellent R²-values. Table 5 summarizes these values.

Compound	R ²	Compound	R ²
Naphthalene	0.9999	Benz(a)-anthracene	0.9998
Acenaphthylene	0.9999	Chrysene	0.9999
Acenaphthene	0.9999	Benzo(b)-fluoranthene	0.9999
Fluorene	0.9999	Benzo(k)-fluoranthene	0.9998
Phenanthrene	0.9999	Benzo(a)-pyrene	0.9999
Anthracene	0.9999	Dibenz(a,h)-anthracene	0.9990
Fluoranthene	0.9999	Indeno(1,2,3-cd)-pyrene	0.9999
Pyrene	0.9990	Benzo(g,h,i)-perylene	0.9996
PCB 28	0.9998	PCB 138	0.9998
PCB 52	0.9997	PCB 153	0.9999
PCB 101	0.9998	PCB 180	0.9999
PCB 118	0.9999		

Tab.5: R²-values for full separation methods calibration

Method 2 details (fast separation)

Since not all regulations request a separation of Dibenz(a,h)anthracene and Indeno(1,2,3-cd)-pyrene a fast method (11 min runtime) was developed to minimize GC cycle times and improve lab efficiency. Table 6 summarizes parameters different from full separation method.

GC parameter	
GC Oven Method	80 °C, hold 1 min, 30 °C/min to 310 °C, hold 2 min
MS parameter	
Det. Volt.	1.4 kV
Loop Time	0.2 s

Tab. 6: Modified parameters for fast method

Sensitivity

Due to higher heating rates in the fast method later eluting compounds generate sharper peaks, which resulted in better S/N ratios for these compounds. Table 7 and 8 compare S/N ratios for PAH and PCBs, respectively.

Compound	fast	full
Naphthalene	119	72
Acenaphthylene	40	20
Acenaphthene	28	18
Fluorene	62	39
Phenanthrene	88	58
Anthracene	87	49
Fluoranthene	50	41
Pyrene	42	32
Benz(a)anthracene	108	44
Chrysene	162	58
Benzo(b)fluoranthene	42	27
Benzo(k)fluoranthene	50	32
Benzo(a)pyrene	29	18
Dibenz(a,h)anthracene	75	33
Indeno(1,2,3-cd)pyrene		26
Benzo(g,h,i)perylene	113	69

Tab. 7: S/N at lowest level (0.5 µg/L) for PAH

Compound	fast	full
PCB 28	80	54
PCB 52	23	13
PCB 101	31	17
PCB 118	25	50
PCB 138	39	34
PCB 153	32	27
PCB 180	20	7

Tab. 8: S/N at lowest level (0.5 µg/L) for PCB

Calibration data

Calibration was done using the same range between 0.5 µg/L and 200 µg/L. Regression results revealed similar R²-values like in full separation method. Lowest R²-value was 0.9995 for Pyrene, whereas the most compounds showed 0.9999.

Comparison between Hydrogen and Helium

Separation

Hydrogen is known to allow higher linear velocities while maintaining the separation efficiency. This has been investigated by resolution determination for Benzo(b)fluoranthene and Benzo(k)-fluoranthene. Hydrogen is capable of separating this pair using a linear velocity of 95 cm/s (Figure 4a). Helium is unable to show peak separation until the velocity is decreased to 40 cm/s (Figure. 4b)

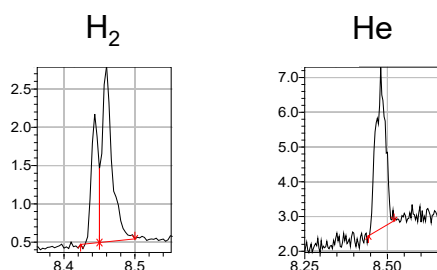


Fig. 4a: Separation of Benzofluoranthenes at 95 cm/s

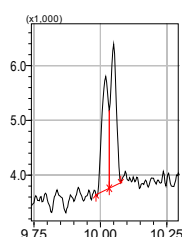


Fig. 4b: Separation of Benzofluoranthenes at 40 cm/s using He

To reach the same efficiency with Helium, the linear velocity needs to be reduced to 40 cm/s. This results in an increase of the retention of 1.5 min. Fig. 3b shows the peak separation.

Sensitivity

Hydrogen is very often claimed to create higher background noise, which results in lower sensitivity, looking at S/N ratios. Therefore, the influence of the carrier gas on the sensitivity was investigated at similar conditions using a 0.5 µg/L standard. Table 9 summarizes S/N ratios using the fast hydrogen method and a similar method using Helium. It is noteworthy that differences in S/N for lower m/z value are more pronounced than for higher m/z values. Nevertheless, the difference between Helium and Hydrogen is acceptable.

