White Paper 046
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Reliable separation and efficient group-type quantitation of volatile petrochemical hydrocarbons (VPH)

This paper describes the analysis of volatile petrochemical hydrocarbons (VPH) in environmental samples by flow-modulated headspace–GC×GC–FID. We explain how inevitable biases observed using traditional one-dimensional GC can be eliminated using a fully automated workflow, for robust and efficient sample quantitation.

Introduction

Contamination of the environment from petroleum hydrocarbons is of major concern from the perspectives of human health and natural ecosystem preservation. Crude oils and refined products are highly complex mixtures containing a wide range of hydrocarbons, as well as compounds containing oxygen, sulfur and nitrogen. The ubiquitous use of petroleum products means there are now multiple ways in which these compounds can enter our environment, so efficient methods are required to monitor their fate, the risk to human health and to plan appropriate remediation strategies.

The lower-molecular-weight hydrocarbons (e.g., BTEX – benzene, toluene, ethylbenzene, xylene isomers) are extremely mobile within the environment and as such, undergo leaching into ground water sources with greater readiness than higher-molecular-weight species.

Risk-based methods have been established for the analysis of total petroleum hydrocarbons (TPH) in environmental media, including those from the TPH working criteria group,[1] the UK Environment Agency[2] and Massachusetts Department of Environmental Protection.[3] These methods state that the aliphatic and aromatic volatile petroleum hydrocarbons (VPH), typically in the range of C_5–C_{10}, must be characterised.

Current methods accomplish this through headspace and/or purge-and-trap techniques coupled with one-dimensional gas chromatography (GC) and detection by flame ionisation detection (FID), photo ionisation detection (PID) or mass spectrometry (MS). However, such techniques are subject to inherent bias due to co-elutions between non-petroleum hydrocarbons and the petroleum hydrocarbons of interest, resulting in quantitative values that either over-estimate or underestimate the target compounds.

Here, we overcome this issue by employing comprehensive two-dimensional GC (GC×GC) for enhanced separation of the petroleum hydrocarbons and improved quantitative precision. In this study, we will show how headspace(HS)–GC×GC–FID with INSIGHT® flow modulation can be used for reliable and fully automated VPH quantitation.

Experimental

Samples: VPH calibration samples consisted of gasoline with a known concentration of BTEX compounds spiked into mineral water at concentrations from 0.1–100 ppm.

Sample preparation: Sample preparation robot (SepSolve Analytical).

GC×GC: INSIGHT flow modulator (SepSolve Analytical); Modulation period (P_M): 2.0 s.

FID: H_2 flow: 10 mL/min; Air flow: 300 mL/min; Temperature: 300°C.

Please contact SepSolve for full analytical parameters.

SepSolve's TPH product package

The analytical equipment and software described here is available as part of SepSolve's TPH product package, comprising GC×GC hardware, software, method statements and consumables. Key aspects of this system for improving VPH analysis are described below, but to find out more on what we can offer for extractable petroleum hydrocarbon (EPH) analysis, read our accompanying white paper: Reliable separation and efficient group-type quantitation of total petrochemical hydrocarbons using GC×GC–FID.

1. Sample introduction

High-throughput labs rely on sample preparation robots (SPR) to increase the productivity, reproducibility and flexibility of their GC–MS analyses. For routine VPH analysis, SepSolve provides an SPR capable of running unattended headspace analysis of up to 360 samples. Control of the SPR is fully integrated into SepSolve's ChromSpace® software and bespoke SPR menus can even be created to tailor settings to specific method requirements.

2. Flow-modulated GC×GC

In VPH analyses, instrumental biases have been observed for specific compound groups according to the technique used (Table 1).[4] Existing techniques that combine the use of FID and PID to quantify aliphatic and aromatic bands are susceptible to inaccuracies due to the practice of subtracting the PID from FID traces, and further error is introduced where peak co-elutions exist. On the other hand, MS detectors typically have a greater response for aromatic compounds, causing aliphatic hydrocarbons in the C_9 to C_{12} range to be over-quantified.

