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L'hydrogène, une alternative à l'hélium comme gaz porteur pour la chromatographie en phase gazeuse couplée à la spectrométrie de masse

Résumé

L'hélium est un gaz inerte commun généralement obtenu comme un sous-produit d'extraction minière de gaz naturel. Cependant, parce que depuis 2012 le ralentissement économique a entraîné une baisse de la production de gaz naturel, les marchés de l'hélium sont confrontés à une pénurie dans de nombreux pays européens où plusieurs laboratoires ont dû faire face à des semaines de non-approvisionnement. Les analystes doivent donc trouver des alternatives à l'hélium. En chromatographie en phase gazeuse (GC), une solution serait de remplacer l'hélium comme gaz porteur par l'hydrogène qui pour des raisons de sécurité, de pureté et de prix peut être produit au moyen d'un générateur de gaz. Cette solution permet à la fois d'anticiper de futures pénuries et de réduire les coûts dus à la consommation d'hélium. Cette étude à long terme a été réalisée pour évaluer les performances et les inconvénients de l'hydrogène comme gaz porteur pour l'analyse des pesticides organochlorés par GC-MS avec ionisation électronique. Après quelques ajustements nécessaires à la mise à niveau du système et pour éviter certains problèmes, cette étude a démontré que l'hydrogène peut être utilisé comme gaz vecteur et qu'il constitue un substitut efficace de l'hélium dans les applications de GC-MS.

Mots-Clés

Hélium, hydrogène, générateur d'hydrogène, gaz porteur, GC-MS.

Hydrogen an alternative to helium carrier gas for gas chromatography-mass spectrometry

Summary

Helium is a common inert gas, and it's usually generated as a by-product from natural gas mining. But because the recession has caused a slowdown in natural-gas production, helium markets are facing a shortage as it occurred in 2012 in many European countries where many laboratories had faced for several weeks without supply. That explains why analysts must find alternatives to helium. In gas chromatography (GC), one solution would be to replace helium by hydrogen as carrier gas using a hydrogen generator for considerations of safety, purity and price. In order to anticipate a potential shortage and to reduce the costs from helium consumption, a long term study was carried to evaluate the performance and the drawback of hydrogen as a carrier gas for the analysis of organochlorine pesticides by GC-MS with electron ionization. After some adjustments made to upgrade the system and to avoid some troubles, this study demonstrated hydrogen as a carrier gas can be used as an effective replacement for helium in GC-MS applications.

Keywords

Helium, hydrogen, hydrogen generator, carrier gas, GC-MS.

I - Introduction

Helium is the second most abundant element in the universe, being present at about 24% of the total elemental mass, which is more than 12 times the mass of all the heavier combined elements. Large amounts of new helium are being created by nuclear fusion of hydrogen in stars but on Earth it is relatively rare, 0.00052% by volume in the atmosphere. Most terrestrial helium present today is created by the natural radioactive decay of heavy radioactive elements. This radiogenic helium is trapped with natural gas in concentrations

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up to 7% by volume, from which it is extracted commercially by fractional distillation. Helium is a finite resource and is one of the only elements with escape velocity, meaning that once released into the atmosphere, it escapes into space.
For many years the United States produced over 90% of commercially usable helium in the world, while extraction plants in Canada, Poland, Russia, and other nations produced the remainder (*table 1*) and 2012, the United States National Helium Reserve accounted for 30 percent of the world's helium. The reserve was expected to run out of helium in 2018.
Helium is used for many purposes that require some of its unique properties (low boiling point, low density, low solubility, high thermal conductivity, inertness). In 2008, world helium total production was about 193 million standard cubic meters and the largest use (about 22%) is in cryogenic applications. Other uses are presented in table 2.
Balloons are perhaps the most well-known use of helium nevertheless they are a minor part of all helium use but higher than chromatography uses.
Helium is the most popular carrier gas for conventional gas chromatography and above all for gas chromatography-mass spectrometry (GC-MS). In recent years, the availability of helium has decreased and its cost has increased significantly, which induces many chromatographers around the world to considered switching to the use of hydrogen. Three gases are commonly used as carrier gas: nitrogen, hydrogen, and helium. There is not a great difference between helium and hydrogen in terms of diffusivity, but hydrogen has about half the viscosity of helium and nitrogen; therefore, when hydrogen is used the best separation is achieved faster allowing a reduction of the analysis time.
The objective of this study was to demonstrate the ability of hydrogen as an alternative carrier gas for GC-MS. The analysis of organochlorine pesticides was the application selected in order to simulate a routine use in laboratory, with high throughput analysis (daily injections for 4 months). To evaluate the performance and the drawback of hydrogen, several parameters were investigated as effect on mass spectrometer background, column efficiency parameters (retention time, calibration linearity, resolution and sensitivity) and the possible impact on compound fragmentation pattern.

Table 1
Helium production worldwide (1).