Compound	m/z	H ₂	He
Naphthalene	128.1	119	423
Acenaphthylene	152.1	40	85
Acenaphthene	153.1	28	73
Fluorene	165.1	62	86
Phenanthrene	178.2	88	103
Anthracene	178.2	87	96
Fluoranthene	202.1	50	99
Pyrene	202.1	42	95
Benz(a)anthracene	228.2	108	211
Chrysene	228.2	162	287
Benzo(b)fluoranthene	252.1	42	40
Benzo(k)fluoranthene	252.1	50	60
Benzo(a)pyrene	252.1	29	35
Dibenz(a,h)anthracene	276.1	75	72
Indeno(1,2,3-cd)pyrene	276.1		
Benzo(g,h,i)perylene	276.1	113	120

Tab. 9: S/N at lowest level (0.5 µg/L) for PAH

Figures 5a and 5b show the base lines for Naphthalene (m/z = 128.1) and Benzo(g,h,i)-perylene (m/z = 276.1) using a fixed scaling. It is evident that the baseline for Naphthalene is much higher using Hydrogen. This trend significantly lowers for Benzo(g,h,i)perylene. Therefore, it can be concluded that lower S/N ratios are mainly caused by low mass compound etched from the source due to use of hydrogen. The difference in signal to noise ratio shrinks with usage of high m/z values.

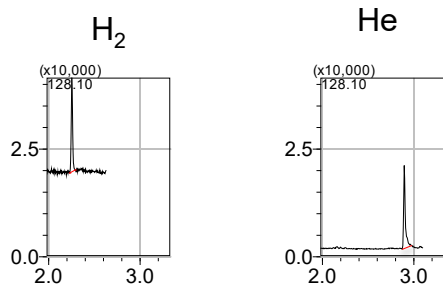


Fig. 5a: Naphthalene peak using fixed y-axis

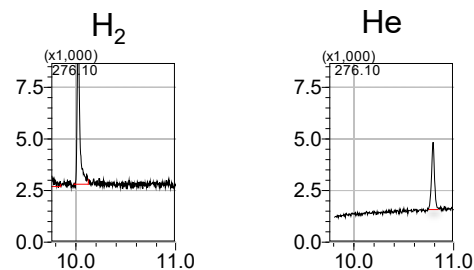


Fig. 5b: Benzo(g,h,i)perylene peak using fixed y-axis

PCBs show the same trend, but the influence of m/z is less pronounced. This is mainly caused by the higher starting m/z value, which is 259.9 for the PCB 28 in contrast to 128.1 for Naphthalene. Table 10 summarizes the determined S/N ratios using Hydrogen and Helium.

Compound	m/z	H ₂	He
PCB 28	255.9	156	174
PCB 52	289.9	23	26
PCB 101	323.9	31	48
PCB 118	323.9	25	49
PCB 153	359.9	39	74
PCB 138	359.9	32	52
PCB 180	393.8	20	23

Tab. 10: S/N ratio for PCBs using Helium and Hydrogen for a 0.5 µg/L sample

Figure 6a and 6b show the baselines for PCB 52 and PCB 180. It is evident that the baseline for hydrogen is only slightly higher than the baseline for helium.

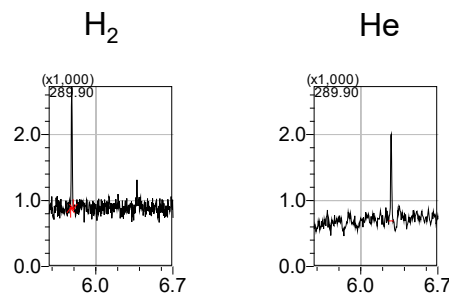


Fig. 6a: PCB 52 peak using fixed y-axis

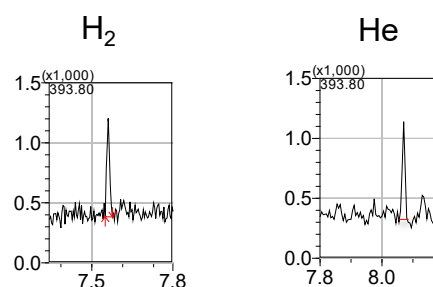


Fig. 6b: PCB 180 peak using fixed y-axis

Conclusion

Excellent sensitivity combined with a high linear dynamic range was shown for the analysis of PCBs, PAHs and VOCs utilizing hydrogen as carrier gas. The high efficiency TMP of GCMS-QP2020 NX enables this sophisticated twinline setup, which allows the parallel analysis of liquid and headspace samples without the need to do any hardware modifications between different applications.