High Flow Hydrogen in GC / MS: Why Not?

Ettore Guerriero*, Marina Cerasa, Simone Serrecchia, Silvia Mosca

Institute of Atmospheric Pollution Research - National Research Council of Italy, Strada Provinciale 35d, 9, Montelibretti (RM) 00010, Italy, ettore.guerriero@cnr.it

1 Introduction

The use of hydrogen in GC/MS is becoming more and more widespread given the enormous benefits that this carrier gas brings to chromatography. In fact, compared to helium, hydrogen brings many advantages and the most obvious are: cheapness, it is inexhaustible, it allows faster chromatographies [1, 2] All the authors in scientific journals and the technical applications of the various GC/MS manufacturers recommend reducing the diameter of the columns for the analysis of the different POPs in order to have a vacuum suitable for mass spectrometry is [3, 4, 5, 6]. In fact, the vacuum in low-resolution mass spectrometers is generally achieved by means of rotary pumps that bring the vacuum to about 1×10^{-3} Torr, sufficient to run the turbomolecular pumps that bring the vacuum up to 1×10^{-7} Torr.

In turbomolecular pumps, the compression of the pumped gas, and therefore the pumping efficiency, varies according to the square of its molecular mass [7]. The resulting compression ratios decrease with the molecular weight of the gas present in the GC/MS system. It is therefore expected that passing from helium to hydrogen as carrier gas, there will be a worsening of the vacuum levels of the mass spectrometer. Normally, optimal voids are between 1×10^{-6} - 1×10^{-7} in this way the average free path of the molecules that must be separated from the analyzer is such as not to create collisions between molecules/ions, increasing the transfer efficiency of the ions to the detector:

a) the collisions would produce a deviation of the trajectory and the ion could lose its charge by hitting the walls of the instrument

b) collisions with other molecules could produce unwanted reactions and therefore increase the complexity of the mass spectrum obtained.

In addition to the difficulty of pumping hydrogen compared to helium, the reduction in diameter is generally recommended by the fact that the Van Deemter equation with hydrogen shows optimal separation speeds around 35-60 cm/s. This also results in high carrier gas flows when considering columns with a diameter of 0.25 mm i.d. that is, flows ranging respectively between 1.25 and 2.5 ml/min. With these hydrogen flows in the mass spectrometer, high vacuum values are observed which can also lead to an automatic shutdown of the mass spectrometer if a maximum vacuum value is provided in the instrument management firmware, beyond which the filament should be switched off to make it safe. the instrument. Use columns with an internal diameter of 0.18 mm or 0.10 mm i.d. with film thicknesses of 0.18-0.10 μm, if on the one hand they preserve the vacuum, they have the contraindication of limiting the chromatographic capabilities by limiting the linear range of quantities of sample that can be analyzed. It therefore happens that in analyzes of environmental or food samples that chromatographic peaks can appear with shoulders due to column saturation, both for high concentrations of analyte and for the presence of interferents present in samples that are not perfectly purified. Furthermore, columns with small diameters are more prone to fouling and are less reproducible. All this happens because the manufacturers of mass spectrometers measure the vacuum incorrectly. In practice, it is forgotten that the vacuum measurement is a function of the residual gas present in the system being measured. Taking into account the correct vacuum measurement, PAHs analyzes were performed using hydrogen as carrier gas with the use of chromatographic columns with an internal diameter of 0.25 mm, increasing the flow of the carrier gas up to a speed of 100 cm/s (5 ml/min). In this way it is possible to have very fast analyzes with separations similar to those obtained with helium as carrier gas at a speed of 30 cm/s but with analysis times halved without invalidating the resulting mass spectrometry.

