

focus on Chromatography

Methane, Ethylene, and Ethane in Water by Headspace-Gas Chromatography (HS-GC) with Flame Ionisation Detection (FID)

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The rapid development of natural gas from unconventional sources in North America has created an energy 'gold rush' not seen in contemporary times. The advent of horizontal drilling technologies and hydraulic fracturing has made this production economical and presents an energy source of sufficient magnitude that could last 100 years.

The technology presents a number of environmental challenges as the wells are drilled vertically through aquifers on their way to the deep shale deposits thousands of feet under the surface, and then turned horizontally and drilled another several thousand feet through the shale deposit. Herein lies the challenge: in the process of drilling the wells and preparing them for production (including 'fracking' to optimise production), opportunities arise for contamination of the clean drinking water aquifers with methane and other low molecular weight organics (e.g., propane and ethane). Correctly drilled and cemented well bores should not be an issue, but any errors in engineering could result in contamination.

It is also possible that methane already exists at a low concentration in the aquifer from diffusion of the gas occurring naturally. There is a need (by property owner and lease holder) to confirm the level of gas in the aquifer before and during drilling, and also after the well is placed into production.

Table 1. Headspace and GC Conditions.

HS Conditions	
Sample Temperature:	90 °C
Equilibration Time:	10 min
Needle Temperature:	110 °C
Transfer Line Temperature:	120 °C
Inject Time:	0.06 min
Withdrawal Time:	0.4 min
Pressurization Time:	1.0 min
HS Mode:	Constant
HS Pressure:	20 psi
GC Conditions	
Oven Temperature	
Initial Temperature:	40 °C
Initial Hold:	4.5 min
Ramp:	40 °C/min
Final Temperature:	205 °C
Final Hold:	1 min
Detector (FID)	
Detector Temperature:	240 °C
Air Flow:	400 mL/min
Hydrogen Flow:	40 mL/min
Range:	1
Attenuation:	-6 (or 1)

Note: The columns are directly connected to the HS transfer line; therefore, inlet parameters are not applicable.

Traditionally, methane in water is determined using US Environmental Protection Agency (EPA) method RSK 175 (RSKSOP175, 2004) or an alternative (Vandegrift, 1998). PerkinElmer's TurboMatrix™ HS and Clarus® 680 GC combination offers a simple, economical and reliable measurement technique to determine methane and other target gases in water. This application note summarises the experimental approach and subsequent results to confirm the viability of the method.

Instrumentation

A PerkinElmer® TurboMatrix Headspace (HS) connected to a PerkinElmer Clarus 680 Gas Chromatograph (GC) with dual flame ionisation detectors (FID) were used in these experiments.

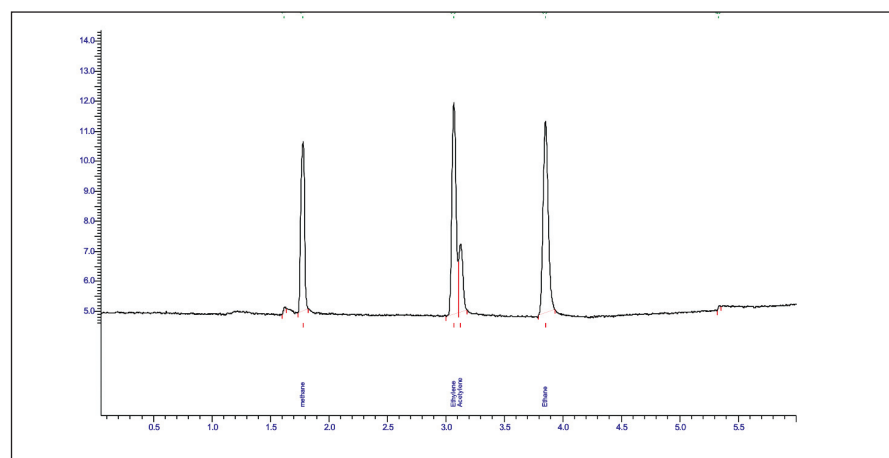


Figure 1: 10 ppb standard (Q PLOT)