USA	Quatar	Algeria
34%	21%	18%
Russia	**Canada**	**Rest of World**
14%	4%	9%

Table 2
Distribution of helium use in various sectors in 1996 and 2012 (1).

Cryogenics	Welding	Pressurisation & Purging	Controlled Atmosphere	Heat Transfer
29%	17%	11%	6%	14%
Party Balloon	**Leak detection**	**Chromatography**	**Airship, weather ballon**	
8%	5%	5%	5%	

II - Experimental

1. Chemicals and reagents

Organochlorine pesticide standards: Aldrin, α-BHC, γ-BHC, β-BHC, δ-BHC, cis-Chlordane, trans-Chlordane,4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin aldehyde, Endrin, Endrin ketone, Heptachlor, Heptachlor epoxide, Methoxychlor. They were supplied by Restek Bellefonte, USA (ref # RK32415 -at 2000 µg/mL in a toluene/hexane mixture).
Internal standard (ISTD) compound was 2,4 dibromo-6-chloro anisole synthesized by Veolia Research Center according to the procedure of Diaz and al modified by Corbi and al. (2-3).
Solvent was hexane of analytical grade from Merck.

2. Sample preparation

Calibration standards were prepared over the calibration range from 0.5 to 10 µg/mL diluted in hexane and spiked with ISTD. ISTD concentration was held at 2 µg/mL.
A simple and fast sample preparation was applied to obtain sludge extract solutions. About 6 grams of dried sludge were weighted into a 500 mL Erlenmeyer. A volume of 250 ml hexane was added. Ultrasonic extraction occurred for 2 hours and the sludge extract was filtered through syringe filters 0.45 µm with GHP membrane (hydrophobic polypropylene membrane). The standard mix was used to spike sludge extract at 0.5 and 1 µg/mL. No clean-up was performed.
In order to avoid any degradation calibration and sludge solutions were stored at - 20°C prior to their use.

3. Instrumentation

Analyses were performed on a 7890/5973N GC-MS from Agilent Technologies equipped with

Gas Chromatograph	
Column	Rxi®-5Sil MS, 20m, 0.18mm ID, 0.18µm (Restek Corp. # 43602)
Injection mode	Splitless (1 min)
Injection volume	2 µl
Injector temperature	250°C
MS	
Ionization	70 eV - Electron Ionization
Transfer line temp.	300°C
Acquisition mode	Full scan; m/z range of 35-550 mass units
Threshold-sampling rate	10 - 3,2
Source temp.	300°C
Quad temp.	150°C
Helium carrier gas	
Flow	Constant at 0.3 ml/min
Oven temperature	70°C (0 min) to 300°C @ 15°C/min (hold 5 min)
Glass liner	Double goose neck
Seal	gold
Hydrogen carrier gas	
Flow	Constant at 0.5 ml/min
Oven temperature	70°C (0 min) to 300°C @ 25°C/min (hold 3 min)
Glass liner	Siltek double goose neck
Seal	Siltek

Table 3
GC-MS instrument conditions.

a 7683 autosampler. Instrument parameters are shown in table 3, they are based on those recommended for US EPA Method 8081B (4).

Helium was provided by cylinders from Air Liquide (France) with purity > 99.9998. Hydrogen was delivered by gas generator from F-DGSi (France) series WM-H2. Regarding the safety, hydrogen generator was link to a hydrogen sensor (Da Vinci, The Netherlands) implemented directly in the GC oven (*Figure 1*).

III - Results and discussion

1. Safety consideration

The first concern when switching to hydrogen carrier gas is understanding and managing the safety issues. Fortunately hydrogen generators minimize much of the risk.
Hydrogen generators produce high purity hydrogen at low pressure (relative to compressed gas cylinders, 10 bar versus 200 bar), which

Figure 1
WM-H2 gas generator from F-DGSi and Hydrogen Sensor.

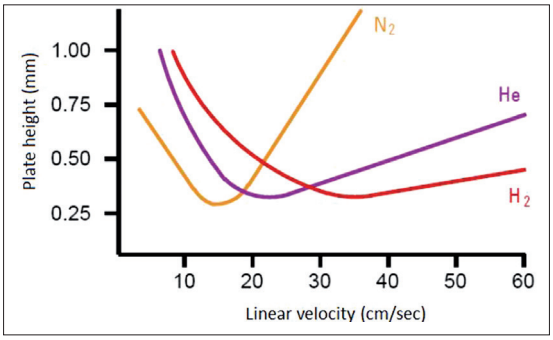


Figure 2
Van Deemter curves for helium, nitrogen and hydrogen (5).

eliminates the risk of high pressure discharge and subsequent self-ignition. Hydrogen is only generated at needed pressure and only on demand. Only a very small volume of hydrogen is stored in the generator: total stored volume is inferior to 50 ml. Generators are also equipped with built-in leak sensors and automatic shut-off features, which turn the unit off if a leak is detected.
Consider using a hydrogen sensor in the GC oven or in the general area the instrument is located. Always turn off the hydrogen at the hydrogen generator every time you shut down the GC or MS. Fan purges the oven before turning on heater to remove any collected hydrogen.

