EVALUATION OF HYDROGEN AS A CARRIER GAS IN THE ANALYSIS OF POLYAROMATIC HYDROCARBONS IN WATER BY LIQUID/LIQUID EXTRACTION – LARGE VOLUME INJECTION – GAS CHROMATOGRAPHY – MASSPECTROMETRY (LLE-LVI-GC-MS)

Dr Diane Turner, Anthias Consulting Ltd.
Richard Stokes, Anthias Consulting Ltd.
Dr Geraint Morgan, The Open University

Contact: Gerard Catchpole – gerard.catchpole@vici.ch

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of structurally related hydrocarbons consisting of two or more fused aromatic/cyclic rings. PAHs are carcinogenic, they persist in the environment and bioaccumulate with potential adverse affects on aquatic life and humans[1]: hence, they are classed as priority hazardous substances under the Water Framework Directive (WFD)[2]. Four PAHs (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene) are also listed in Annex III of the Persistent Organic Pollutants (POPs) Regulation[3].

PAHs naturally occur in fossil fuels and materials like bitumen, used in road construction, coal tar pitch, creosote; in addition, raw materials used to manufacture plastic and rubber contain them. Atmospheric emissions of PAHs from combustion sources and road transport are significantly higher than those from water, but, after rainfall, the run-off leads to the contamination of surface waters. A lot of environmental contamination in soil and sediment comes from natural sources and past industrial activity, these can also contribute to the contamination of water. The monitoring of PAHs in water is important to check that exposure does not present a risk to organisms, including humans. There is different legislation for the maximum allowable PAH concentrations, depending on the country, the matrix and source of the water; from ground water and drinking water to surface, sediment and wastewater[4,5]. In this White Paper the lowest extracted calibration concentration will be 10 ng/L.

Different techniques are used for different water sources[5]. Most methods either use liquid-liquid extraction (LLE) or solid phase extraction (SPE) followed by separation and detection using high performance liquid chromatography (HPLC) with fluorescence detection (FLD) or ultra-violet detection (UVD); gas chromatography (GC) with flame ionisation detection (FID) or mass spectrometry (MS). The most common methods use LLE with GC-MS[5] and therefore these techniques were selected for this White Paper. LLE is usually a manual method and requires a concentration step prior to injection into the GC-MS to obtain enough sensitivity. An alternative to a manual concentration step is to perform a large volume injection (LVI) into the GC inlet.

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

This requires a programmable temperature vaporiser (PTV) in order to purge the excess solvent in the inlet and concentrate the sample, prior to splitless transfer to the column for separation and detection.

The most common carrier gas used for this application is helium. However, helium is a limited resource and, as such, is expensive with increasing costs and reducing availability, especially in developing countries. The need for the monitoring of PAHs is very high, however, particularly in environment laboratories the cost per analysis needs to be very low; therefore, reducing the sample analysis time is important as it helps meet the increasing need for higher sample throughput. As more scientific evidence gathers on the toxicity of chemicals like PAHs, there is always a potential for stricter regulations, resulting in a reduction in concentration limits and therefore the need for more sensitive analysis methods. To summarise, there is a need for quicker, more sensitive methods, enabling a higher throughput of samples while reducing costs and making the analytical methods more accessible to all.

Helium (He), is one of the three most common gases used as the mobile phase in GC, alongside nitrogen (N_2) and hydrogen (H_2). How good each of these gases is at separating against the analysis time can be summarised by the van Deemter plot (Figure 1). The smaller the Height Equivalent of a Theoretical Plate (HETP) the better the column efficiency, whereas, higher linear velocities equate to shorter run times. Although nitrogen produces the best separations, this is only possible at low velocities resulting in longer run times. The most common carrier gas, helium, is widely used as it is inert and although not producing such a good separation as nitrogen can be used at higher velocities. Hydrogen is becoming more common in GC methods, as although there are concerns over safety, its reactivity causing a high background signal due, for example, to higher column bleed and potential reactions with analytes, it produces better separation over a larger velocity range than helium and can result in faster analyses with better signal to noise ratios. The use of gas generators can alleviate some of the hydrogen concerns by producing high quality gas on demand.

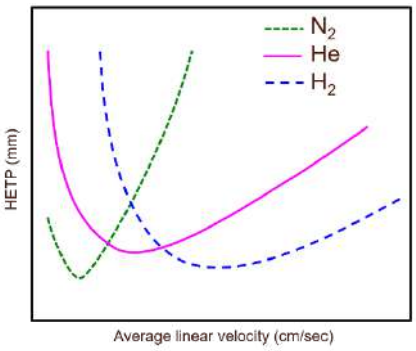


Figure 1: Representation of the van Deemter plots for N_2, He and H_2

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

AIMS

The aim of this White Paper is to optimise and produce a robust and repeatable method for the analysis of PAHs in water, using GC-MS and hydrogen carrier gas produced in situ by a hydrogen generator. Then, the aim is to determine if hydrogen is suitable as the carrier gas for the separation and detection of PAHs in water.

EXPERIMENTAL

A PAH stock standard was prepared by diluting 50 µL of the SV Calibration Mix #5/610 PAH Mix (PN31011, Restek, Belfont, PA, USA) to 10 mL in acetone. 1 mL of this initial stock solution, was further diluted, in acetone, to 100 mL, in an amber volumetric flask, to create a 0.1 µg/mL solution. An internal standards stock solution at a concentration of 0.2 µg/mL was prepared by diluting 100 µL of the SV Internal Standard Mix (PN31206, Restek, Belfont, PA, USA) to 10 mL with acetone, then a further dilution of 1 mL of this to 100 mL in acetone in an amber volumetric flask.