2 Materials and Methods

The tests were performed on a triple quadrupole GC/MS/MS equipped with an autosampler and PTV injector. Helium 5.0 (99.9990%) and hydrogen from an electrolytic cell hydrogen generator with silica gel residual water abatement system was used as carrier gas to which a further moisture reduction system based on molecular sieves. For the polycyclic aAromatic hydrocarbons (PAH) a column with a specific phase was used for their separation, 60 meter long with 0.25 mm i.d. and 0.1μm of phase thickness. The tests were performed using a PAH standard containing 27 analytes (PAH-STKB) and a 14-component peruterate PAH standard (LS429IS). The mixture of standards was diluted in toluene to form 5 calibration solutions with concentration from 2 pg/μl to 1000 pg/μl while keeping the concentrations of the labeled standards constant at 100pg/μl. The tests were performed with a column suitable for the analysis of PAHs of 60 m x 0.25 mm i.d. and 0.1 μm.

3 Results

First, we went to see the vacuum values in switching from helium to hydrogen by observing a high worsening of the vacuum with high flows of hydrogen. The following are the vacuum levels measured by the GC/MS system used:

Table 1: Different values including the vacuum obtained from the tune of the MS/MS spectrometer with different flows of He and H_2

He Flow 1.1 ml/min.		H_2 Flow 1.1 ml/min.		H_2 Flow 3.0 ml/min.	
EI Ion Source Type	EI	EI Ion Source Type	EI	EI Ion Source Type	EI
Polarity	Positive	Polarity	Positive	Polarity	Positive
Electron Lens Voltage	30 V	Electron Lens Voltage	30 V	Electron Lens Voltage	15 V
Electron Energy	40 eV	Electron Energy	40 eV	Electron Energy	70 eV
Emission Current	80 µA	Emission Current	80 µA	Emission Current	50 µA
Ion Guide Frequency	1711.6	Ion Guide Frequency	1711.6	Ion Guide Frequency	1711.6
Q1 Frequency	1093.3	Q1 Frequency	1093.3	Q1 Frequency	1093.3
Collision Cell Frequency	1850.4	Collision Cell Frequency	1850.4	Collision Cell Frequency	1850.4
Q3 Frequency	1092.1	Q3 Frequency	1092.1	Q3 Frequency	1092.1
Multiplier Voltage	1209.4 V	Multiplier Voltage	1203.0 V	Multiplier Voltage	1454.9 V
Detector Gain	3.0×10^5	Detector Gain	3.0×10^5	Detector Gain	1.1×10^6
MS Transfer Line	289.9 °C	MS Transfer Line	289.9 °C	MS Transfer Line	300.0 °C
Filament Selection	1	Filament Selection	1	Filament Selection	1
Ion Source Temperature	349.9 °C	Ion Source Temperature	349.9 °C	Ion Source Temperature	349.9 °C
Foreline Pressure	80 mTorr	Foreline Pressure	99 mTorr	Foreline Pressure	172 mTorr
Ion Gauge Pressure	3.8×10^{-6} Torr	Ion Gauge Pressure	1.1×10^{-5} Torr	Ion Gauge Pressure	2.5×10^{-5} Torr