Targets	Potential instrument bias	
	GC–PID/FID	GC–MS
Individual target analytes (e.g., BTEX)	High	No bias
C_5–C_8 aliphatics	Low	No significant bias
C_9–C_{12} aliphatics	Low	High
C_9–C_{10} aromatics	High	No significant bias

Table 1

Observed biases in 1D GC techniques for VPH analysis from a round-robin study conducted by the Massachusetts Department of Environmental Protection.[4]

With the enhanced separation of the aliphatic and aromatic compounds achieved by flow-modulated GC×GC–FID, these historical biases are anticipated to be eliminated. GC×GC involves coupling two columns with different stationary phases to allow separation of a mixture based on two different separation mechanisms. The sample is therefore separated in two dimensions, reducing the risk of co-elutions (Figure 1).

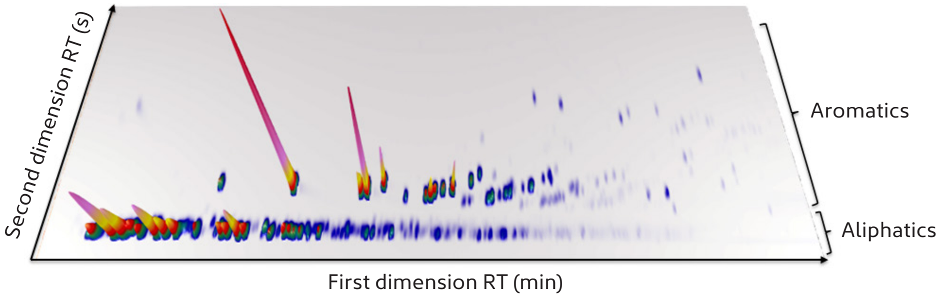


Figure 1

HS–GC×GC–FID surface chart for the analysis of a water sample spiked with gasoline.

The function of the modulator in GC×GC is to 're-inject' the effluent of the primary column onto a secondary column (with a different stationary phase) in sharp, narrow bands, whilst simultaneously preserving the separation attained in the primary column. There are two main types of modulator – thermal and flow modulators. Thermal modulators require a cold jet to trap the analytes, before a hot jet re-injects them on to the secondary column. However, thermal modulators are unsuitable for VPH analysis as they require expensive liquid nitrogen to capture the most volatile components and may also suffer from reliability issues (e.g., ice blockages within the cold jets).

On the other hand, flow modulators work using a simple, valve-based approach to 'fill' and 'flush' a sample loop. Flow modulation delivers increased method robustness – specifically the repeatability of retention times – through precise flow control by a dedicated EPC for each column. Flow modulators are therefore better suited to routine GC×GC analyses and comparisons across large sample batches. Here, the INSIGHT flow modulator was shown to provide excellent repeatability for HS–GC×GC–FID of a spiked water sample (Figure 2), with RSD values <10% across eight replicate injections.