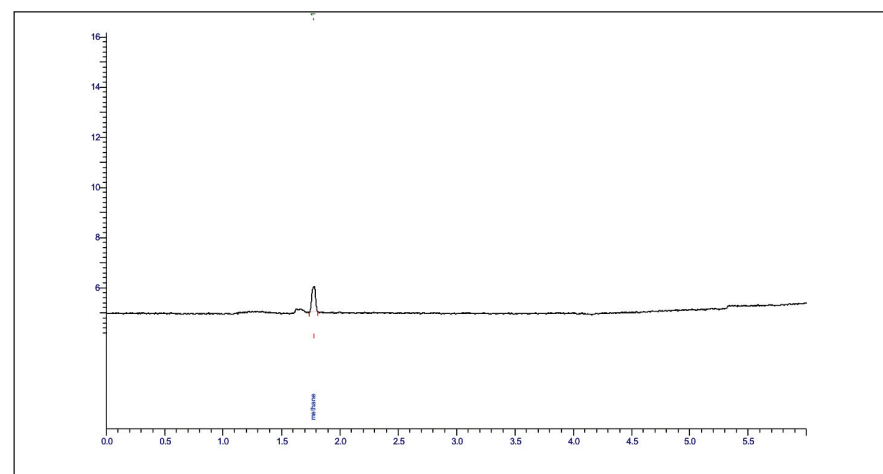


Figure 2: Chromatogram of blank (15mL water)

Since detection is performed using an FID, the technique of column confirmation may be employed to confirm identity of components. An Elite-Q PLOT column with dimensions 30m x 0.32mm (PerkinElmer Part No. N9316359) was used for quantitation and the Elite-U PLOT column with dimensions 30m x 0.32mm was used for confirmation. These columns were directly connected to the deactivated fuse silica headspace transfer line via a 'Y' connector.

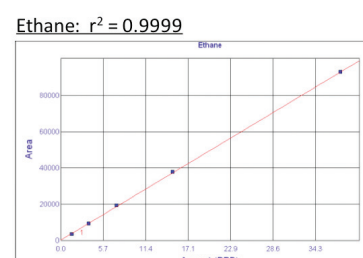
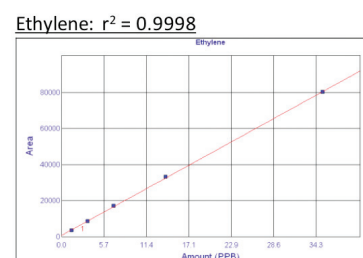
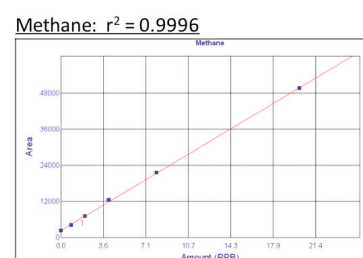


Figure 3: Calibration curves

Experimental Conditions

A stock standard was used for these experiments (Supelco® Part No. 23437). This stock standard contained methane, ethylene, acetylene and ethane in approximately one molar percent concentration in nitrogen for each component.

The headspace and GC operating conditions are displayed in Table 1. To validate the method, the following experiments were performed:

1. **Background:** Blank air and water were investigated for interferences. Since methane may be present in ambient air, four 22mL Headspace Crimp Vials (PerkinElmer Part No. N9306079) containing 15mL of the deionised (DI) water, used in preparing standards, were investigated to determine the concentration of the methane in the blank samples.

2. **Calibration:** A five-point calibration curve was created establishing method linearity and reporting limits. Five headspace vials were prepared with 15mL of DI water then capped using PTFE silicone septa. A 2µL, 5µL, 10µL, 20µL and 50µL volume of the stock standard was inserted through the septum (PerkinElmer Part No. N9303992) into the water of five of the vials, respectively, attaining concentrations as described in Table 3.

3. **Accuracy:** Four water samples were prepared as quality controls from 5 to 50 ppb to confirm method accuracy.