It is observed that the vacuum measured by the Pirani (Foreline Pressure) between the rotary pump and the turbomolecular passes from a value of 80 mTorr with 1.1 ml/min of helium to 99 mTorr with 1.1 ml/min of hydrogen up to 172 mTorr with 3.0 ml/min of hydrogen. The high vacuum found in the chamber hosting the quadrupoles is measured with an Ion Gauge and from the value of $3.8x10^{-6}$ Torr in the presence of He it is reduced to $1.1x10^{-5}$ Torr with the same flow of 1.1 ml/min of H_2 having a worsening of the vacuum by a factor of 3. Using hydrogen at a flow of 3 ml min there is a worsening of the vacuum, compared to the flow of 1.1 ml min of He by a factor of 6.6. We proceeded to evaluate the worsening in spectrometric resolution in passing from the conditions of 1.0 ml min of helium, conditions normally used in GC MS, to the conditions found by our method of 5.0 ml/min of hydrogen.
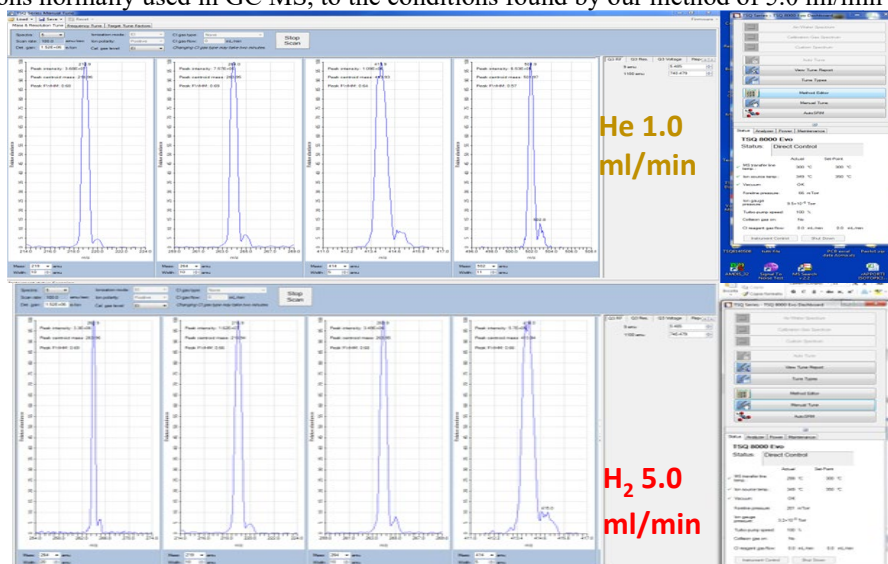

Figure 1: Above there is the standard tune obtained with a helium flow of 1.0 ml/min, below the standard tune with 5.0 ml/min of H_2. The mass intervals representing the typical fragments of perfluoroterbutylamine are shown, i.e. the m/z: 69, 219, 264, 414 and 502. At the top, each spectrometric peak is parameterized automatically by the software and the intensity of the signal, the maximum m/z detected on the centroid and the resolution of the peak at half height (Peak FWHM). On the right there is the low vacuum value at 51 mTorr and the high vacuum value at $2.7 x10^{-6}$ for helium while for hydrogen there is a low vacuum at 201 mTorr and a high vacuum at $3.2 x10^{-5}$.

From Figure 1 listed above it can be observed that the resolutions do not practically undergo significant variations as the vacuum varies. In practice, with hydrogen carrier gas flows at 5.0 ml/min, 11-times worsening of the vacuum is measured compared to the vacuum obtained with a helium flow of 1.0 ml min. By measuring the resolution of the characteristic fragments of Perfluoroterbutylamine it is observed that the resolution of the mid-height peaks (FWHM)