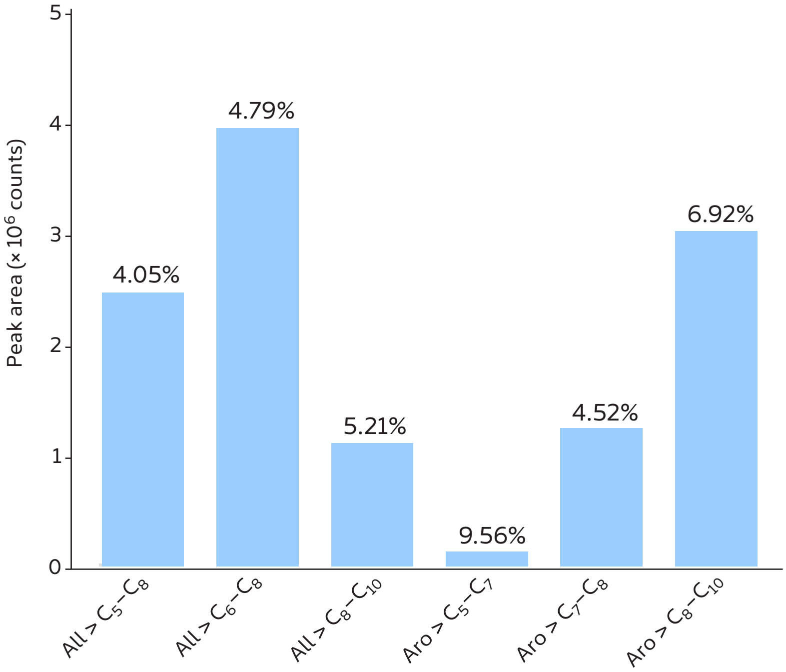


Figure 2

Repeatability results for eight replicate gasoline spike injections at 100 ppb.

3. Software

A key part of the package is SepSolve's ChromSpace GC×GC software platform, for fast, simple data processing and full LIMS compatibility. The availability of full instrument control and data processing in a single software platform is a key advantage of ChromSpace, resulting in streamlined workflows and simplified training requirements for analysts. A key feature that is covered in detail in this document is the use of 'stencils' defined by a banding standard, allowing real-world samples to be quickly integrated and quantified.

Results and discussion

The workflow for VPH data analysis using ChromSpace contains four fundamental steps: (1) Creation of stencil regions; (2) Quantitative method set-up; (3) Batch processing; and (4) Review and reporting of quantitative results. These are described separately in the following sections.

Step 1: Creation of stencil regions

The structured ordering of GC×GC chromatograms produces bands of chemical classes; thus, the petroleum aliphatic and aromatic compounds elute in separate regions of the GC×GC colour plot (Figure 3). Furthermore, non-petroleum compounds elute in separate bands, removing the potential for error from co-elutions.

Bands for group-type VPH analysis are defined by equivalent carbon numbers (e.g., aliphatics >C5–C6, >C6–C8, etc.). A banding standard consisting of individual aliphatic and aromatic compounds is used to define the regions and create a stencil, which can then be automatically applied to real samples.

Within ChromSpace, stencils are easily constructed and annotated for use in quantitative methods. Figure 3 shows a completed VPH stencil applied to both a banding standard (Figure 3, top) and a water sample spiked with gasoline (Figure 3, bottom). Stencil regions can easily be assigned to hierarchical groups; for example, all aromatic regions can be assigned to an 'Aromatics' group, allowing quantitative results to be reported for the entire class as well as the individual regions.

ChromSpace allows results to be reported automatically in the form of either a simple area percent table (Figure 4) or full quantitative analysis through group-

