

Application Note: An evaluation of hydrogen as a carrier gas in the analysis of the halogenated pesticide-herbicide mixture listed in US EPA Method 551.1

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Introduction

Pesticide is a general term for substances which are used to poison pests (weeds, insects, mould, rodents, etc.). The pesticides most acutely dangerous to man are insecticides and rodenticides, although pound for pound, herbicides are the most widely used type of pesticide.¹ Since World War II, herbicide and insecticide application to crops had grown to an estimated 660 million pounds of active ingredient in 1993.²

Without proper safeguards, pesticides have the potential to seriously threaten many groundwater drinking supplies. Approximately 50% of the U.S. population obtains its drinking water from groundwater sources and as much as 95% of the population in agricultural areas use groundwater as its source of drinking water. The Safe Drinking Water Act sets standards for drinking water and mandates the Environmental Protection Agency set Maximum Contamination Levels (MCLs) for a number of pesticides in public water supplies. USEPA Method

551.1 involves the determination of the concentration of halogenated pesticides/herbicides in drinking water by liquid-liquid extraction followed by gas chromatography with electron capture detection and using helium as the carrier gas. It is routinely used in water quality laboratory test houses.

Helium (He) is just one of the commonly used carrier gases for GC analyses, the others are nitrogen (N_2) and hydrogen (H_2). For any separation or purification application, the ultimate goal is to achieve maximum separation of the target species in the shortest period of time within budgetary constraints. Indeed, this is true for all analytical laboratories performing gas chromatographic (GC) analyses. The van Deemter plot (**Figure 1**) represents a plot of the height equivalent per theoretical plate (H) against the linear velocity (\bar{u}) for the common carrier gases. Effectively this represents an evaluation of the carrier gas separation performance vs. the inverse of analysis time. Lower H and higher \bar{u} are preferred for fast, higher resolution analyses.

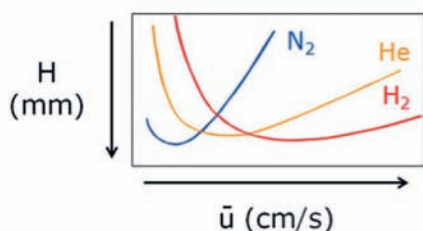


Figure 1: A representation of the van Deemter plots obtained for a range of GC carrier gases.

Helium has been widely used to date due to its low reactivity with analytes and its more favourable van Deemter characteristics than N_2 . However, helium is in short supply; its primary application is to cool magnets within medical imaging systems. In the last 10 years helium has become increasingly expensive as supplies diminish.

To date, the use of hydrogen in GC systems has widely been avoided, due to concerns over safety, high background noise and potential reactions with analytes. However for many GC applications, hydrogen carrier gas permits higher resolving power than helium over a larger velocity range and volumetric carrier gas flows, thus improving the quality and speed of chromatographic separation. With helium becoming prohibitively expensive for routine analysis and the clear advantages offered by hydrogen, many chromatographers are transitioning to hydrogen carrier gas.

The innovative design in Parker dhFNS hydrogen generators permits safe on-site generation of ultra-high purity (>99.99995%) hydrogen gas from deionised water, using proton exchange membrane technology. Novel safety and operational features such as leak detection, automatic shut down and consistent purity and flow control offers significant benefits over expensive, cumbersome high pressure cylinders which must be changed on a frequent basis.

Method 551.1 contains a list of analytes which includes: 12 commonly observed chlorination disinfection by-products, 8 commonly used chlorinated organic solvents and 16 halogenated pesticides and herbicides. In this Application Note, we will focus solely on the halogenated pesticides and herbicides; the original method was therefore modified to improve the speed of analysis and the separation of these species.

Detection is normally carried out by a GC- μ ECD (microcell Electron Capture Detector), enabling the detection of concentrations down to parts per trillion (ppt). However, this detection technique relies upon retention time alone for identification purposes. In this study a GC-MS system was also used to confirm the presence and identity of each analyte.

Method 551.1 utilises helium as the carrier gas; however, this Application Note will evaluate the use of an on-site generated hydrogen carrier gas, supplied by a Parker dhFNS 110H-MD hydrogen generator, for the analysis and detection of these compounds.