The samples, calibration standards and blanks were prepared by adding 50 ± 1 mL of Milli-Q water to 60 mL vials plus 2.0 mL of pentane. For the calibration standards, 5, 25, 50, 125, 250 or 500 µL of the PAH stock solution (0.1 µg/mL) was added to create calibration standards at 10, 50, 100, 250, 500 and 1000 ng/L, respectively. The vials were immediately capped and placed in a sonicator at room temperature for 20 minutes. After allowing to settle, 1.5 mL of the concentrated extract was transferred to a 2 mL amber autosampler vial (Chromacol, Thermo Fisher Scientific, MA, USA), using a 2 mL calibrated syringe (Trajan Scientific and Medical, Victoria, Australia), 50 µL of the internal standard stock solution (0.2 µg/mL) was also added and the vial capped.

The analyses were performed on an Agilent 7890 GC with 5975C XL inert MSD (Agilent Technologies Inc., Santa Clara, CA, USA), Optic 3 PTV (GL Sciences, Tokyo, Japan) cooled with liquid nitrogen and a CTC Analytics CombiPal autosampler (CTC Analytics AG, Zwingen, Switzerland) installed with a 250 µL syringe (Trajan Scientific and Medical, Victoria, Australia). Hydrogen carrier gas was supplied by a VICI DBS NM Plus hydrogen generator.

The GC-MS method was optimised so as to use the lowest operating temperatures, thus minimising any reactions with hydrogen. The autosampler injected 200 µL of extract, at 25 µL/s, into the Optic 3 inlet, held at 5 °C. A deactivated, sintered glass liner with taper (PN 2414-1007, GL Sciences, Tokyo, Japan) was installed and operated with a vent flow of 150 mL/min and a sample sweep/column flow of 1 mL/min. After the majority of the solvent had evaporated, measured with the solvent monitor with a threshold set to 75, the sample was transferred to the column in splitless mode. The inlet was heated to 320 °C at a ramp rate of 10 °C/s and a transfer column flow of 2 mL/min.

These parameters were held for a transfer time of 2 minutes, after which the split exit was reopened at 30 mL/min. Separation of the PAHs was performed on an HP-5MSUI column (30 m x 0.25 mm x 0.25 µm film thickness) (PN 19091S-433UI, Agilent Technologies Inc., Santa Clara, CA, USA) with the hydrogen carrier gas set to constant flow at 1.6 mL/min.

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

The GC oven was programmed from 50 °C, with a 2 min hold, to 340 °C at 25 °C/min and held for 0.5 min. The total run time was 14.1 minutes. Compounds eluted through a heated transfer line, held at 280 °C, into the MS,with the ion source set at 230 °C and the quadrupole at 150 °C. An autotune was used with a gain factor of 2.00 and a 4 minute solvent delay. Acquisition was in selected ion monitoring (SIM) mode, using the SIM groups, dwell times, quantification and qualifier ions listed in Table 1. The compound name cells are coloured to indicate the deuterated internal standard that was used, also with the same colour.

Table 1: The retention times, SIM group numbers, quantification and qualifier ions used for each PAH. The colours cluster the compounds that use the same deuterated internal standard, also present in the cluster.

Compound name	Retention time (min)	SIM group number	Dwell time (ms)	Quantification ion (u)	Qualifier ion (u)
Naphthalene-d8	5.627	1	25	136.1	108.1
Naphthalene	5.649	1	25	128.1	102.0
Acenaphthylene	7.193	2	25	152.1	76.1
Acenaphthene-d10	7.335	2	25	164.1	160.1
Acenaphthene	7.366	2	25	153.1	152.1
Fluorene	7.873	3	110	166.1	165.1
Phenanthrene-d10	8.788	4	40	188.2	160.1
Phenanthrene	8.810	4	40	178.1	152.0
Anthracene	8.860	4	40	178.1	152.0
Fluoranthene	9.976	5	100	202.1	101.0
Pyrene	10.195	5	100	202.1	101.0
Benzo[a]anthracene	11.378	6	30	228.1	226.0
Chrysene-d12	11.389	6	30	240.2	236.2
Chrysene	11.413	6	30	228.1	226.0
Benzo[b]fluoranthene	12.367	7	35	252.1	126.1
Benzo[k]fluoranthene	12.390	7	35	252.1	126.1
Benzo[a]pyrene	12.639	7	35	252.1	126.1
Perylene-d12	12.686	7	35	264.1	132.0
Indeno[1,2,3-cd]pyrene	13.496	8	40	276.1	138.1
Dibenzo[a,h]anthracene	13.518	8	40	278.1	139.1
Dibenzo[g,h,i]perylene	13.681	8	40	276.1	138.1

RESULTS & DISCUSSION

Procedural blanks were analyzed before and after the calibration, the replicate Calibration Standard Level 1 standards, the replicate Calibration Standard Level 3 standards and between each sample type to check for carryover. For most peaks no carryover was found, however, fluoranthene, benzo (a), (b) and (k)anthracene was detected but only after the highest concentration standard and it was below the calibration range.

