

# Analysis of Hydraulic Fracturing Fluids with the Agilent Intuvo 9000 GC and Agilent 5977B GC/MSD

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## Abstract

The Agilent Intuvo 9000 GC coupled with the Agilent 5977B GC/MSD system is a combination of a technologically advanced GC with high-efficiency mass detection. The Intuvo 9000 GC features a Guard Chip for column protection, ferrule-free, click-and-run connections, and a direct heating oven that reduces the turnaround time and overall footprint of the GC. This makes the instrument well suited for bench-scale studies in university research laboratories. Analysis of water samples from oil and gas wells can be carried out efficiently with GC/MS. These systems characterize volatile and semivolatile organic compounds while offering good resolution. This Application Note presents a study conducted with an Intuvo 9000 GC and 5977B GC/MSD system to analyze hydraulic fracturing water samples. These contained produced and flowback water from three sites in various US states. Compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX) were identified using MS along with long chain hydrocarbons (C7 to C35). The study concludes that this GC/MSD system is appropriate for a wide range of student research applications with great performance, repeatability, reliability, and ease-of-use.

## Introduction

Hydraulic fracturing (fracking) refers to a process in which rocks such as sandstone, shale, and coalbed methane are injected with a mixture of chemicals (surfactants, emulsifiers, and stabilizers). This perforates the rock formation to enable or increase the flow of oil and gas to the wells. The flowback and produced waters are the by-products of the fracturing process, constituting a complex matrix of hydrocarbons, salts, metals, and other trace constituents. The water samples usually consist of a wide variety of hydrocarbons, surfactants, emulsifiers, chemical stabilizers, and proprietary compounds used by the oil and gas companies. Many of the chemicals are reported nonspecifically as general families, such as alkyl ethoxylates or proprietary substances, which are highly complex in nature.

This Application Note focuses on the characterization of such samples using an Intuvo 9000 GC coupled to a 5977B GC/MSD system. The aim of this study was to develop a sample preparation protocol, and to optimize the GC/MS system for analyzing oil and water samples. We intended to challenge the Intuvo Guard Chip system with these samples. Another objective was to see if a microfluidics GC system and software/hardware interface were suitable for these types of samples and yet easily applicable to student use. Because students are often in training, they do not have the skilled abilities of experienced GC analysts.

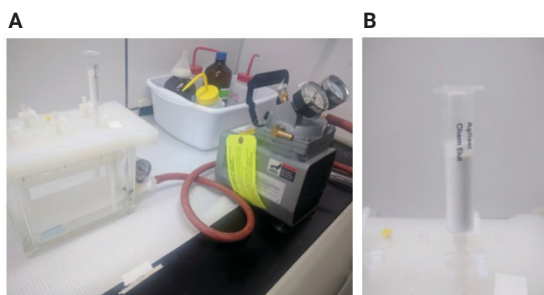
## Experimental

### Sample preparation

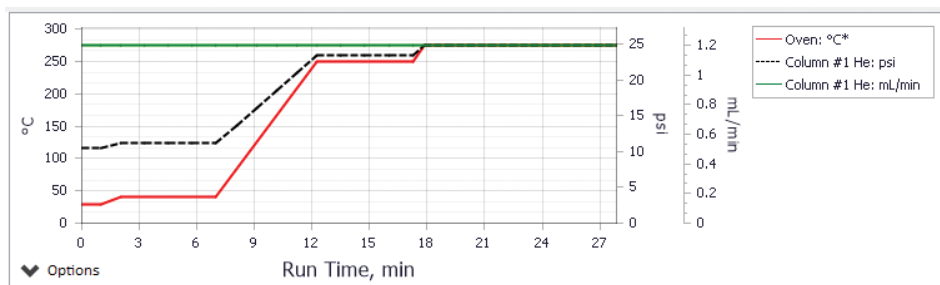
Three different hydraulic fracturing samples from sites named Virginia Lee, Marmot, and OK Preserve were prepared using supported liquid extraction (SLE) in a vacuum manifold under a pressure of 15 psi. A 2-mL aliquot of the fracking water sample was loaded onto an Agilent Chem Elut 1 mL SLE cartridge made of diatomaceous earth (p/n 12198002) (Figure 1). After the column adsorbed the water content in the sample (no breakthrough), 2 mL of methylene chloride was added to the column under vacuum pressure to elute the compounds that partitioned into the diatomaceous earth. The eluted methylene chloride was placed in a clean, 2-mL amber GC vial, and stored at  $-20\text{ }^{\circ}\text{C}$  for analysis.