is practically similar, oscillating between 0.66 m/z and 0.68 m/z. Having ascertained that the mass spectrometer could support high hydrogen flows without significantly affecting the spectrometric resolution, the chromatographic separations for PAHs were evaluated considering above all the benzo[b,j,k]fluoranthenes, isomers difficult to separate.
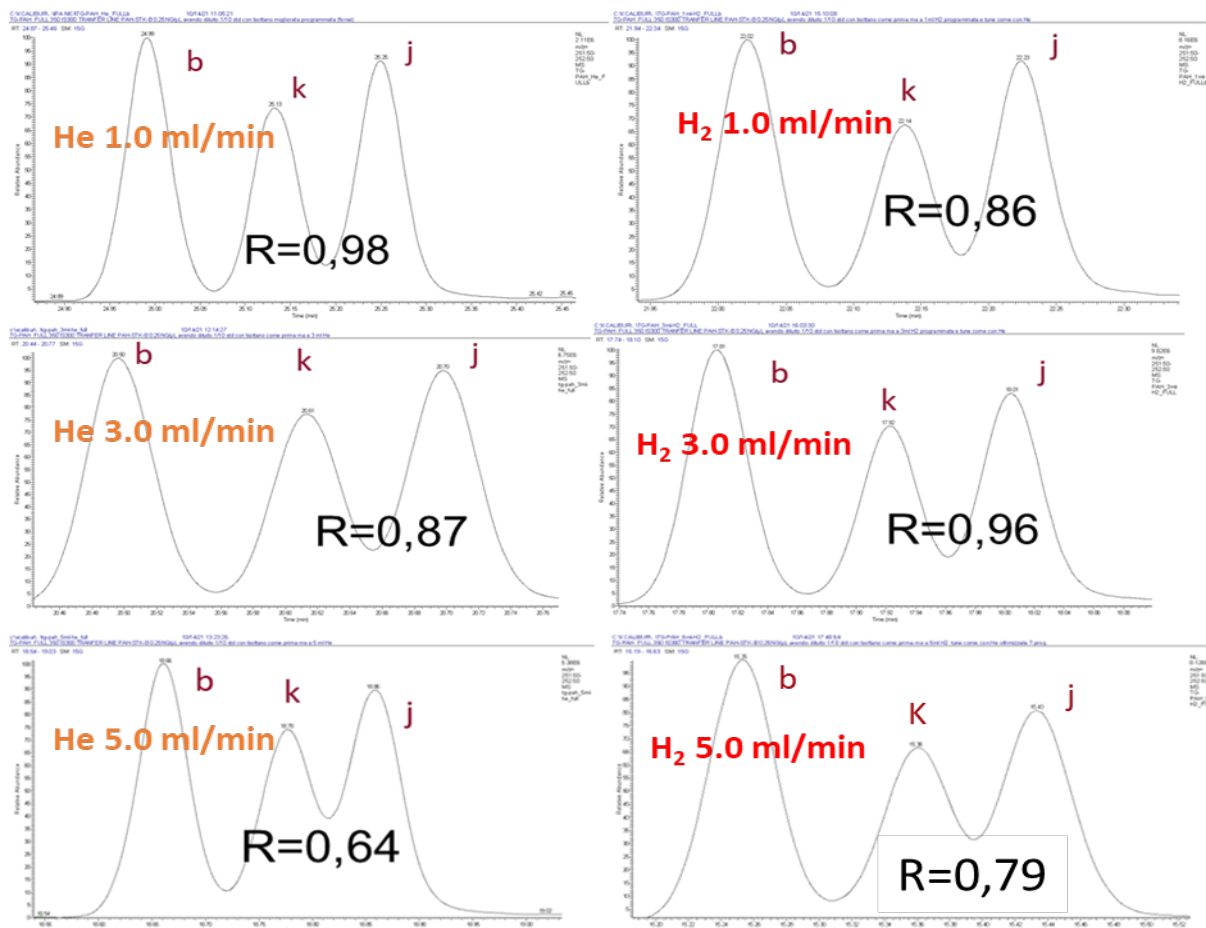

Figure 2: Chromatogram obtained by recalling the mass 252 of benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(j)fluoranthene related to the analysis of the PAH-STKB standard at 250 pg/µl using He as carrier gas with constant flow of 1.0 ml/min, 3.0 ml/min and 5.0 ml/min using the TG-PAH column on the left. Right: chromatogram obtained using H_2 as carrier gas with constant flow of 1.0 ml/min, 3.0 ml/min and 5.0 ml min. The resolution R of the peaks is calculated between the isomers K and J.