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

Extracted calibration standards were prepared and analyzed at six different levels, from 10 to 1000 ng/L. A chromatogram of extracted Calibration Standard Level 3 is shown in Figure 2 and shows good separation and peak shapes. As a fast ramp was used to reduce the run time, baseline resolution was not seen for the isomers. Phenanthrene and anthracene had a resolution of 0.67 and benzo[b] and [k]fluoranthene had a resolution of 0.40, but both were enough to differentiate them in all calibration standards, as can be seen in the extracted ion chromatograms (EICs) of 178 u and 252 u for these pairs, respectively, in Figure 3.

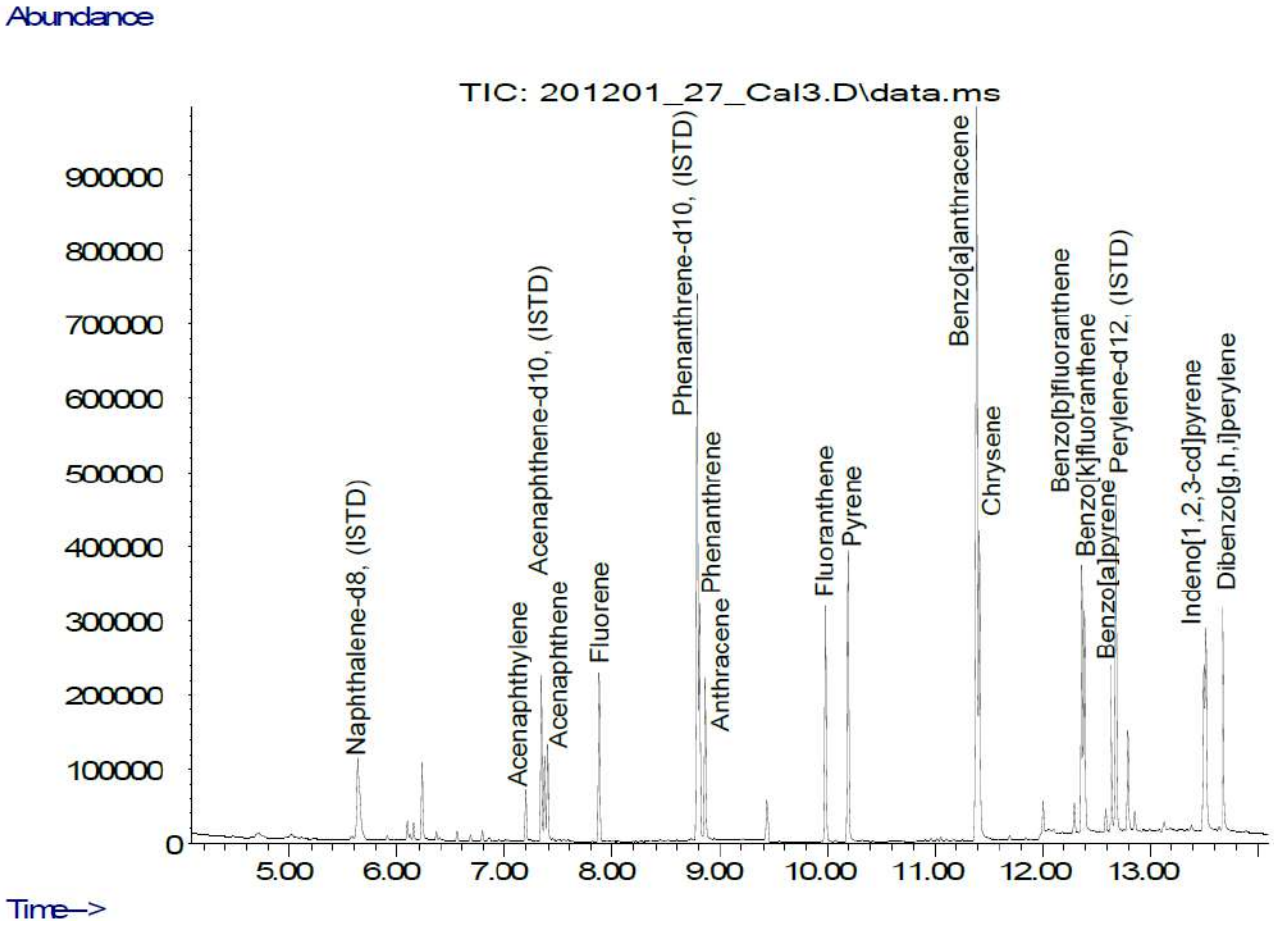


Figure 2: TIC of extracted Calibration Standard Level 3 at 100 ng/L of PAHs and 200 ng/L of internal standards by LLE-LVI-GC-MS