### Method development on the Intuvo 9000 GC and 5977B GC/MSD coupled system

The Intuvo 9000 GC was configured with an Agilent HP-5ms Ultra Inert column. The Intuvo 9000 GC also features a Guard Chip for column protection. The oven was ramped from 30 to  $275\text{ }^{\circ}\text{C}$  over a 20 minute period, as shown in the temperature profile in Figure 2. Simultaneously, the Guard Chip was held at  $55\text{ }^{\circ}\text{C}$  until the oven reached  $55\text{ }^{\circ}\text{C}$ , then the two were ramped to final temperatures of  $250\text{ }^{\circ}\text{C}$  for the Guard Chip and  $275\text{ }^{\circ}\text{C}$  for the column. It was recommended that the Guard Chip be run at approximately  $25\text{ }^{\circ}\text{C}$  higher than that of the oven. However, we found that running at the same temperature as the oven gave good chromatographic results for the semivolatile compounds present in the samples.



**Figure 1.** Vacuum manifold system (A) with SLE cartridge fitted on top. Agilent Chem Elut 1 mL cartridge (B).



**Figure 2.** Graphic representation of column temperature, He pressure, and flow.

The Intuvo 9000 GC also features cycle time optimization that has a fast-cooling option set by default to minimize the delay between runs using a rapid heating and cooling technology. Thus, it was easy to reach a starting temperature of 30 °C for good chromatographic separation of the BTEX compounds.

**Table 1.** GC/MS system parameters.

Parameter	Value
<b>Intuvo 9000 GC</b>	
Inlet	Inert split/splitless in splitless mode, 250 °C splitless, 10.549 psi
Inlet pressure	10.549 psi
Purge flow to split vent	100 mL/min at 0.25 minutes
Septum purge flow	3 mL/min
Gas saver	30 mL/min after 2 minutes
Intuvo Guard Chip	55 °C for 7.5 minutes, then 40 °C/min to 250 °C
Column	Agilent Intuvo HP-5ms Ultra Inert, 30 m × 250 µm, 0.25 µm (p/n 19091S-433UI-INT)
Column flow	1.2 mL/min (helium)
Oven	30 °C (hold: 1 minute) 10 °C/min to 40 °C (hold: 5 minutes) 40 °C/min to 250 °C (hold: 5 minutes) 40 °C/min to 275 °C (hold: 10 minutes) Total run time: 27.875 minutes
Injection volume	1 µL
Bus temperature	275 °C
MSD connector	275 °C
MSD transfer line	275 °C
<b>5977B GC/MSD</b>	
Operating mode	Scan (normal scanning) with positive electron ionization
MS source temperature	230 °C
MS quad temperature	200 °C
Solvent delay (MS start time)	2.90 minutes
Low mass	<i>m/z</i> 50
High mass	<i>m/z</i> 500
Scan speed	1562 u/s
Data processing software	Masshunter Qualitative Analysis Version 8.0

## Results and discussion

Figure 3 shows GC/MS-produced chromatograms for the three analyzed hydraulic fracking samples. The Intuvo 9000 GC showed good compound repeatability in terms of peak shape and retention times.

Figure 4 shows repeatability test results for the Virginia Lee samples, with compound peaks overlapping between different runs within fractions of one second, and an average peak width of three seconds. The chromatograms of the hydraulic fracking samples revealed the presence of straight-chain alkanes ranging from C7 to C35. This allowed us to compare the series of compounds called gasoline range organic compounds (GROs) with the diesel range organic compound (DRO) series.

Virginia Lee sample analysis revealed GROs, which are C6 to C10 *n*-alkanes, and DROs, which are C11 to C35 *n*-alkanes, as shown in Figure 4. The ratio of GRO/DRO alkanes is considered an

important parameter in characterizing the samples used in petroleum studies. Here we saw differences for the Virginia Lee sample, which contained considerably more GRO compounds than

the other samples. This measurement is critical to studies of petroleum reserves and, in the case of hydraulic fracturing, to the safe storage of these oil and water samples.