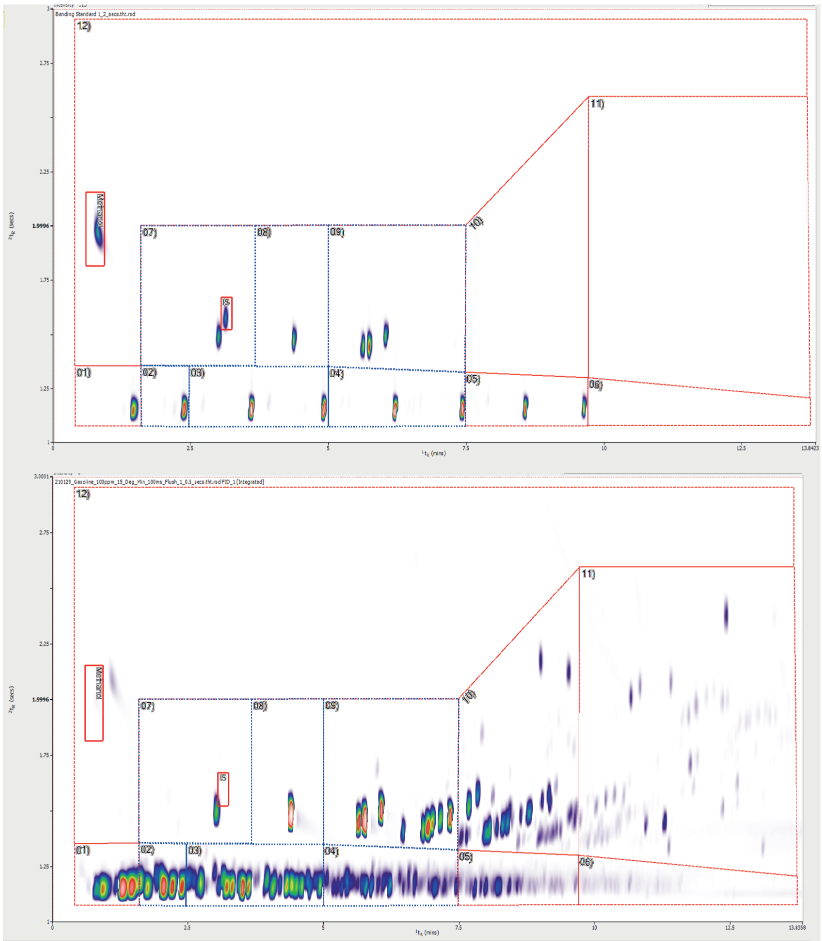
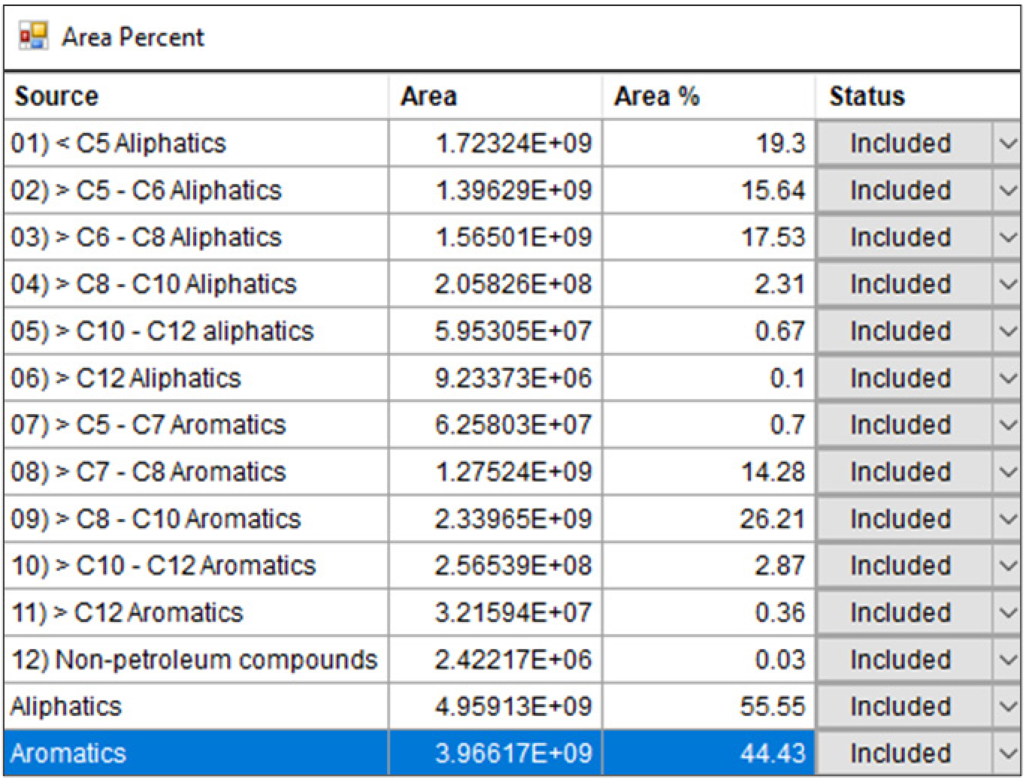


Figure 3

ChromSpace screenshots showing the VPH banding standard (top) and gasoline spike extract (bottom) with stencil regions applied. The normal VPH range of >C_5–C_{10} is shown by the blue stencils, while the red stencils indicate additional groups (e.g., <C_5 aliphatics) that can be classified using this GC×GC–FID method. The numerical labels in each stencil region correspond to the analyte classes listed in Figure 4.

type calibrations. It is important to note that the enhanced separation provided by GC×GC–FID enables additional classes to be included in the single analysis, such as the Aliphatics <C5, which would ordinally co-elute with methanol and interfere with quantitative results.