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

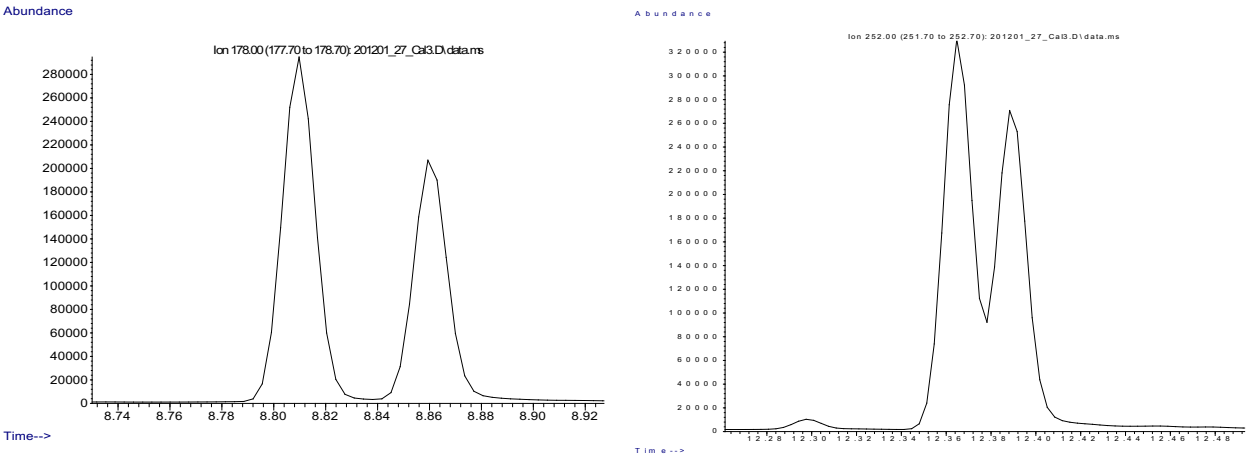
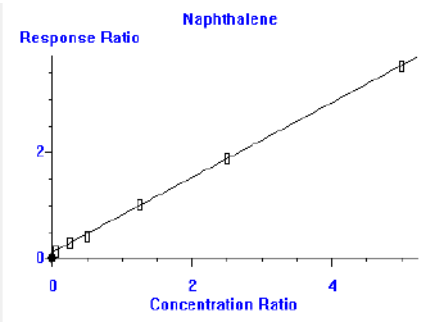
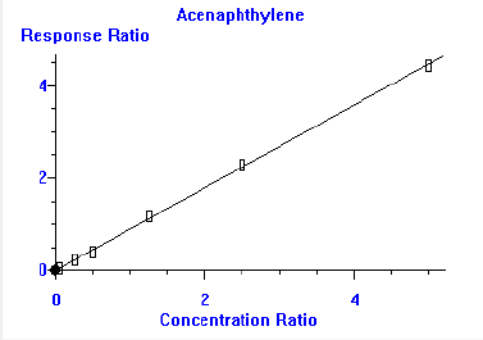


Figure 3: EICs of 178 u for phenanthrene and anthracene (left chromatogram) and 252 u for benzo[b]fluoranthene and benzo[k]fluoranthene (right chromatogram).

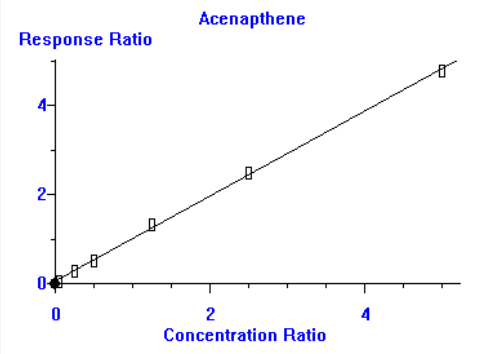
The target peaks were normalized against the internal standards, each present at a concentration of 200 ng/L. The calibration curves for all PAHs can be seen in Figure 4; whilst, the curve fits and correlation coefficients can be seen in Table 2. All PAHs had correlation coefficients >0.999.

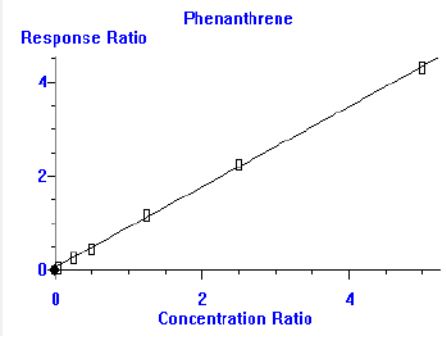
All were linear, except for the last two compounds, dibenzo[a,h]anthracene and dibenzo[g,h,i]perylene. It is thought that these higher molecular weight compounds at high concentration could have dropped out of solution in the low molecular weight, volatile extraction solvent pentane, while waiting for analysis. This was the last calibration standard run after numerous blanks. It is less likely that they were not transferred from the inlet onto the column, as carryover was not seen in the solvent blank analyzed after the higher concentration standards, as discussed above. Further validation of the method would clarify this. It is possible with the autosampler used, as well as with other GC autosamplers, and it is recommended in future analyses, to shake the sample vials in the agitator, at room temperature, immediately before injection to ensure the extract is properly mixed and all PAHs are in solution.

