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The Analysis of 16 EPA PAHs by GC/MS using Hydrogen Carrier Gas

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Objective

The objective of this technical paper is to optimize and produce a robust and repeatable method for the analysis of 16 EPA PAHs by GC/MS using generated hydrogen carrier gas over helium. This yields vastly improved analytical performance with shortened run times, while eliminating laboratory hazards associated with high pressure vessel usage, storage and handling.

Introduction

Hydrogen is the choice of carrier gas for many applications, due to faster analysis times (compared with nitrogen and helium) with no reduction in resolution. In fact resolution is normally improved. However hydrogen's use as a GC/MS carrier gas has long been avoided. Reactions in the ion source, lack of pumping ability, and high background noise have all been cited as reasons not to use hydrogen as a carrier gas. Modern technology has to some extent allayed these concerns, but still helium continues to be used for many established methods. Generated hydrogen offers an analytically superior, cost effective and safe solution over and above cylinder fed helium.

One of the most common analytical studies performed in many environmental laboratories is the analysis of Polynuclear Aromatic Hydrocarbons (PAHs). PAHs are a group of compounds consisting of more than one benzene ring, found in fossil fuels, tar and various oils, as well as being formed by the incomplete combustion of carbon containing compounds, such as wood, coal and diesel, to name but a few.

The Environment Protection Agency (EPA) has designated 16 PAHs as primary pollutants. The detection and quantification of these compounds, especially in water and soils, is of paramount importance for human health and the environment, due to their toxic and carcinogenic nature. Parker manufactures a range of hydrogen generators providing ultra high purity hydrogen gas without the safety concerns associated with high pressure cylinders. These generators improve analytical performance, shorten run times and maximize productivity.

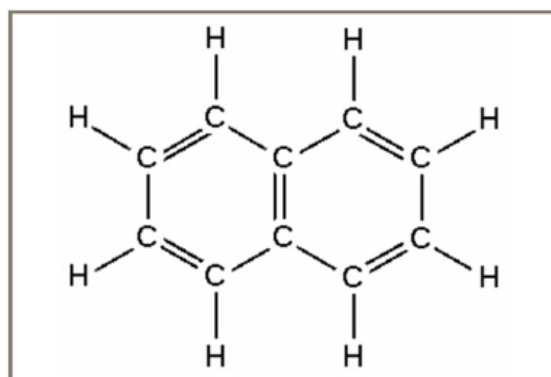
Analytical Considerations

Analysis of the 16 EPA PAHs is normally carried out using GC-FID or GC/MS, with varying detection limits depending upon the medium in question and the analytical technique employed. GC/MS is favorable as it can eliminate non-required peaks, leaving only analytical information of interest, utilizing Single Ion Monitoring (SIM) mode. This is especially important in complex matrices, where peaks of similar composition may lead to false interpretation.

In any modern analytical laboratory, sample throughput and productivity are of utmost importance, where time is money. Employing hydrogen as a carrier gas is very common in GC-FID workflows, yielding superior chromatography, as well as reduced run times. While its use within GC/MS workflows is less common, with the correct conditions, it has the potential to deliver superior performance benefits over and above helium, with the added incentive of enhanced safety and cost savings.

Typical GC/MS analyses uses helium which, as well as having vagaries in supply, often at elevated cost, also necessitates the use of cumbersome, heavy, high pressure cylinders (up to 200 bar g) which must be changed on a regular basis.

A Parker hydrogen generator produces ultra high purity carrier gas at a constant pressure and flow rate, with minimal stored volume, eliminating laboratory hazards associated with high pressure storage vessels, such as cylinders.



Naphthalene

Experimental

Analysis performed on a Shimadzu QP2010s using SIM mode and splitless injection

Hydrogen supplied from a Parker 110H-MD generator

Column supplied by Phenomenex - Zebtron ZB5MS
0.25mm x 0.25µm

Injector - 300°C

Interface - 320°C

Ion Source - 250°C

Flow rate - 3ml/min (H₂)

Injection volume - 1µl

Oven Program:

40°C (hold 1minute)

100 °C @ 15 °C/min (hold 10 minutes)

225 °C @ 5 °C /min (hold 0 minutes)

320 °C @ 15 °C /minute (hold 2 minutes)