4. **Precision:** Five 40 ppb standards were prepared from the stock standard, and analysed for precision.

Table 2. Repeatability of Four Blanks for Methane.

Sample Name	Area (Methane)
15 mL Water Blank	2093.5
15 mL Water Blank	2163.7
15 mL Water Blank	2337.4
15 mL Water Blank	2124.3
Average	2179.7
%RSD	5%

Table 3. Standard concentrations in Parts Per Billion (ppb) or µg/L.

Level No.	Methane	Ethylene	Ethane
1	0.80	1.40	1.50
2	2.00	3.50	3.75
3	4.00	7.00	7.50
4	8.00	14.00	15.00
5	20.00	35.00	37.50

subtract for the presence of methane in air. Since the headspace vials are sampled in air, this air is trapped in the vial. The concentration of methane in air is below the reporting limit. *Table 2* tabulates the precision of methane in the blank.

Figure 3 graphically demonstrates the results of the external standard calibration curve of each component. The linearity achieved was excellent with a correlation coefficient (r^2) of 0.9996 and better. *Table 3* contains the concentrations of the standards used to prepare these curves.

Table 4 tabulates the results of the quality control study. These controls were processed using the five-point calibration for each component. *Table 5* represents the results of the precision study at Level 4.

Discussion

In this experiment, the blank was used as a point on the calibration curve to correct for the presence of methane in ambient air (subtracting the blank), which improves accuracy for the low level methane amount and allows for very easy sample preparation essentially filling the vial with a known amount of water and capping it.

The reporting limit of 1 ppb methane in water was achieved. The lowest point of the curve prepared for this application for methane was 0.8 ppb, and 1st order is maintained through this point.

The recoveries obtained in this experiment from four quality control samples are from 90% to 98%. This accuracy is excellent and incorporates errors due to method and operator. Since these gaseous standards and quality control samples are prepared manually with a gas-tight syringe human error is a contributory factor; therefore, the accuracy is exceptional.

Instrument and method repeatability (precision) is 2.1% for methane which is an acceptable repeatability for this application.

Conclusions

Examining the results of these experiments, the PerkinElmer TurboMatrix HS and PerkinElmer Clarus 680 GC provide a viable solution determining methane and other low molecular weight hydrocarbons in water delivering accuracy, precision and ease of use.

Table 4. Repeatability of Peak Area Calculations Using Level 4 Concentration (Refer to Table 2).

Methane			Ethylene			Ethane		
Actual Amt.	Calc. Amt.	%Dev	Actual Amt.	Calc. Amt.	%Dev	Actual Amt.	Calc. Amt.	%Dev
2.00	2.05	2.50	3.50	3.43	-2.00	3.75	3.59	-4.27
10.00	10.72	7.20	17.50	18.68	6.74	18.75	19.91	6.19
14.00	15.19	8.50	24.50	26.40	7.76	26.25	28.43	8.30
20.00	20.69	3.45	35.00	36.44	4.11	37.50	39.14	4.37

Table 5. Repeatability of Peak Area Calculations Using Level 4 Concentration (Refer to Table 3).

Conc. Level	Methane Area	Ethylene Area	Ethane Area
4	43180	70067	80441
4	44330	70199	81390
4	43421	67911	79164
4	44331	71017	82016
4	42184	66722	76234
Average	43489	69183	79849
% RSD	2.1	2.6	2.9

Results

Figure 1 demonstrates separation of the four gases in the stock standard on the Elite-Q PLOT column. The concentration of the standard represented in *Figure 1* is 10 parts per billion (ppb). Since acetylene is not a target analyte of this application, and acetylene is not found in samples, it is recommended that a standard mix be used not containing this analyte to avoid integration challenges between ethylene and acetylene.