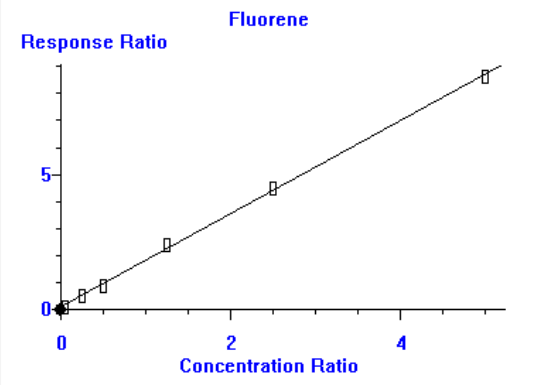


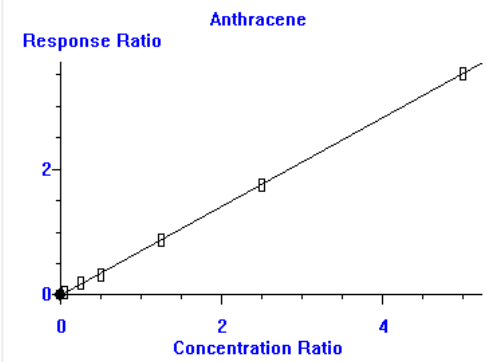


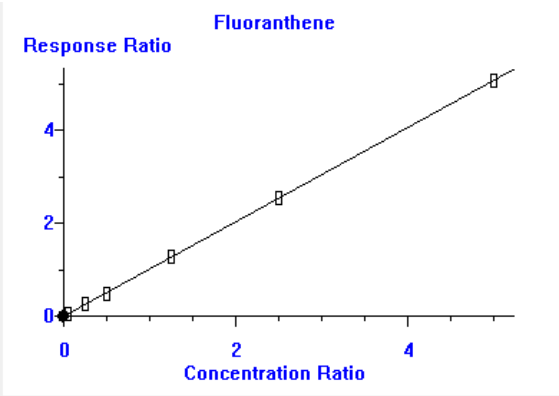
VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

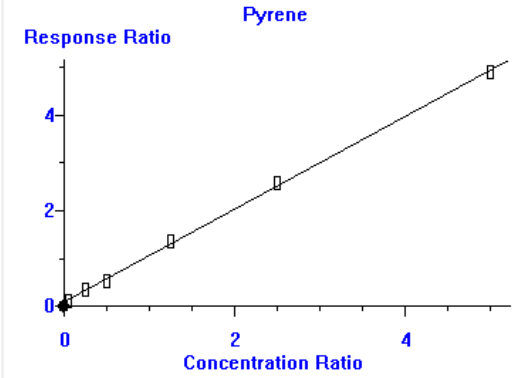




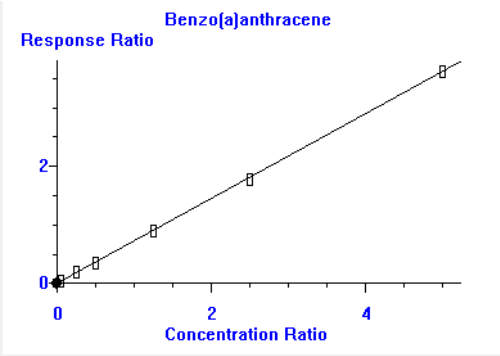


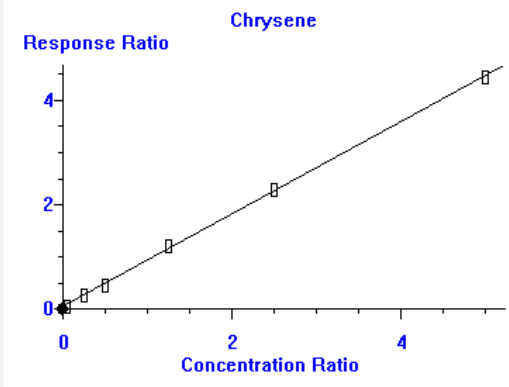


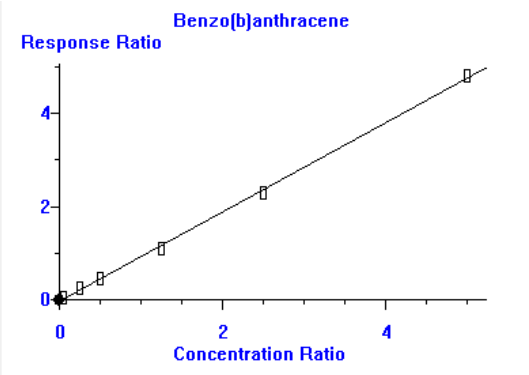


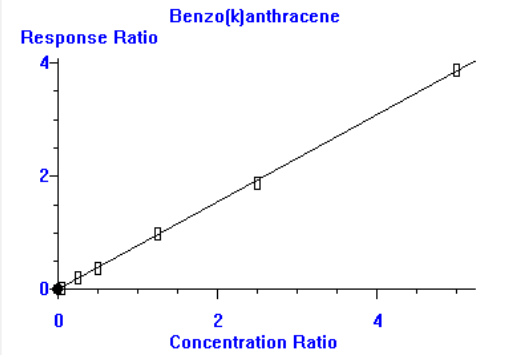


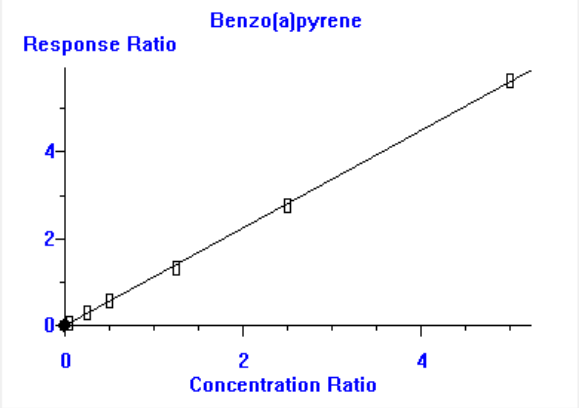
VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