Experimental

Mixed standards were prepared in methyl tertiary butyl ether (MTBE) at four different concentrations (1, 10, 50 & 100 µg/L). The standard solutions each contained: hexachlorocyclopentadiene, trifluralin, hexachlorobenzene, atrazine, simazine, γ -BHC (lindane), heptachlor, alachlor, metolachlor, bromacil, cyanazine, heptachlor epoxide, methoxychlor, endrin, endrin aldehyde and endrin ketone. With a 1 µL splitless injection these concentrations were the equivalent of 1 - 100 pg on-column injections, respectively.

The analyses were performed using an Agilent 7890 GC fitted with a µECD & 5975C (XL inert) MSD (www.agilent.com). Hydrogen was supplied from a Parker dhFNS 110H-MD hydrogen generator (www.parker.com/dhfn) and helium was supplied from a cylinder (Air Products, BIP).

An injection volume of 1 µL was introduced in splitless mode with the inlet temperature set at 200°C via a G4513A autosampler.

A deactivated focus liner (4.0 mm i.d., split/splitless, tapered) with a glass wool insert was used in the inlet. Separation was performed on a Restek Rtx-624 column (30 m x 0.25 mm i.d. x 1.4 µm).

For hydrogen, the initial GC oven temperature was set at 35°C and held for 2 minutes. The temperature was then raised at a rate of 10°C/min to 300°C. A constant carrier flow rate of 1 mL/min was used. The µECD temperature was set at 290°C and nitrogen make-up gas flowed through the detector at 30 mL/min. The data acquisition rate was set at 10 Hz.

For helium, the oven temperature program gave coelutions for many of the peaks, therefore a different program was used. The initial GC oven temperature was set at 35°C and held for 2 minutes, the temperature was then raised at a rate of 20°C/min to 170°C and then immediately raised at 10°C/min to 250°C for 5 min, then 10°C/min to 300°C for 10 min. The remaining parameters were set as for hydrogen.

Results

The chromatograms obtained at concentrations of 1 and 100 µg/L, analysed by GC-µECD using H₂ and He carrier gases, are shown in the **Figures 2 and 3** respectively.

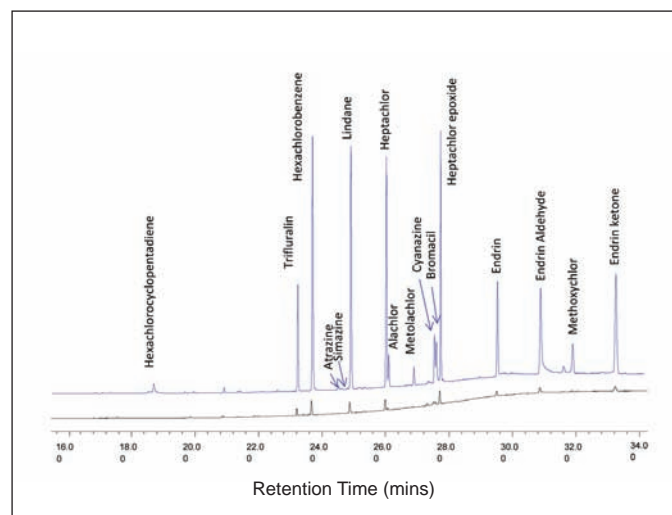


Figure 2: Offset chromatograms of the standard mix analysed with a GC-µECD using H₂ carrier gas at concentrations of 1 and 100 µg/L. Each of the 16 species are labelled.

The peak areas measured for seven replicates of 1 µg/L (1 pg on-column) were used to calculate Limits of Detection (LODs). A mean concentration for each compound was calculated and the standard deviation (σ_{n-1}) of this mean was then determined. The LOD was then calculated by multiplying the standard deviation with the value (3.14) for the Students t-test at 99 % confidence level. The repeatability of the seven replicates of 1 µg/L was calculated as the % relative standard deviation against the mean concentration.

Table 1 reports the retention times, LODs and repeatability values for the analysis with both helium and hydrogen carrier gases. All compounds that were detected with helium could also be detected with hydrogen as the carrier gas.