Total run time = 48.33 minutes

Sampling time - 1 minute

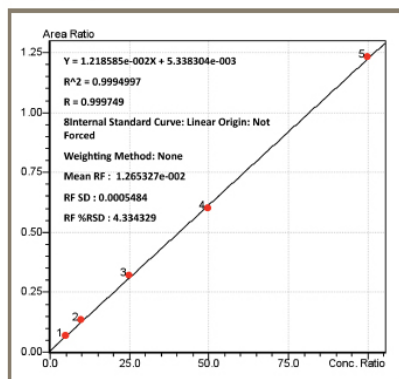
Control mode - Linear velocity

Results

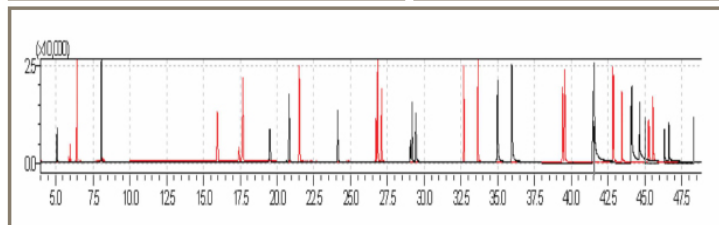
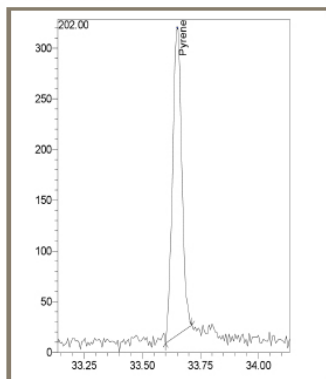
Detection limits of 1ppb were easily achieved, with excellent baseline resolution. 10 replicates were run at this level, with typical RSD's of <0.1, and signal / noise (s/n) ratios varying between 5 and 20 (typically <10).

Standards were prepared in Dichloromethane over a range of 5 to 100ppb. Calibration over this range showed excellent linearity with all compounds being >0.995.

Benzo[ghi]perylene

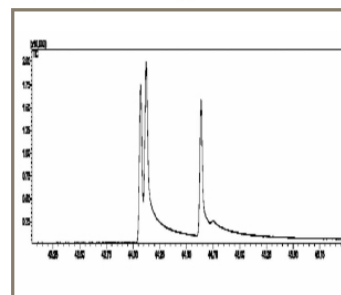


1 ppb Pyrene

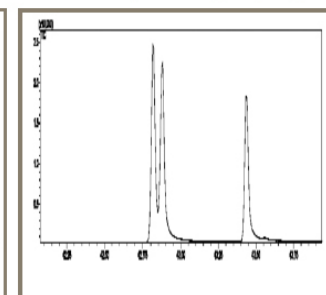


Typically, late eluting PAHs tend to tail, sometimes quite badly, making integration difficult, and peak asymmetry poor. In the example shown below, you can see clearly that the use of hydrogen carrier gas minimizes tailing, making integration easier to perform. As you can see from the comparison of the two chromatograms to the left, hydrogen has many advantages over helium when it comes to chromatographic performance:

Late compound tailing - Helium



Elimination of peak tailing - Hydrogen



- **Shorter run times, in this case, a saving of over 5 minutes**
- **Increase in sensitivity, which is important for trace level analysis**
- **Less peak tailing of later compounds, which is important for peak integration**
- **Near baseline resolution of later co-eluting peaks**

Conclusion

In conclusion, hydrogen carrier gas, supplied by a Parker domnick hunter 110H-MD generator, provides all the necessary requirements needed to perform the analysis of low level Polynuclear Aromatic Hydrocarbons by GC/MS, with many distinct advantages over helium carrier gas.

As well as the analytical benefits, safety issues are also addressed through the elimination of the containment and handling of heavy, high pressure storage vessels, not to mention the danger of running out of gas unexpectedly. Instrument downtime through loss of gas and further column damage and loss of vacuum within the GC/MS system are extremely undesirable outcomes. Moreover, the volume of stored gas in a hydrogen generator is very small, and has built in safety features in case of a leak, shutting down the flow of hydrogen and removing the danger of the lower explosive limit being reached.

With the price of helium ever increasing, and vagaries in supply, there is a compelling case for ultra high purity generated hydrogen as a GC/MS carrier gas. With maximized instrument uptime of prime importance to many analytical laboratories, the use of hydrogen is a viable and safe alternative over and above helium.

Throughout this paper we have displayed a robust, repeatable and reliable method utilizing hydrogen as a carrier gas to reduce peak tailing, lower limits of detection, provide superior baseline resolution of co-eluting compounds with excellent calibration coefficients, over much reduced analytical run times.

Acknowledgements

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