2. Experimental Set-up

Two parameters guided our choice of a hydrogen generator instead of cylinders: the safety aspect and low specification for water and oxygen.
Prior to switching from helium to hydrogen, it was necessary to change the external tubing connections (gas line and split line) of the GC system. Chromatographic quality stainless steel tubing is often recommended for H2 plumbing or use new 1/8th copper that has been cleaned for GC use (dirty tubing will cause huge contamination problems, as H2 appears to carry dirt out of metal more than it does).
By installing inside the GC oven, a hydrogen sensor with alarm if a leak occurred the gas generator will stop. Concerning the injector, split vent and septum purge vent were connected to exhaust. Standard glass liner and inlet seal were replaced by Siltek-treated.
Regarding Mass spectrometer detector, standard 3 mm draw out lens were replaced by the larger 6 mm hole (Agilent # G2589-20045). Hydrogen method with 6 mm draw out and overnight cleaned source gave much better peak shape and lower background.

3. Switching of helium to hydrogen method (EI GC-MS)

There are two options when switching from helium to hydrogen. The first is to duplicate helium analysis with little to no loss of efficiency. The second is to take advantage of the higher linear gas rate available with hydrogen to speed up chromatographic run (*Figure 2*). This second option does not fit to the current study: shortening runs include decreasing stationary phase thickness, changing the temperature program, decreasing column length or column internal diameter. The GC-MS parameters between both methods were set to similar operating conditions with only some slight changes to accommodate for the carrier gas differences (*Table 3*).
For method conversion to hydrogen gas carrier, Van Deemter curves (*Figure 2*) are used in order to take into account gas properties (mainly viscosity and diffusivity). These curves show that hydrogen linear velocity is 1.75 faster compared to the one of helium. Method with hydrogen gas carrier must be carried out 1.75 times more quickly than those using helium with constant effectiveness. For the same peak elution order, this factor will be also applied to the oven temperature program. Temperature program rates are multiplied by this factor and Isothermal times are divided.
Previous factor for hydrogen can round up 2 and it is valid when using the same column for both methods. For different column dimensions with the same phase ratio (beta), use formulas of table 4. There is also method-translator software developed by Dr. Leonid Blumberg. This software is available as free-ware from the web (6).

4. Chromatographic performance

Switching from helium to hydrogen carrier gas is illustrated in the chromatograms of organochlorine pesticide mixture shown in Figures 3 and 4.

The performance results for both carrier gases are presented in table 5 for 15 compounds.
Hydrogen carrier gas allowed acceleration of the analysis with a reduction of around 5 min in retention times and lower peak width (factor 2) leading to a better efficiency. The resolution was greatly improved for three critical pairs. Endrin ketone/Methoxychlor ranged from 0.76 to 1.64 getting a correct resolution (R > 1.5). For others

Table 4
General formula to calculate temperature program for same elution temperatures

General formula							
Column 1: initial column used - Column 2: new column							
New temperature program rate (2)	=	Old temperature program rate (1)	x	Length column 1 / Length column 2	x	Gas velocity 2 / Gas velocity 1	
New iso times (2)	=	Old iso times (2)	x	Length column 2 / Length column 1	x	Gas velocity 1 / Gas velocity 2	

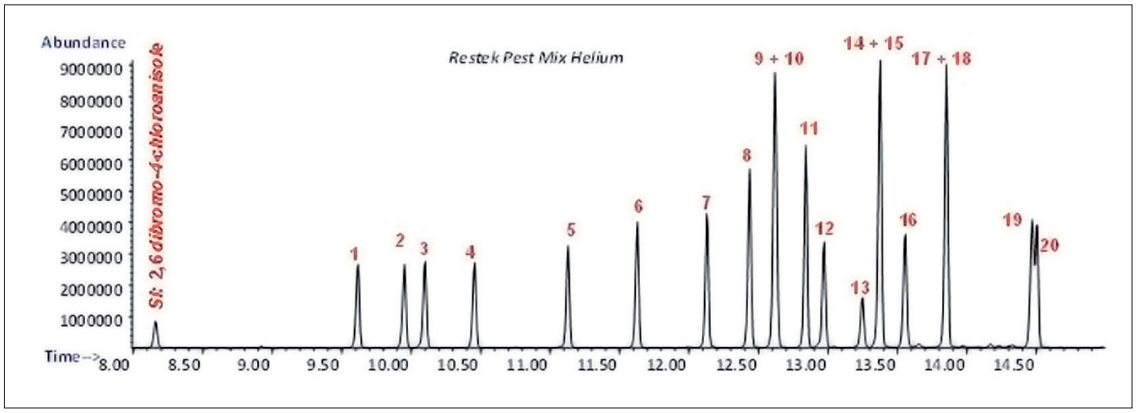


Figure 3
Total Ion Chromatogram of organochlorine pesticide mix using helium gas carrier.