It can be seen that the hexachlorocyclopentadiene peak could not be accurately detected at 1 µg/L concentration level for both carrier gases. However, at a concentration of 10 µg/L, hexachlorocyclopentadiene could be detected with both carrier gases with a signal to noise ratio of around 3. Simazine could not be easily determined with the helium carrier gas at any

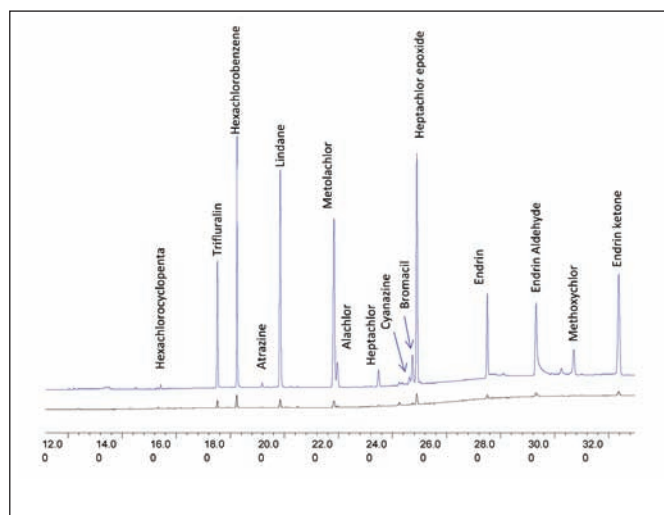


Figure 3: Offset chromatograms of the standard mix analysed with a GC-µECD using He carrier gas at concentrations of 1 and 100 µg/L. Each of the 15 species are labelled with the exception of simazine which could not be determined.

concentration possibly due to a co-elution and the fact that this analyte gives a lower response with the µECD than most of the other pesticides analysed.

The LODs with the helium carrier gas were found between 0.09 - 0.42 µg/L with similar results for the hydrogen carrier gas with LODs between 0.17 - 0.49 µg/L. Generally, helium gave a slightly lower LOD than hydrogen except for atrazine which had a lower LOD with hydrogen, but overall, for these pesticides switching from helium to hydrogen as the carrier gas is not greatly detrimental to their limits of detection.

For helium the repeatability was below 9.7%, for all compounds at the 1 µg/L concentration level, with the exception of hexachlorocyclopentadiene and simazine. With the hydrogen carrier gas, repeatability was better than 10% for most compounds and lower than 16.3% for all compounds except hexachlorocyclopentadiene. Therefore, the repeatability with hydrogen was not quite as good as with helium but adequate for many applications.

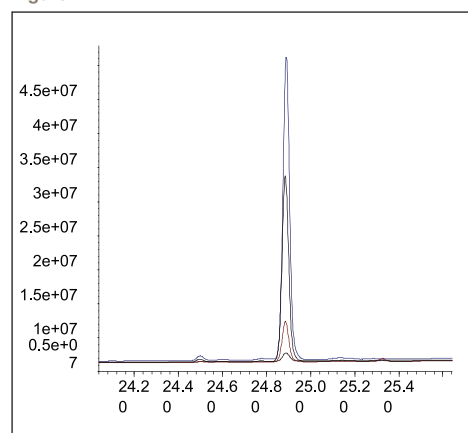
Table 1: The retention times, LODs and repeatability values for both Helium and Hydrogen carrier gases calculated using 1 µg/L standards.

No.	Compound name	Hydrogen			Helium		
		RT (min)	LOD (µg/L)	Repeatability (% RSD)	RT (min)	LOD (µg/L)	Repeatability (% RSD)
1	Hexachlorocyclopentadiene	18.698	N/a	N/a	13.497	N/a	N/a
2	Trifluralin	23.219	0.30	9.5	17.523	0.12	3.8
3	Hexachlorobenzene	23.683	0.26	8.1	18.235	0.13	4.2
4	Atrazine	24.498	0.17	5.5	19.177	0.42	6.4
5	Simazine	24.598	0.30	9.6	N/a	N/a	N/a
6	γ-BHC (Lindane)	24.889	0.28	9.1	19.849	0.13	4.2
7	Heptachlor	26.005	0.32	10.1	21.839	0.13	4.0
8	Alachlor	26.079	0.35	11.2	21.963	0.13	4.0
9	Metolachlor	26.872	0.38	12.0	23.492	0.14	4.4
10	Cyanazine (Bladex)	27.528	0.51	16.3	24.629	0.23	7.2
11	Bromacil	27.585	0.33	10.6	24.744	0.20	6.5
12	Heptachlor epoxide	27.723	0.27	8.7	24.906	0.14	4.4
13	Endrin	29.517	0.27	8.4	27.512	0.09	2.9
14	Endrin aldehyde	30.876	0.26	8.4	29.318	0.21	6.7
15	Methoxychlor	31.886	0.49	15.7	30.713	0.31	9.7
16	Endrin ketone	33.246	0.36	11.4	32.377	0.19	5.9