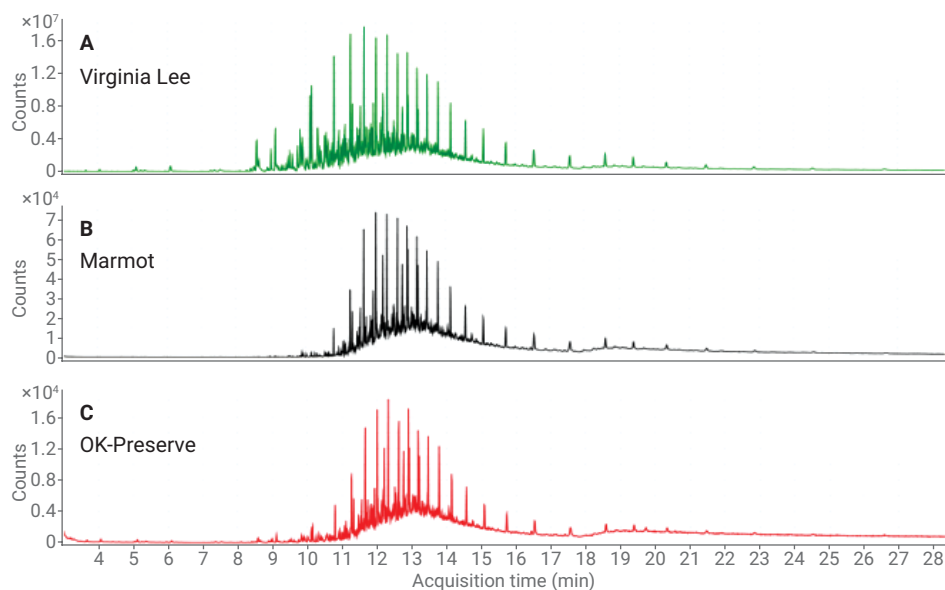


Figure 3. GC chromatograms showing compound peaks in hydraulic fracking samples.

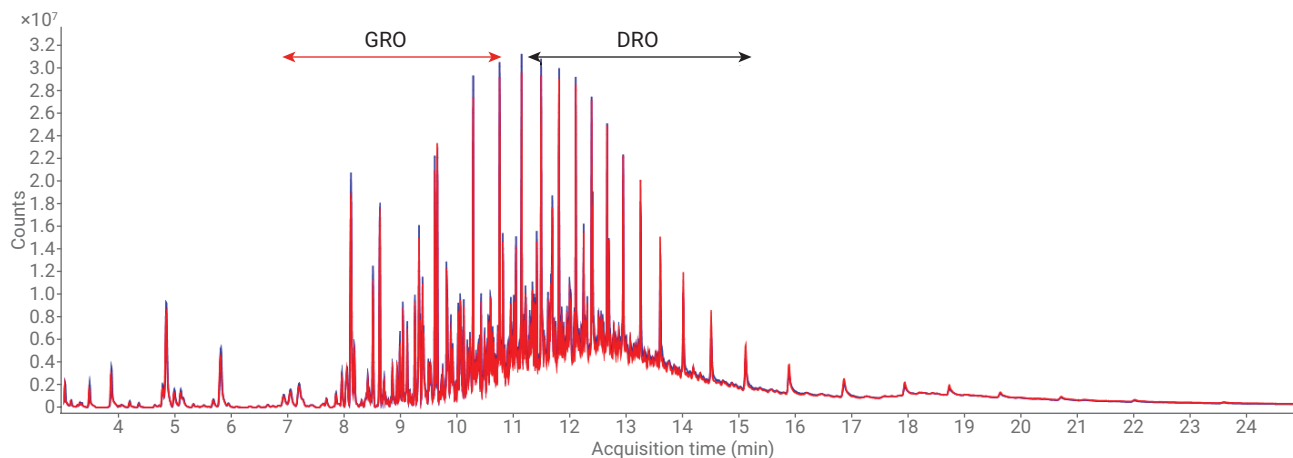
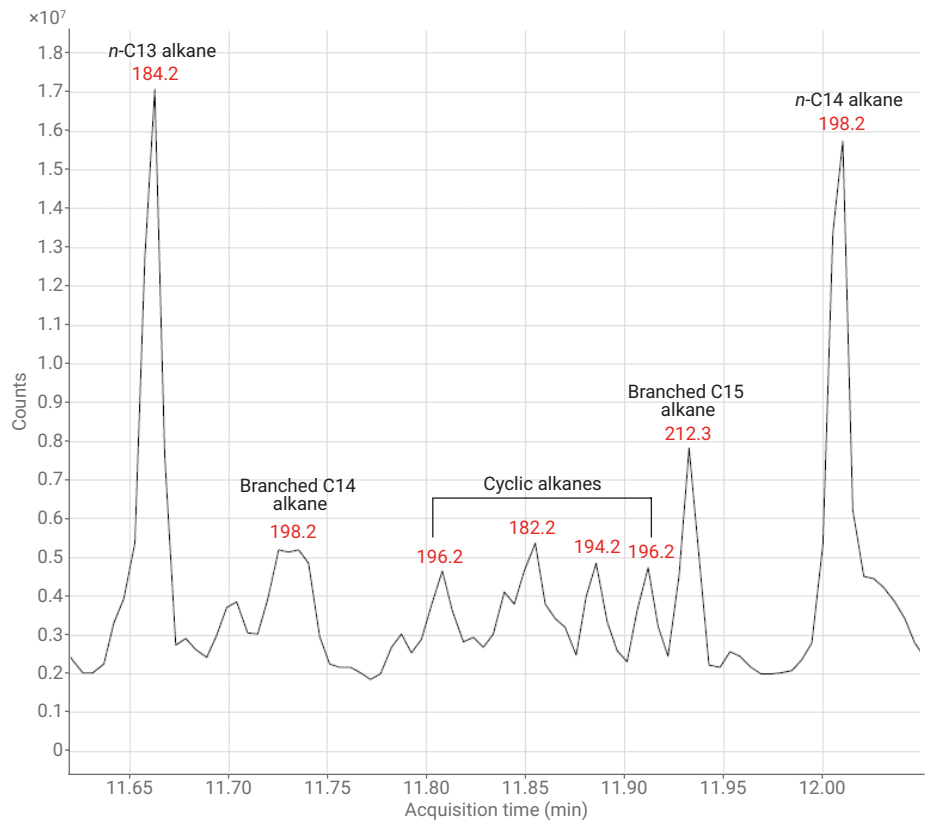