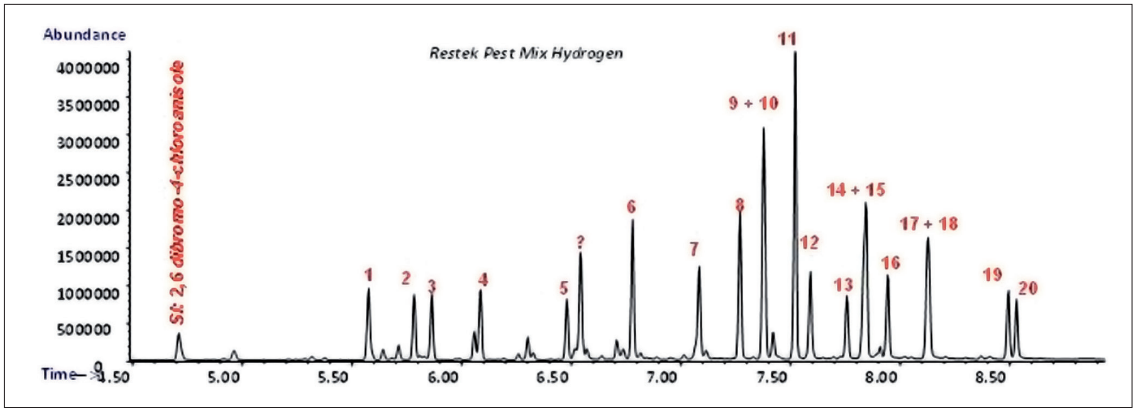


Figure 4
Total Ion Chromatogram of organochlorine pesticide mix using hydrogen gas carrier. 1: α-BHC, 2: γ-BHC, 3: β-BHC, 4:δ-BHC, 5: Heptachlor, 6: Aldrin, 7: Heptachlor epoxyde, 8: cis-Chlordane, 9: trans-Chlordane, 10: Endosulfan I, 11: 4,4'DDE, 12: Dieldrin, 13: Endrin, 14: 4,4'DDD, 15: Endosulfan II, 16: Endrin Aldehyde, 17: Endrin sulfate, 18: 4,4' DDT, 19: Endrin Ketone, 20: Metoxychlor

compounds, the use of hydrogen have enabled to differentiate the peaks of each pair (in *Figure 5*)
Sensitivity differences between hydrogen and helium, as assessed by signal-to-noise ratio (S/N), were attributed to increased noise with hydrogen carrier gas. This effect can be seen by careful inspection of the total ion chromatograms shown in Figures 3 and 4, where the baseline level is higher with hydrogen than with helium. Sensitivity decreased around a factor 2 (basic compensation based on ion focus and thinner peaks) when hydrogen was used as a carrier gas.
Regarding calibration (linearity, dynamic range and relative standard deviation), no significant difference was observed between both carrier gases. All values for the coefficient of determination (R2) were greater than 0.99 that indicates a good statistical fit to a quadratic calibration. All compounds showed relative standard deviations (RSD) of R2 less than 1%.
To assess analytical precision, recoveries have been determined for each calibration range. The statistical values were based on data of each point in the multi-point calibration (*Table 6*).

Most compounds showed RSD of mean recovery less than 10%. At lower concentration, with hydrogen the recovery was slightly better than with helium. Therefore with hydrogen, despite reduced response for many compounds, recoveries were excellent and reasonable precision was attained for most compounds even at low concentration (0.5 µg/mL).

5. Hydrogen and Mass spectrometer

5.1 Hydrogen and background

First time using hydrogen as a carrier gas in GC-MS through former helium lines may result in a higher initial MS background. Hydrogen can act as a scrubber in the flow system because it can displace contaminants that can be adsorbed on roughened or unwept areas when using helium carrier (*Figure 6*).
In order to have a good understanding of this phenomenon, a daily manual tune was performed by recording peak number in full mass spectra scanned from 10 to 700 amu. Results in Figure 6 show that with helium, the number of peaks was low and quite stable throughout the time and in accordance with Agilent specifications when all system was «clean». As soon as we switched from helium to hydrogen, the scrubber effect appeared with a jump of 250% of the peak number. This scrubber effect remained for 2 weeks before reaching a conventional background. The scrubber effect time may be reduced by changing after a few days some parts of the injector port. During experiments, the gold seal and the liner were checked after two weeks and both were dramatically "dirty". They were replaced by others fully deactivated and protected with a Syltek coating. They significantly contributed to scrubber effect reduction.

5.2 Mass Spectrum Recognition

With hydrogen carrier gas, it was observed that

Table 5

Comparison of chromatographic parameters with both carrier gases. Each parameter was measured for 75 analyses carried out on 5 standard solutions (15 injections of each calibration range).