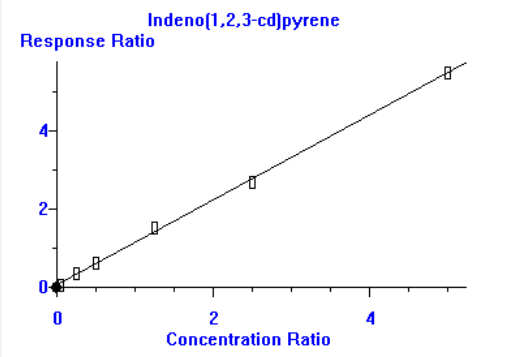












VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

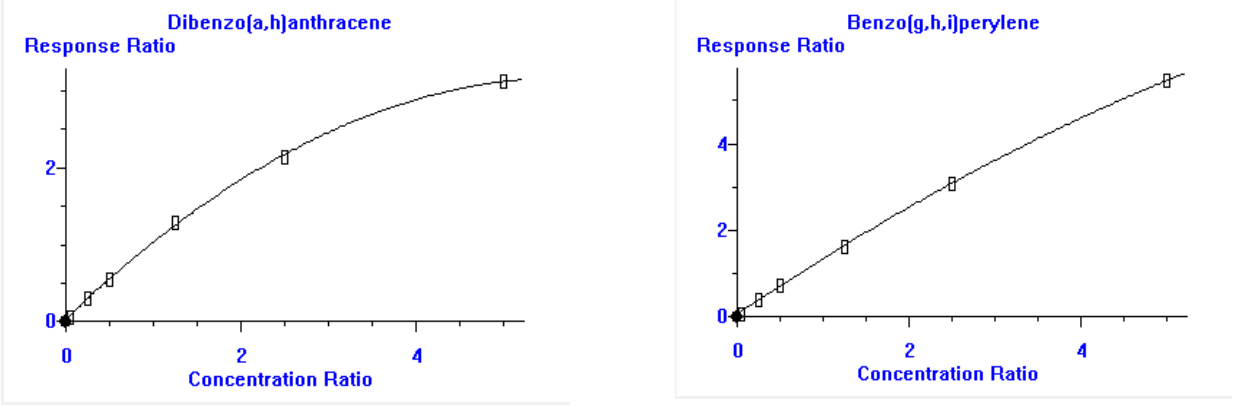


Figure 4: Calibration curves for all PAHs

The Limit of Detection (LOD) was determined by analysing 6 replicate extracted Calibration Standard Level 1 standards at a concentration of 10 ng/L. Concentrations were determined from the calibration curves, from these the standard deviation was calculated and multiplied by the students t-test for 99

% statistical confidence for n-1. The LOD for each residual solvent can be seen in Table 2 and these range from 0.73 to 3.31 ng/L. Further method development and validation could reduce these further, especially with the recommendations discussed in this White Paper.

Table 2: The retention times, curve fit, correlation coefficients, LODs, repeatability and accuracy determined for the PAHs.

Compound name	Retention time (min)	Curve fit*	R^2	LOD** (ng/L)	Repeatability (% RSD)***	Accuracy (%)****
Naphthalene	5.649	Linear	0.999703	3.13	16.70	86.3-101.1
Acenaphthylene	7.193	Linear	0.999310	2.19	9.65	91.9-108.5
Acenaphthene	7.366	Linear	0.999131	2.20	10.64	84.9-102.9
Fluorene	7.873	Linear	0.999140	2.10	9.70	84.6-101.9
Phenanthrene	8.810	Linear	0.999389	1.98	9.70	79.0-96.7
Anthracene	8.860	Linear	0.999886	1.22	8.99	100.8-118.8
Fluoranthene	9.976	Linear	0.999907	1.73	9.70	93.4-115.6
Pyrene	10.195	Linear	0.999337	3.31	9.48	90.0-111.1
Benzo[a]anthracene	11.378	Linear	0.999881	1.05	9.50	96.7-118.8
Chrysene	11.413	Linear	0.999517	1.97	10.05	83.5-104.1
Benzo[b]fluoranthene	12.367	Linear	0.999144	1.03	11.64	86.5-111.3
Benzo[k]fluoranthene	12.390	Linear	0.999711	1.53	10.47	84.7-111.6
Benzo[a]pyrene	12.639	Linear	0.999667	0.73	8.64	88.0-107.8
Indeno[1,2,3-cd]pyrene	13.496	Linear	0.999083	2.20	12.64	86.2-113.1
Dibenzo[a,h]anthracene	13.518	Quadratic	0.999332	2.05	14.71	80.4-102.1
Dibenzo[g,h,i]perylene	13.681	Quadratic	0.999839	2.39	13.71	92.2-110.1

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

Where:
* = 6 point calibration, linear or quadratic regression, not forced through 0,0
** = Extracted Calibration Standard Level 1, n=6, concentration STDEV x 3.365,
*** = Extracted Calibration Standard Level 3, n=6, ((STDEV x Mean) x 100) of peak areas
**** = Calibration Standard Level 3, n=6, %recovery = (conc/known conc) x 100%

The repeatability and accuracy were both determined from the analysis of 6 replicate, extracted Calibration Standard Level 3 standards, at a concentration of 100 ng/L. The repeatability was determined from the area of each peak, without normalization against the internal standards, and the results are presented in Table 2. These show %RSD of <10% for most PAHs, with the exceptions of the most volatile PAH, naphthalene and the last three eluting PAHs. For an LVI method, a poorer repeatability for the more volatile compounds is to be expected, hence the need for a volatile internal standard. In this case naphthalene-d8 was used as the internal standard for Napthalene.