From the images in Figure 2 it is observed that the maximum resolution of the peaks is obtained at 1.0 ml/min for helium while using hydrogen as carrier gas the maximum resolution is obtained at a flow of 3.0 ml/min. It can also be noted that working at higher flows there is a loss of resolution but the benzofluoranthene isomers are still quantifiable. Working at flows at 5.0 ml/min with hydrogen, the resolution necessary for the Benzofluoranthenes is obtained, but the analysis time and the elution temperatures of the PAHs are drastically reduced until the elution of the dibenzopyrenes is obtained in more than half the time and at temperatures of 310 °C against the 320 °C necessary in the use of helium as carrier gas (Figure 3).
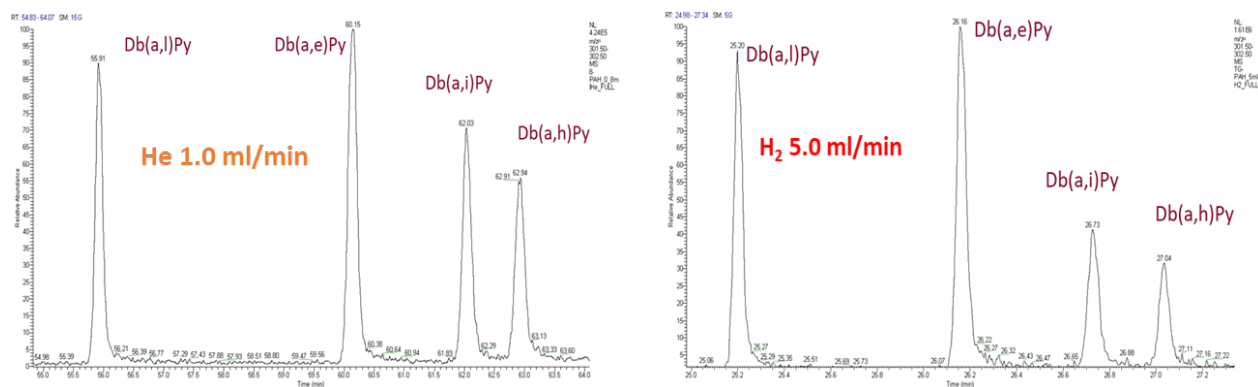
Figure 3: Chromatogram obtained by recalling the mass 302 of dibenzo(a,l)pyrene, dibenzo(a,e)pyrene, dibenzo(a,i)pyrene and dibenzo(a,h)pyrene related to the analysis of the PAH-STKB standard 250 pg/µl using He as carrier gas with constant flow of 1.0 ml/min and H_2 at 5 ml min using the Rxi-XLB column.

4 Discussion

The vacuum measurement performed with the Pirani is based on the thermal capacity of the residual gas present at the measurement point. The heat capacity of a gas is a function of the specific heat and mass of a gas which per unit of volume is related to its density. Table 2 shows the conversion factors for He and H_2 relating to a Pirani which is often calibrated in N_2. The same goes for the wrong vacuum measurement in mass spectrometers, for high vacuum meters. In the case of measurement performed through a hot cathode ion gauge , there are different conversion factors due to the different ionization of the residual gas present in the mass spectrometer which are shown below:

Table 2: Multiplication factor to obtain the actual pressure for helium, hydrogen and nitrogen by measuring the vacuum [8]

Ion Gauge hot cathode					
Gas	Formula	Correction factor vs N_2	Gas	Formula	Correction factor vs N_2
Acetone	(CH3)2CO	3.60	Hydrogen Chloride	HCl	1.50
Air	- - -	1.00	Hydrogen Fluoride	HF	1.40
Ammonia	NH3	1.30	Isobutylene	C4H8	3.60
Argon	Ar	1.29	Krypton	Kr	1.94
Benzene	C6H6	5.90	Methane	CH4	1.40
Bromine	Br2	3.80	Neon	Ne	0.30
Bromomethane	CH3Br	3.70	Nitric Oxide	NO	1.30
Carbon Dioxide	CO2	1.42	Nitrogen	N2	1.00
Carbon Disulfide	CS2	5.00	Nitrogen Oxide	NO	1.16
Carbon Monoxide	CO	1.05	Nitrous Oxide	N2O	1.50
Carbon Tetrachloride	CCl4	6.00	Oxygen	O2	1.01
Chlorine	Cl2	0.68	Phosphine	PH3	2.60
Deuterium	D2	0.35	Propane	C3H8	4.20
Helium	He	0.18	Sulfur Dioxide	SO2	2.10
Hydrogen	H2	0.46	Sulfur Hexafluoride	SF6	2.50
Hydrogen Bromide	HBr	2.00	xenon	xe	2.87