(n=75)	Retention time (min)				Peak width (s)				Resolution		Calibration			
	He carrier		H2 carrier		He carrier		H2 carrier				He carrier		H2 carrier	
	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	He	H2	R^2	RSD (%)	R^2	RSD (%)
alpha-BHC	9,6	0,05	5,6	0,09	0,028	7,8	0,015	6,5			0,999	0,03	0,998	0,05
gamma-BHC	9,9	0,05	5,8	0,17	0,028	3,9	0,015	6,6	3,05	3,20	0,999	0,06	0,998	0,10
beta-BHC	10,1	0,18	5,9	0,46	0,029	8,4	0,015	8,1			0,999	0,03	0,997	0,13
delta-BHC	10,5	0,04	6,1	0,59	0,028	5,2	0,015	5,1			0,999	0,05	0,998	0,04
Heptachlor	11,1	0,05	6,5	0,00	0,027	5,6	0,014	11,7			0,995	0,14	0,995	0,09
Aldrin	11,6	0,04	6,8	0,00	0,027	8,6	0,014	3,9			0,999	0,06	0,999	0,04
Heptachlor epoxide	12,1	0,03	7,1	0,06	0,028	8,0	0,014	7,7			0,998	0,07	0,998	0,08
Endosulfan I	12,6	0,65	7,3	0,69	0,027	8,4	0,014	4,2			0,998	0,04	0,998	0,13
4,4'-DDE	12,8	0,04	7,5	0,03	0,026	5,1	0,013	2,7			0,998	0,11	0,997	0,17
Dieldrin	13,0	0,01	7,6	0,02	0,028	11,2	0,015	9,3			0,998	0,07	0,997	0,19
Endrin	13,2	0,15	7,7	1,06	0,029	7,4	0,014	10,1	2,68	5,99	0,981	0,98	0,992	0,79
4,4'-DDD	13,4	0,05	7,8	0,05	0,026	2,7	0,014	5,3			0,997	0,10	0,996	0,19
4,4'DDT	13,8	0,05	8,1	0,06	0,026	4,4	0,015	7,7			0,993	0,12	0,992	0,30
Endrin ketone	14,5	0,05	8,5	0,03	0,028	4,5	0,015	5,1	0,76	1,64	0,998	0,05	0,996	0,24
Methoxychlor	14,5	0,04	8,5	0,02	0,025	6,9	0,013	4,0			0,992	0,25	0,990	0,43

Table 6

Summary of precision results. Recovery = relative % of expected amount.

(n=15)	Spike	He carrier		H2 carrier		Spike	He carrier		H2 carrier	
		Mean Rec.(%)	RSD (%)	Mean Rec. (%)	RSD (%)		Mean Rec.(%)	RSD (%)	Mean Rec. (%)	RSD (%)
alpha-BHC	0.5 µg/mL	121,6	2,7	95,5	7,5	1 µg/mL	106,9	3,0	97,3	5,9
gamma-BHC		120,1	3,7	96,7	6,8		107,3	4,7	98,2	4,4
beta-BHC		116,7	4,2	102,6	11,1		104,7	2,5	98,1	4,7
delta-BHC		118,9	3,4	109,8	7,9		107,1	3,4	98,3	4,6
Heptachlor		156,3	3,1	106,2	9,8		119,1	3,7	100,7	5,6
Aldrin		125,3	2,5	107,4	9,8		108,1	2,9	100,9	5,3
Heptachlor epoxide		133,6	2,0	109,7	8,5		111,3	3,0	100,5	5,3
Endosulfan I		136,5	1,5	117,1	4,1		114,3	3,5	103,6	3,6
4,4'-DDE		130,0	2,0	122,0	3,0		111,3	2,3	103,2	3,4
Dieldrin		121,5	4,7	107,7	2,0		107,9	4,6	101,4	5,2
Endrin		154,3	6,4	113,7	2,6		111,3	2,3	103,2	3,4
4,4'-DDD		142,0	0,8	117,5	0,0		107,9	4,6	101,4	5,2
4,4'DDT		166,3	2,4	122,3	5,9		124,7	4,3	104,5	7,0
Endrin ketone		129,9	1,6	116,4	3,9		109,1	4,1	102,7	5,6
Methoxychlor		167,6	2,3	117,9	5,2		124,4	3,9	103,5	6,4

due to its higher diffusivity compared to helium, the mass spectrometer pump must work at a higher rate to reach a stable vacuum level. This may increase the number of background molecules which can collide with the ions formed, leading to a potential reduction in sensitivity and a change in the relative abundance of ions within the mass spectrum.

Despite literature indicates that the mass spectral patterns of some compounds are known to change when hydrogen carrier gas is used, no significant change was evidenced in the mass spectral pattern for the target compounds. Nevertheless small changes were observed in the fragmentation behavior for two pesticides: Heptachlor and trans-Chlordane. Recognition probability has switched from 98% to 79% for Heptachlor and from 93% to 82% for trans-Chlordane respectively from helium to hydrogen. With hydrogen carrier gas, the ion m/z=66 of trans-Chlordane mass spectra (*Figure 7*) was the second most abundant ion. Those changes in abundance may explain the lower percentage in recognition nevertheless the mass spectrum is even easily recognized by the analyst.