It has previously been discussed that it is believed that the last two PAHs were dropping out of solution, which will affect the repeatability of the injection, especially when not normalized against an internal standard and although not seen in the calibration curves it is likely the case for Indeno[1,2,3-cd]pyrene too. The accuracy was calculated by determining the concentration of each compound for each replicate using their calibration curves, then comparing to the known concentration to determine the recoveries, the lowest and highest recoveries are shown in Table 2. Across all PAHs, the lowest recovery was 79% and the highest 118.8% which is acceptable[4] and will improve with further method development following the recommendations made and further method validation.

To test the method, tap water and water from a puddle on a tarmac surface in a car park were analyzed. No PAHs were determined in the tap water samples and therefore tap water was also used as a matrix spike where three tap water samples were spiked at three different concentrations, at Calibration Standard Levels 1, 3 and 6. The sample analysis and matrix spike results are shown in Tables 3 and 4 and a chromatogram of the puddle water is shown in Figure 5.

Table 3: Sample of puddle water from a tarmac surface results

	Retention time (min)	Concentration (ng/L)*	Qualifier ion value (%)
Phenanthrene	8.856	6.270	99
Fluoranthene	10.022	11.867	96

**Result from determination from the calibration curve, uncertainty not reported as not calculated in this limited method validation.*

In the puddle water, from a tarmac surface of a car park, two PAHs were identified and quantified as shown in Table 3. These were present at low concentration, one of which was below the lowest calibration standard but above the LOD. However, as no uncertainty value has been calculated with this limited method validation then the accuracy of the result is uncertain. But the identification of two PAHs does show that this method does have potential for this application.

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

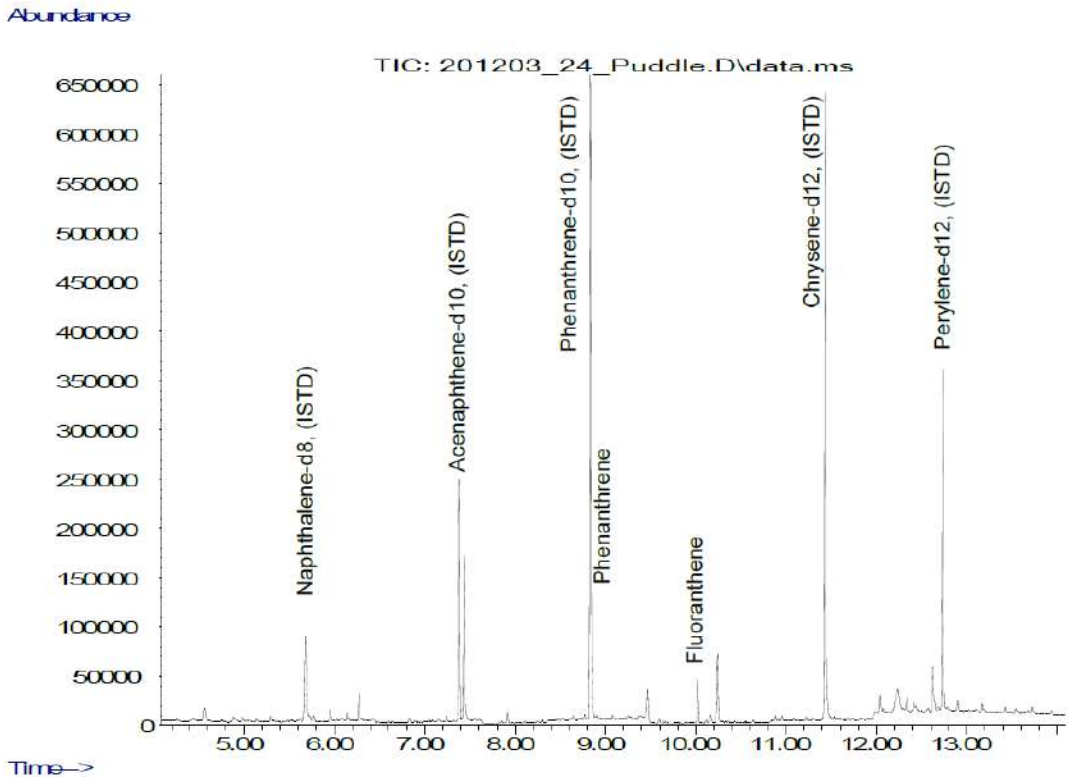


Figure 5: Chromatogram of the puddle sample

Table 4: Matrix spike results for tap water sample spiked at Calibration Standard Levels 1 (10 ng/L), 3 (100 ng/L) and 6 (1000 ng/L).