Figure 4. Repeatability of the Virginia Lee sample (red and blue traces) showing the presence of alkanes ranging from C7 to C35 that fall under gasoline and diesel range organics.

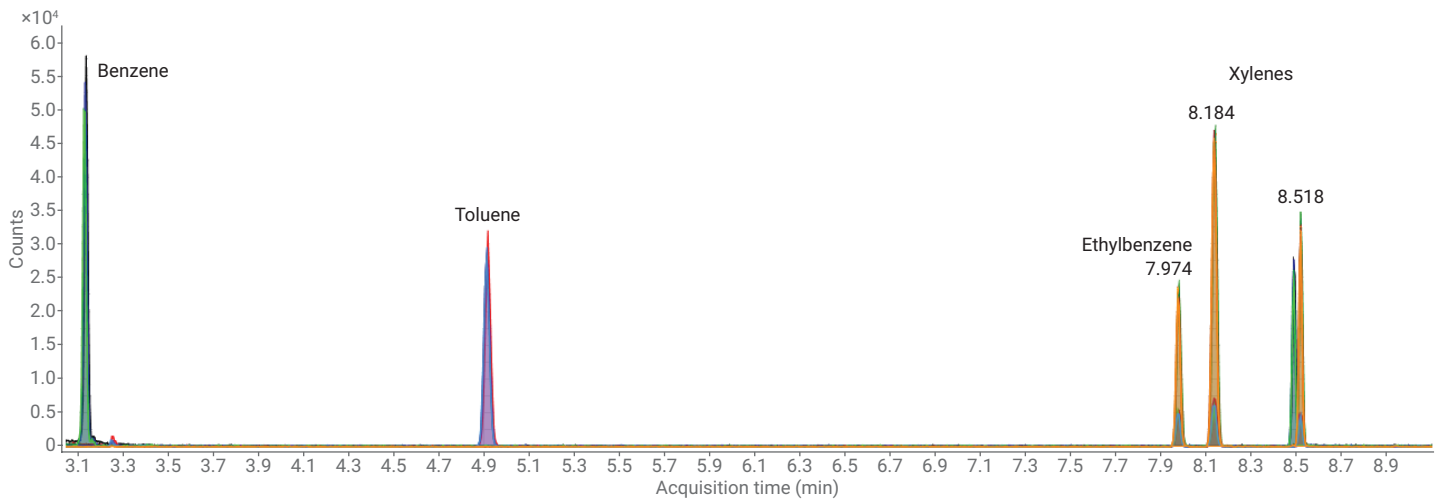
The peak patterns of these chromatograms were analyzed to identify branched-chain and straight-chain isomers of the alkanes and alkenes present in the samples. Figure 5 is an example of peak analysis showing *n*-alkanes, branched isomers, and cyclic alkanes.