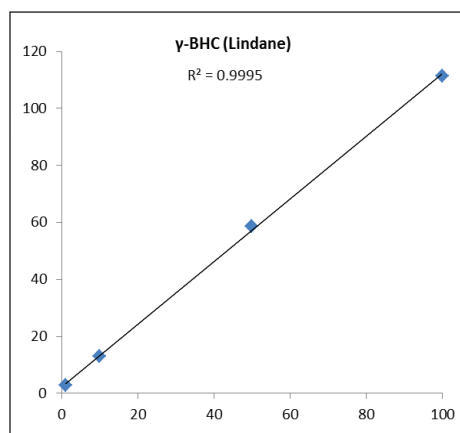
The chromatograms for γ-BHC (lindane) using hydrogen and helium as the carrier gas are shown in **Figure 4** along with their respective correlation coefficients. Similarly **Figure 5** illustrates the plots for heptachlor epoxide.

For both lindane and heptachlor epoxide the calibration curve correlation coefficient was better when using hydrogen as the carrier gas than when using helium, with 0.999 vs. 0.998 respectively for both analytes.

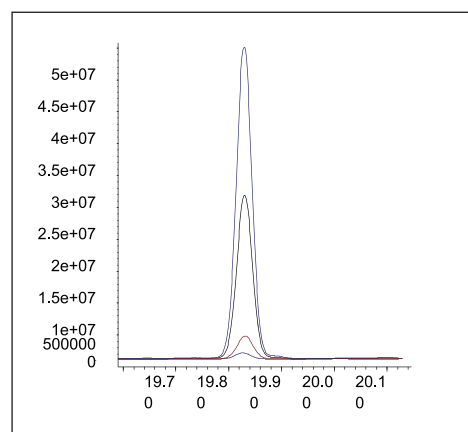
Figure 4:



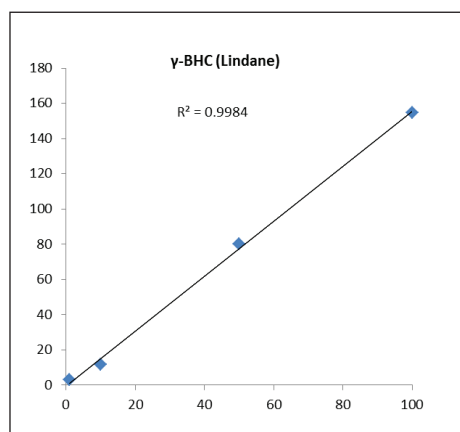
A) Chromatograms of γ-BHC (Lindane) analysed with a GC-µECD using H₂ carrier gas at concentrations of 1, 10, 50 and 100 µg/L (Retention time 24.88 min).



B) A linear calibration curve of the compound with a correlation coefficient of 0.9995.

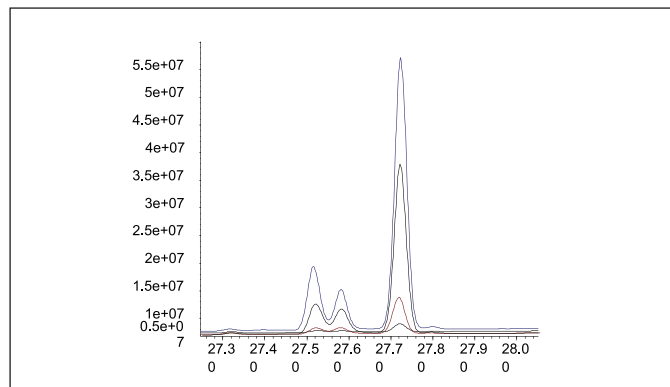


C) Chromatograms of γ-BHC (Lindane) analysed with a GC-µECD using He carrier gas at concentrations of 1, 10, 50 and 100 µg/L (Retention time 19.85 min).