Compound name	L1 Determined conc (ng/L)	L1 Recovery (%)	L3 Determined conc (ng/L)	L3 Recovery (%)	L6 Determined conc (ng/L)	L6 Recovery (%)
Naphthalene	12.4727	124.7	96.2270	96.2	930.308	93.0
Acenaphthylene	9.3403	93.4	92.4857	92.5	864.638	86.5
Acenaphthene	10.6778	106.8	95.7402	95.7	875.488	87.5
Fluorene	10.5361	105.4	98.6407	98.6	898.560	89.9
Phenanthrene	10.7712	107.7	92.9988	93.0	837.079	83.7
Anthracene	8.7856	87.9	88.8128	88.8	865.986	86.6
Fluoranthene	9.3590	93.6	87.6381	87.6	875.886	87.6
Pyrene	12.4587	124.6	103.0020	103.0	925.105	92.5
Benzo[a]anthracene	9.4913	94.9	90.7740	90.8	892.227	89.2
Chrysene	10.4642	104.6	102.6640	102.7	957.460	95.7
Benzo[b]fluoranthene	8.6361	86.4	87.1207	87.1	895.974	89.6
Benzo[k]fluoranthene	8.7631	87.6	84.4872	84.5	897.585	89.8
Benzo[a]pyrene	8.8859	88.9	93.9491	93.9	1004.02	100.4
Indeno[1,2,3-cd]pyrene	8.96589	89.7	82.5076	82.5	1009.77	101.0
Dibenzo[a,h]anthracene	7.60672	76.1	71.3599	71.4	1218.1	121.8
Dibenzo[g,h,i]perylene	8.46742	84.7	78.8022	78.8	1091.42	109.1

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

Good recoveries were determined for all PAHs across the three matrix spike levels, which closely followed recovery values determined in the method validation. For the last eluting PAHs, the recoveries were higher than expected, this could be due to the reasons previously dicussed, but, on this occasion the sample extracts were analysed immediately after being prepared rather than waiting in the autosampler for a longer period of time, which could explain the higher recoveries and also emphasises earlier recommendations to mix the extract just before analysis.

CONCLUSIONS

The method developed using generated hydrogen as the carrier gas for the LLE-LVI-GC-MS determination of PAHs in water shows very good potential in speed and separating capacity. No adverse effects were observed concerning possible reaction of hydrogen carrier gas with analytes or the stationary phase of the GC column. The purity of the carrier gas as provided by the VICI DBS NM Plus hydrogen generator was fully satisfying. Changing from helium supported by pressure bottles to on-site generated hydrogen proved to be feasible without troubles and allowed steady operation with reduced efforts for system maintenance and eliminated safety issues.

The calibration curves showed very good linearity, although the last two eluting peaks showed quadratic fits, but, with further method development and ensuring that no PAHs dropped out of solution while awaiting analysis they could also show linear regression curves.

The last target compound eluted in less than 14 minutes, which is much earlier than conventional methods where the analysis takes 30-40 minutes[6]. This new method, with hydrogen, is at least twice as fast. The carrier gas flow rate was limited by the pumping capacity of the MS vacuum turbo pump, as higher flows produce a reduction in sensitivity. If a higher performance pump was utilised for this application higher flow rates in-line with the van Deemter curve for hydrogen could be used, resulting in even shorter run times.

Excellent peak shape, due to the use of hydrogen as a carrier gas was demonstrated, along with good peak separation; although, co-elution of two pairs of isomers were seen, but even with a conventional, 40-minute method baseline resolution is not achieved for these[6]. However, there was still enough peak separation for automated integration at all the concentration levels analysed. Changing from a 0.25 mm to a 0.18 mm internal diameter column could also reduce analysis time and improve peak resolution further.

By using LVI into the GC-MS, a manual sample preparation step was removed, making the total sample preparation time much shorter too. This method also has the potential for further method miniaturisation and using a fully automated LLE step using a robotic GC autosampler, such as was used in this White Paper or a newer version, prior to LVI. Therefore, the use of hydrogen as a carrier gas along with large volume injection enables the total sample analysis time to be greatly reduced and could at least double the sample throughput depending on the conventional method used.

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200

As well as the analytical advantages, there are also safety aspects that are addressed when comparing hydrogen to helium. The amount of stored gas in a generator is very small, compared to the high pressure (up to 200 bar) heavy, cumbersome cylinders that helium is supplied in. A VICI DBS generator will shut down in the event of a leak, therefore removing the danger of the lower explosive limit being reached.

With the price of helium constantly increasing, and variability in supply, this White Paper shows that there is no reason why generated hydrogen should not be considered as an alternative to helium as the carrier gas in GC-MS applications, in particular for the **analysis of PAHs in water by LLE-LVI-GC-MS**.

REFERENCES

1. Environment Agency, Polycyclic aromatic hydrocarbons (PAHS): sources, pathways and environmental data, October 2019
2. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union [online] pp. L226/1-L226/14. Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013L0039&from=EN
3. Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC. Official Journal of the European Union [online] pp. L158/7-L158/24. Available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2004:158:0007:0049:EN:PDF
4. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union [online] pp. L226/1-L226/14. Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013L0039&from=EN
5. Joint Research Centre, Institue for Reference Materials and Measurement, European Commission, Polycyclic Aromatic Hydrocarbons (PAHs) Factsheet 4th edition, JRC 66955 https://ec.europa.eu/jrc/sites/jrcsh/files/Factsheet%20PAH_0.pdf
6. Agilent Technologies Inc., GC/MS Analysis of European Union (EU) Priority Polycyclic Aromatic Hydrocarbons (PAHs) using an Agilent J&W DB-EUPAH GC Column with a Column Performance Comparison 5990-4883EN https://www.agilent.com/cs/library/applications/5990-4883EN.pdf

VICI AG International address: Parkstrasse 2, CH-6214 Schenkon, Switzerland
web: www.vicidbs.com email: sales@vicidbs.com phone: +41 41 925-6200