Area Percent

Source	Area	Area %	Status
01) < C5 Aliphatics	1.72324E+09	19.3	Included
02) > C5 - C6 Aliphatics	1.39629E+09	15.64	Included
03) > C6 - C8 Aliphatics	1.56501E+09	17.53	Included
04) > C8 - C10 Aliphatics	2.05826E+08	2.31	Included
05) > C10 - C12 aliphatics	5.95305E+07	0.67	Included
06) > C12 Aliphatics	9.23373E+06	0.1	Included
07) > C5 - C7 Aromatics	6.25803E+07	0.7	Included
08) > C7 - C8 Aromatics	1.27524E+09	14.28	Included
09) > C8 - C10 Aromatics	2.33965E+09	26.21	Included
10) > C10 - C12 Aromatics	2.56539E+08	2.87	Included
11) > C12 Aromatics	3.21594E+07	0.36	Included
12) Non-petroleum compounds	2.42217E+06	0.03	Included
Aliphatics	4.95913E+09	55.55	Included
Aromatics	3.96617E+09	44.43	Included

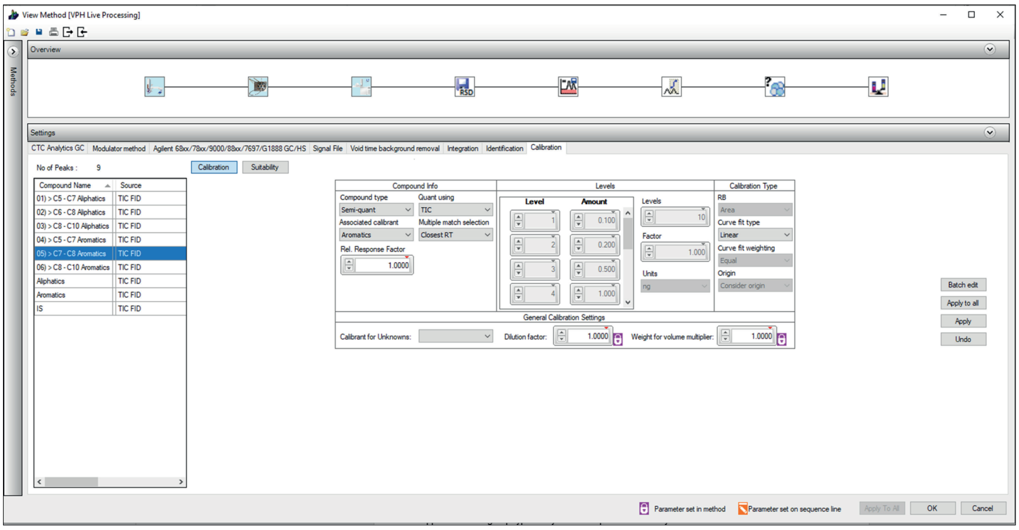
Figure 4

Area percent table in ChromSpace providing an overview of sample composition for the gasoline sample.

Step 2: Quantitative method set-up

In order to apply a calibration using the stencil, quantitative parameters must also be stored within the method (Figure 5). The region names are automatically transferred from the stencil to allow integration and calibration parameters to be added quickly. As can be seen in Figure 5, semi-quantitation can also be used, in this case allowing the '>C7–C8 Aromatics' class to be quantified using the calibration curve for the total aromatics.

The icon-based method overview shows each component of the method. A unique feature of ChromSpace is the ability to save processing parameters in a method alongside the acquisition parameters (Figure 5), enabling real-time data processing to be performed while the sample is acquiring. This saves valuable time by allowing all processed results to be viewed as soon as the acquisition sequence has completed. In Figure 5, all instrument settings have been saved alongside the quantitative parameters, meaning that background subtraction, integration and quantitation will be applied as the data acquires and results will be available immediately without any user intervention.