6. Sample analysis with hydrogen carrier gas

In order to check if the contamination was faster when using hydrogen as carrier gas, experiments were carried out with the injections of complex and loaded samples: non-spiked and spiked sludge extracts.

6.1 Non-spiked sludge extract

Even with a very complex matrix like sludge (*Figure 8*), hydrogen carrier gas use leads to a better resolution compare to helium. The most

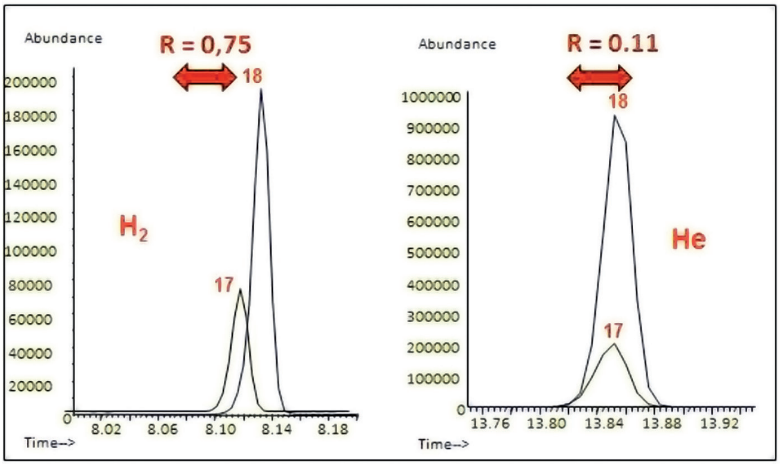


Figure 5
Endrin sulfate/4,4'-DDT pair.

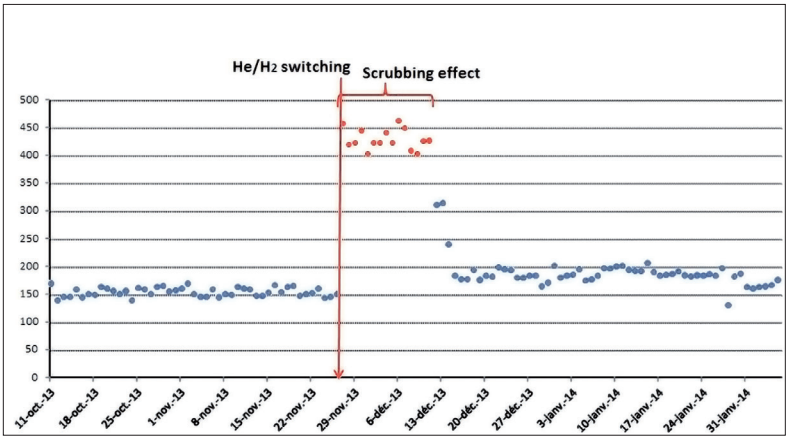


Figure 6
Evolution of scanned peak number during experimentation.

Spike	He carrier		H2 carrier		Spike	He carrier		H2 carrier		Spike	He carrier		H2 carrier	
	Mean Rec. (%)	RSD (%)	Mean Rec.(%)	RSD (%)		Mean Rec.(%)	RSD (%)	Mean Rec.(%)	RSD (%)		Mean Rec.(%)	RSD (%)	Mean Rec.(%)	RSD (%)
2 µg/mL	98,9	3,1	98,5	2,8	5 µg/mL	99,7	2,0	102,0	2,4	10 µg/mL	100,2	1,6	98,8	2,9
	99,2	2,6	97,3	5,9		99,6	2,9	101,7	3,7		100,2	2,0	98,9	3,4
	97,9	2,2	96,4	3,9		99,6	2,5	101,8	3,9		100,2	1,5	98,7	4,3
	98,1	2,0	97,3	3,9		99,9	2,8	101,7	2,0		100,2	1,9	99,2	2,4
	103,0	6,8	99,0	12,4		99,1	4,5	100,9	4,1		100,3	3,3	99,7	5,6
	99,3	2,5	96,7	4,9		99,3	2,1	101,1	4,4		100,4	2,6	100,3	3,1
	100,1	3,0	96,2	6,8		98,9	2,1	101,5	4,3		100,4	2,5	99,9	3,0
	101,3	3,9	96,5	4,5		99,2	2,9	101,8	3,0		100,0	2,0	101,7	2,8
	100,6	2,9	93,9	8,7		99,0	3,0	100,8	6,5		100,3	1,9	100,7	2,4
	97,8	2,7	95,6	5,3		99,5	2,9	100,7	1,7		100,7	2,8	99,8	4,4
	104,6	9,4	97,3	11,9		97,4	15,7	104,3	8,9		100,6	10,5	99,9	4,7
	101,4	3,0	95,5	8,8		98,3	2,5	100,6	4,3		100,4	2,9	100,5	4,1
	105,7	7,3	96,9	11,7		99,1	5,3	99,2	6,4		100,3	4,1	101,2	5,8
	97,8	2,8	95,4	8,9		99,6	3,5	100,4	4,5		100,4	3,2	100,6	4,6
	105,0	7,5	98,4	15,4		99,1	6,6	99,0	6,9		100,6	4,8	100,8	7,1

Figure 7
Mass spectra of trans-Chlordane.