Figure 2 is a chromatogram of a water blank (15mL volume). To compensate for the methane present in ambient air, this point was incorporated on the calibration curve to

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Optimal Drying of Aqueous HPLC Fractions

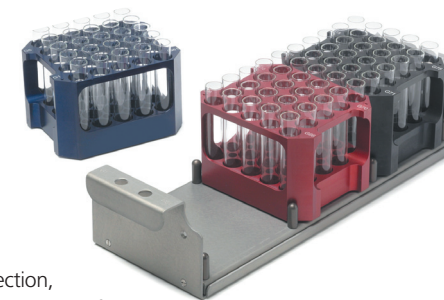
A white paper is available from **Genevac** that details a high throughput methodology, using its HT Series II centrifugal evaporator, for drying HPLC fractions containing water.

HPLC purification fractions can be notoriously difficult to dry. The acetonitrile or methanol seems to evaporate easily enough but the water presents more of a challenge. Genevac have developed a multiple stage method to enable HPLC purification fractions to be easily dried in the fastest safe way possible.

For a copy of this white paper please visit the Genevac website or contact the company.

The HT Series II centrifugal evaporators benefit from Genevac's 20+ years of experience in solvent removal with leading edge features that provide superior sample protection, flexibility for multiple applications, consistency of results, robust build quality, ease-of-use, rapid high-throughput results and low maintenance. Genevac has developed a number of technological innovations on the HT Series II that assist labs looking to efficiently and safely dry aqueous HPLC fractions.

These include Dri-Pure® that eliminates the unwanted effects of solvent bumping; SampleGuard® that prevents heat damage to samples while ensuring rapid evaporation and Auto-Defrost & Drain that enables volatile solvents to be collected and safely disposed of. A technical brochure describing their HT Series II Centrifugal Evaporator range in more detail is available at www.genevac.com/en/NewsPg.asp?S=6&V=1&Page=95



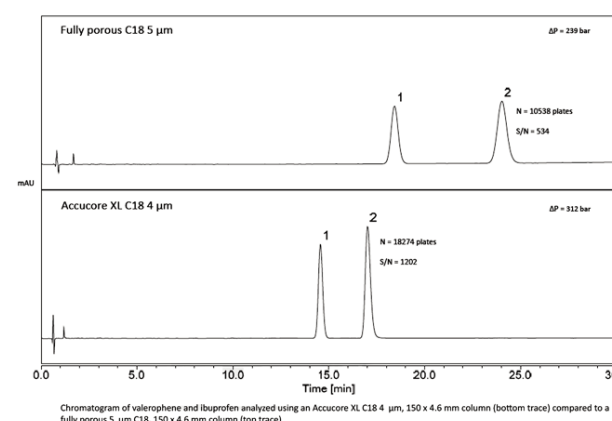
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New Columns Designed to Improve Performance of Conventional HPLC Methods Introduced

Thermo Fisher Scientific Inc have introduced Thermo Scientific Accucore XL HPLC columns, engineered to significantly increase the performance of conventional HPLC separations without modifying the instruments or methods. Tests in Thermo Fisher's internal laboratory show that Accucore XL HPLC columns, based on Core Enhanced Technology using 4µm solid core particles, allow users of conventional HPLC methods to enjoy performance far beyond that of columns packed with 5µm, 4µm or even 3µm fully porous particles.

Core Enhanced Technology™ is a combination of Thermo Fisher's state-of-the-art particle technology and extensive experience in phase bonding and packing. The columns feature solid core particles, tight control of particle diameter, advanced bonding technology and automated packing processes. Very high separation efficiencies using standard HPLC instruments and conditions provide increased peak resolution and lower limits of detection. An ultra-stable packed bed results in exceptionally robust columns that demonstrate excellent retention and response reproducibility.

"The Accucore XL HPLC column range is targeted at those labs desiring better sensitivity, resolution and robustness when compared to conventional 3 and 5µm HPLC columns," said Darren Thomas, Thermo Fisher Business Director and General Manager, Chromatography Consumables. "Accucore XL HPLC columns can achieve these improvements with no modification to the customer's current method. Consequently, customers can see better results and an enhanced return on their investment."



Chromatogram of valerophene and ibuprofen analyzed using an Accucore XL C18 4 µm, 150 x 4.6 mm column (bottom trace) compared to a fully porous 5 µm C18, 150 x 4.6 mm column (top trace)

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