No of Peaks : 9

Compound Name	Source
01) > C5 - C7 Aliphatics	TIC FID
02) > C6 - C8 Aliphatics	TIC FID
03) > C8 - C10 Aliphatics	TIC FID
04) > C5 - C7 Aromatics	TIC FID
05) > C7 - C8 Aromatics	TIC FID
06) > C8 - C10 Aromatics	TIC FID
Aliphatics	TIC FID
Aromatics	TIC FID
IS	TIC FID

Compound Info
Compound type: Semi-quant
Quant using: TIC
Associated calibrant: Aromatics
Multiple match selection: Closest RT
Rel. Response Factor: 1.0000

Levels

Level	Amount
1	0.100
2	0.200
3	0.500
4	1.000

Levels: 10
Factor: 1.000
Units: ng

Calibration Type
RB: Area
Curve fit type: Linear
Curve fit weighting: Equal
Origin: Consider origin

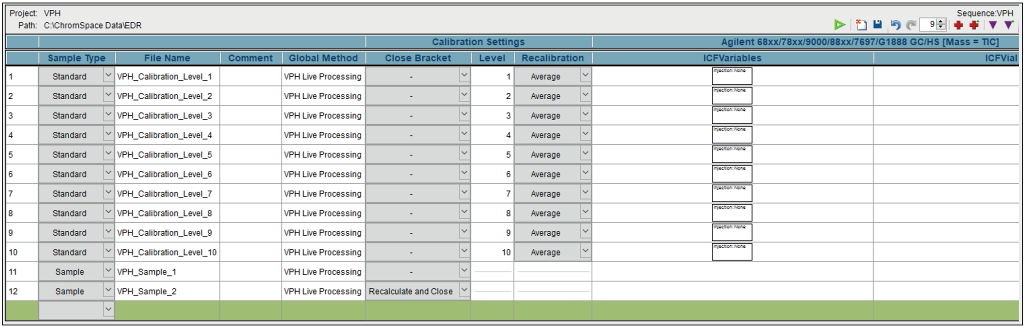
General Calibration Settings
Calibrant for Unknowns:
Dilution factor: 1.0000
Weight for volume multiplier: 1.0000

Figure 5

Quantitative method parameters in ChromSpace software. The top panel contains an icon-based method overview, showing all the instrument control and data processing settings contained within this single method.

Step 3: Batch processing

Once a method is saved, sample analysis and data processing can be run in unattended batches. As previously mentioned, data processing can be performed off-line post-analysis or in real time while the sample is acquiring (as shown in the method in Figure 5). All sequences are stored under the 'History' tab and can be easily archived to a back-up system.


Project: VPH
Path: C:\ChromSpace Data\EDR
Sequence:VPH

					Calibration Settings			Agilent 68xx/78xx/9000/88xx/7697/G1888 GC/HS [Mass = TIC]	
	Sample Type	File Name	Comment	Global Method	Close Bracket	Level	Recalibration	ICFVariables	ICFVial
1	Standard	VPH_Calibration_Level_1		VPH Live Processing	-	1	Average	Injection: None	
2	Standard	VPH_Calibration_Level_2		VPH Live Processing	-	2	Average	Injection: None	
3	Standard	VPH_Calibration_Level_3		VPH Live Processing	-	3	Average	Injection: None	
4	Standard	VPH_Calibration_Level_4		VPH Live Processing	-	4	Average	Injection: None	
5	Standard	VPH_Calibration_Level_5		VPH Live Processing	-	5	Average	Injection: None	
6	Standard	VPH_Calibration_Level_6		VPH Live Processing	-	6	Average	Injection: None	
7	Standard	VPH_Calibration_Level_7		VPH Live Processing	-	7	Average	Injection: None	
8	Standard	VPH_Calibration_Level_8		VPH Live Processing	-	8	Average	Injection: None	
9	Standard	VPH_Calibration_Level_9		VPH Live Processing	-	9	Average	Injection: None	
10	Standard	VPH_Calibration_Level_10		VPH Live Processing	-	10	Average	Injection: None	
11	Sample	VPH_Sample_1		VPH Live Processing	-				
12	Sample	VPH_Sample_2		VPH Live Processing	Recalculate and Close				