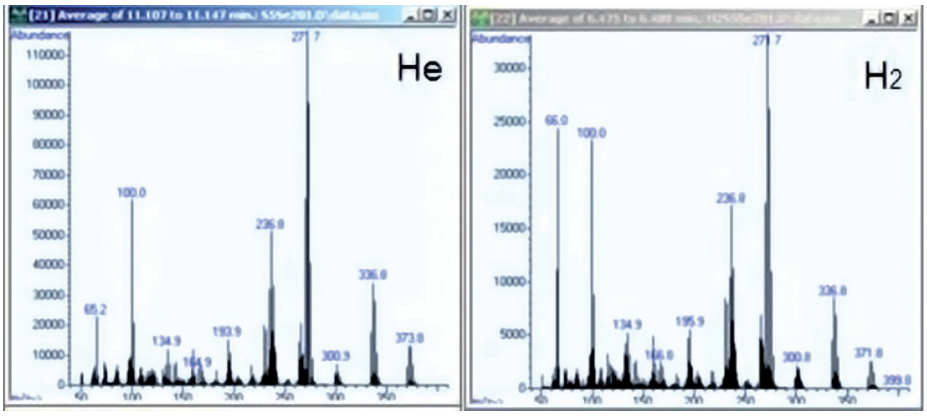


Figure 8
Overlaid Total Ion Chromatograms of sludge extract with both carrier gases.

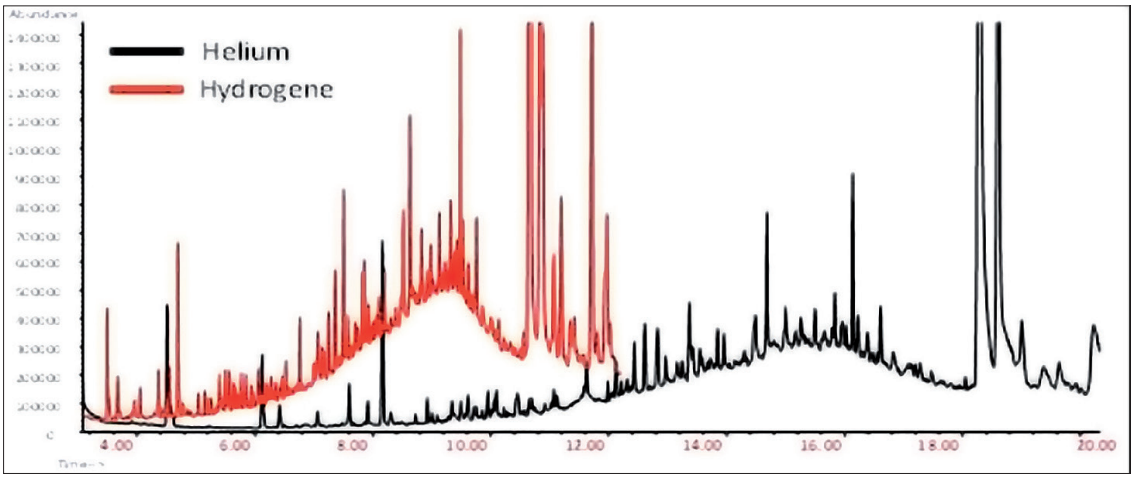
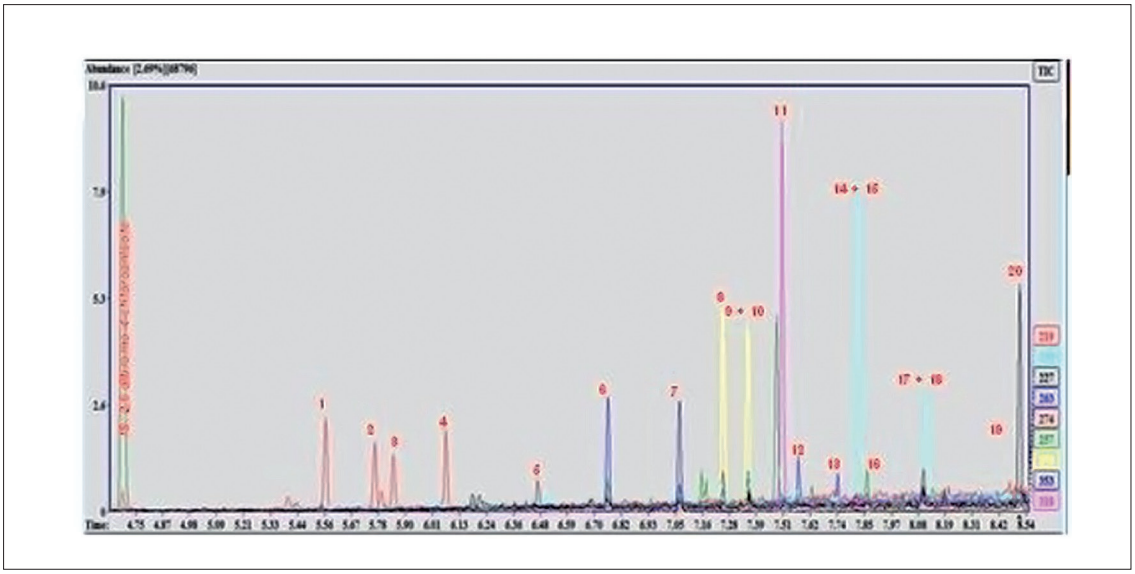