Pirani			
Gas	cal/g	density g/l	Conversion factor
He	1,241	0,179	1,450
H2	3,419	0,090	1,010
N2	0,249	1,250	1,000

In practice, the value displayed with H_2 on the spectrometer is overestimated by 2.5 times and applying the formula

$$P\ eff = P\ measured\ /\ K\ Correction\ factor$$

we obtain that the actual pressure measured of 2.7×10^{-6} Torr with a helium carrier gas at 1.0 ml/min is 1.5×10^{-5} Torr, while with 5.0 ml/min of hydrogen carrier gas, the measured pressure is 3.2×10^{-5} Torr and the actual pressure becomes 7.0×10^{-5}. Therefore, the ratio between the two different vacuum conditions is not 11-times as erroneously estimated without considering the actual pressures but is only 4.6-times.

5 Conclusions

From the experimental tests carried out on the available GC/MS it is clear that high hydrogen flows partially reduce the vacuum of the mass spectrometer and this reduction does not affect the spectrometric performance of the instrument. Probably the high gas flow rates can be pumped by the vacuum system especially if the GC/MS system is equipped with oversized pumps inserted by the manufacturer in order to be able to perform chemical ionization with additional gas. By using high hydrogen flows, it is possible to considerably reduce the analysis times by also reducing the analysis temperatures and therefore reducing the bleeding of the chromatographic columns which allows the good quantification of analytes that normally elute from the GC columns with difficulty. It is emphasized that the use of hydrogen compared to helium reduces the analysis costs not so much for the economy of hydrogen but above

all because by reducing the analysis times, using it at high flows, it reduces the analysis times and therefore the use of personnel and increases the number of analyzes per instrument, reducing amortization times.

6 References

1. P Benedetti, E Guerriero, S Mosca, M Rotatori. 2017. Analysis of Polychlorodibenzo-p-Dioxins and Polychlorodibenzofurans in Stationary Source Emissions in GC – MS / MS Using Hydrogen a s the Carrier Gas. J. Sep. Sci. 40 (17), 3469-3478. https://doi.org/10.1002/jssc.201700026.
2. JA Muñoz-Guerra, P. Prado, SV García-Tenorio . 2011. Use of hydrogen as a carrier gas for the analysis of steroids with anabolic activity by gas chromatography – mass spectrometry J. Chromatogr. A, 1218 (41), 7365-7370
3. Agilent EI GC / MS Instrument Helium to Hydrogen Carrier Gas Conversion. 07-22-22. User Guide https://www.agilent.com/cs/library/usermanuals/public/user-guide-coverting-ei-gcms-instruments-5994-2312en-agilent.pdf
4. The use of Hydrogen Carrier Gas for GC / MS. 07-22-22. Technical Note https://resources.perkinelmer.com/lab-solutions/resources/docs/TCH_010288_01-.pdf
5. S Rana, RK Garg, A Singla. 2014. Rapid analysis of urinary opiates using fast gas chromatography – mass spectrometry and hydrogen as a carrier gas Egypt. J. Forensic Sci., 4, 100-107
6. J Heseltine. 2010. Hydrogen as a Carrier Gas for GC and GC – MS. LCGC North America-01-01-2010, Vol 28, (1), 16–27
7. Alca technology. 2021. Turbomolecular pumps. https://www.alcatechnology.com/blog/. Turbomolecular-pumps /
8. RL Summers. Technical Note TND 5285, Summers Lewis Research Center, (1969) National Aeronautics and Space Administration [https://ntrs.nasa.gov/citations/19690019953]