Figure 6

A VPH sequence in ChromSpace. Here, this is performed after analysis, but it can also be carried out in real time by saving the data-processing parameters alongside the acquisition parameters.

Step 4: Review and reporting of quantitative results

Finally, once a quantitative method is run, results are launched from the results browser of ChromSpace, providing all the quantitative information at a glance, including region list, sample list, calibration curves and interactive colour plot. Results can be easily exported either as a custom report, a simple .csv file or directly to a LIMS interface. Full LIMS import and export capability enables alignment of ChromSpace with existing laboratory protocols. An example of the excellent linearity achieved using HS–GC×GC–FID is shown in Figure 7 for VPH in mineral water across a concentration range of 100 ppb–100 ppm.

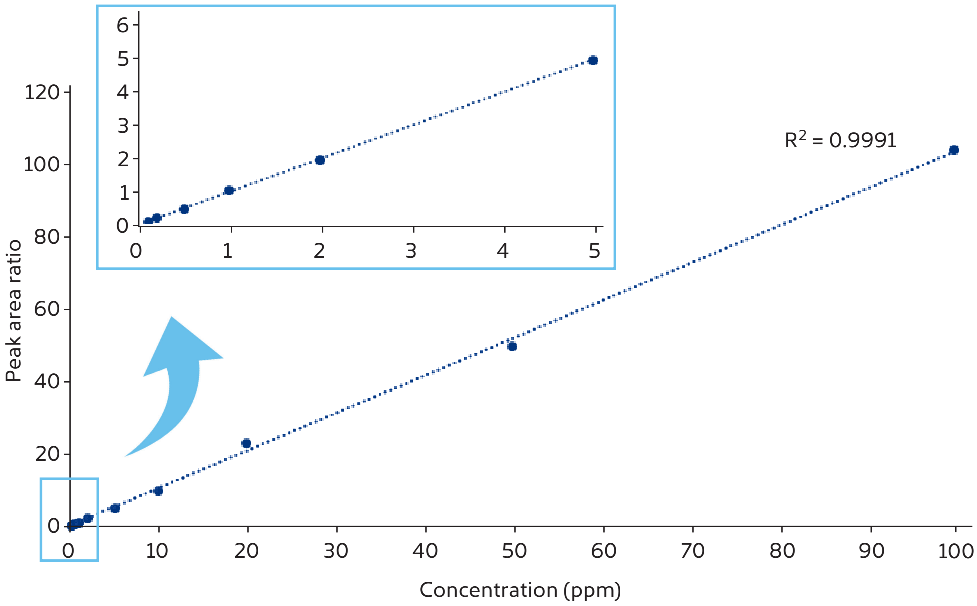


Figure 7
VPH calibration curve for gasoline spiked into mineral water showing excellent linearity across a concentration range of 100 ppb to 100 ppm.

Conclusions

This study has shown HS–GC×GC–FID to be a versatile and powerful approach to the group-type analysis of VPH in environmental samples. Key features are:

- High productivity through fully automated sample introduction, analysis and data processing.
- Improved confidence due to elimination of method biases observed with conventional 1D GC methods, through enhanced separation and structured ordering of GC×GC.
- Excellent repeatability and low running costs through INSIGHT flow modulation.
- Fast and flexible set-up of quantitative methods in ChromSpace GC×GC software.
- Streamlined group-type data processing and reporting in real time – a key consideration for contract laboratories routinely running large numbers of VPH analyses.
- A turnkey solution (including method protocol and column set) that can be supplied as a complete system or as an upgrade to an existing GC–FID.

References

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