Figure 9
RIC of organochlorine pesticides in sludge extract



abundant compound families were pointed out for both carrier gases and their mass recognition were satisfactory (*table 7*). Siltek glass liner use has avoided the possible degradation of compounds in the injection port whose the surface may react as catalyst with specific compounds.

6.2 Spiked sludge extract

The two levels of spiked sludge extracts were injected in order to check the potential impact between the matrix, the compounds of interest and the carrier gas hydrogen. The reconstructed ion chromatogram (RIC) of spiked sludge extract

	Positive mass spectrum recognition
PAHs	Yes
PAHs (C1-C3)	Yes
Hydrocarbone (C11-C32)	Yes
Fatty acids(C16, C18, C18-1, C18-2)	Yes
Phtalates	Yes
Sterols and derivatives	Yes
Linear alkyl benzene	Yes

Table 7
Spectral recognition of the most abundant compound families.

(n=100)	He carrier		H2 carrier	
	Mean	RSD (%)	Mean	RSD (%)
alpha-BHC	0,233	3,1	0,177	4,9
gamma-BHC	0,191	6,7	0,130	5,3
beta-BHC	0,213	4,1	0,132	6,8
delta-BHC	0,195	6,1	0,136	5,8
Heptachlor	0,166	8,0	0,094	9,5
Aldrin	0,189	4,2	0,187	6,6
Heptachlor epoxide	0,279	5,1	0,168	9,1
Endosulfan I	0,459	9,8	0,289	9,6
4,4'-DDE	0,596	15,2	0,771	9,0
Dieldrin	0,098	6,8	0,072	7,9
Endrin	0,043	8,6	0,061	11,6
4,4'-DDD	0,960	13,5	0,575	10,4
4,4'DDT	0,626	14,8	0,280	11,4
Endrin ketone	0,185	14,7	0,076	13,9
Methoxychlor	0,882	15,4	0,373	13,1

Table 8
RF means over a testing period with the two carrier gases.

is presented in Figure 9.
From a chromatographic point of view there was no difference between organochlorine compounds from standard solution compared to those of spiked sludge extract. Concerning the mass spectra recognition, the same results were obtained than with standard solutions.

6.3 Quality control (QC) throughout study

Regular standard solution injections were carried out (series from 5 to 40 injections at each time) in order to check and to prevent instrument drift due to a fouling of the column or of the injector. For each of compounds, response factors (RF) were determined from generated data. Most organochlorine compounds showed RSD of response factor mean less than 15% and by comparing between both gases, obtained RSD were in the same range (*table 8*).
At this step, by using particular precautions expressed in section above and considering obtained results, hydrogen may be used as carrier gas for GC-MS.

IV - Conclusion

A long term study demonstrated hydrogen as a carrier gas can be used as an effective replacement for helium in GC-MS applications. In general

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terms it allows speeding up the analysis without the loss of resolution, and therefore makes it possible to reduce costs.
When switching from a system previously under helium to hydrogen with MS detector, some adjustments were made to upgrade the system and to avoid some troubles like higher level of background. After a short equilibration period, the system was operational. MS tuning was essentially equivalent, and passed all acceptance criteria with both hydrogen and helium. From a chromatographic point of view, all parameters were enhanced while the run time was divided by a factor 2 compared to helium. Calibration linearity, repeatability and recovery were excellent with hydrogen carrier gas. The simulation of high throughput analyses of sludge demonstrated that hydrogen may be used as a conventional carrier gas and no problem occurred when preventive and curative maintenance was made. In addition, the use of passive material in the injection port was a benefit leading to a passive system when a complex matrix was injected. Due to the nature of this gas, the sensitivity was below to this obtained with helium. That could impact fragmentation pattern by the decrease of specific ion, nevertheless no significant modification was observed and mass spectra recognition was done for all organochlorine compounds. Anyway this loss of sensitivity may be compensated by a selective MS tune and large volume injection mode, where 10 µL injection may easily obtain better sensitivity compare to helium.

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