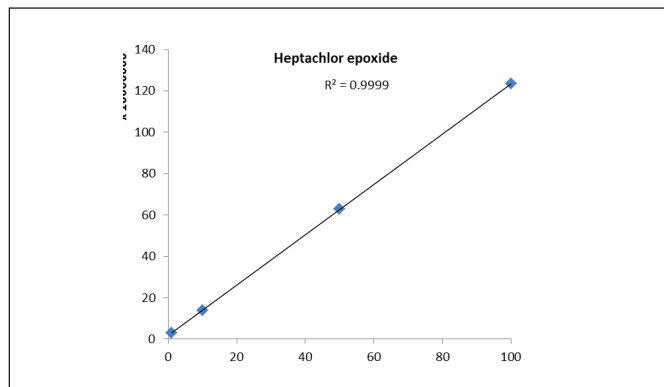


D) A linear calibration curve of the compound with a correlation coefficient of 0.9984.

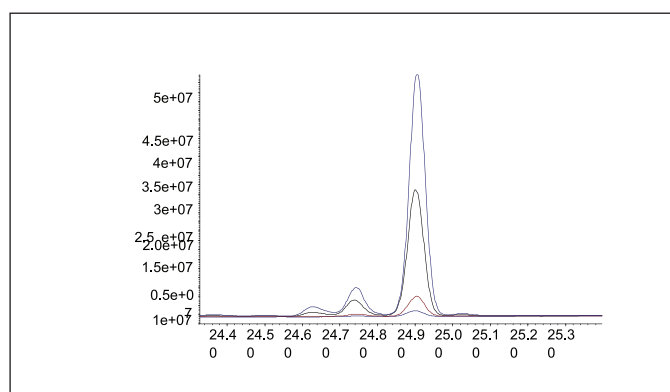
Figure 5:



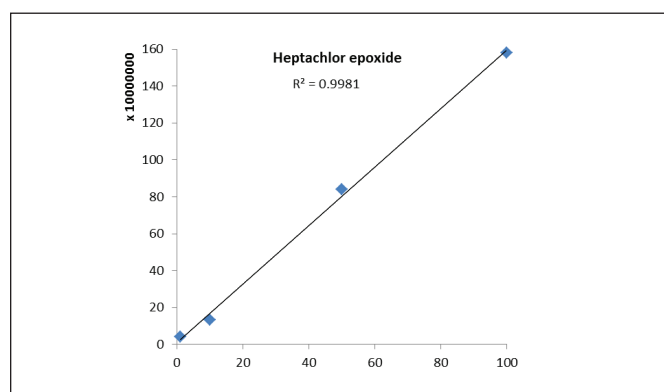
A) Chromatograms of heptachlor epoxide analysed with a GC-μECD using H₂ carrier gas at concentrations of 1, 10, 50 and 100 μg/L (Retention time 27.72 min)



B) A linear calibration curve of the compound with a correlation coefficient of 0.9999.



C) Chromatograms of heptachlor epoxide analysed with a GC-μECD using He carrier gas at concentrations of 1, 10, 50 and 100 μg/L (Retention time 24.91 min)



D) A linear calibration curve of the compound with a correlation coefficient of 0.9981.

Conclusion

The detection of these halogenated pesticides and herbicides by GC-μECD and hydrogen carrier gas shows similar method performance results to those obtained with helium carrier gas, with no significant reduction in detection limits, repeatability or calibration curve correlation coefficients, which is more than adequate for many applications. Method optimisation could improve the performance further. With the price of helium constantly increasing and difficulties in obtaining a consistent supply, there is no reason why hydrogen should not be considered as an alternative to helium for carrier gas for this GC application.

The ultra-pure hydrogen supplied from a Parker dhFNS 110H-MD hydrogen generator has been used for this application. Looking at the safety of generated hydrogen to cylinder helium, the amount of stored flammable hydrogen gas in the generator is very small compared to the safety of moving and storing heavy, high pressure (up to 200 bar) helium supply cylinders. A generator will also shut down in the event of a leak, therefore removing the danger of the lower explosive limit being reached.

References

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