### BTEX analysis

This study also looked at analyzing BTEX compounds. These are common contaminants of drinking water that may leach into the water table from oil and gas wells and petroleum production sites. A BTEX standard of 200 ppb concentration in methylene chloride was analyzed using the GC/MS system as a reference, as shown in Figure 6.



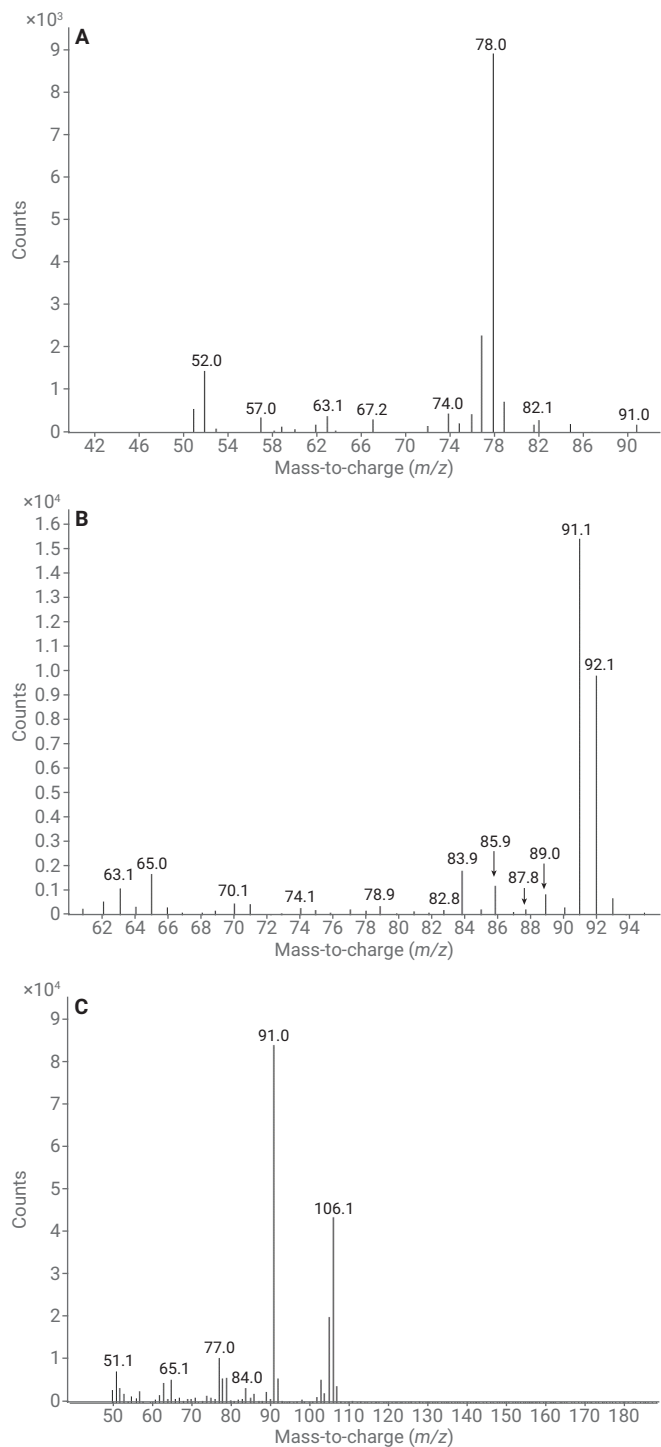
**Figure 5.** Analysis of peak patterns in a chromatogram of hydraulic fracking sample (Virginia Lee) with corresponding *m/z* values.



**Figure 6.** Chromatogram showing benzene (RT 3.15 minutes), toluene (4.95 minutes), ethylbenzene (RT 7.97 minutes), and xylenes (*p*-xylene and *m*-xylene at 8.134 minutes; *o*-xylene at 8.518 minutes).

BTEX chromatograms showed good repeatability between consecutive runs with sharp and symmetric peaks. We found that it was quite important to use a high purge flow (100 mL/min) with a short purge time (0.25 minutes) to get sharp nontailing peaks that were reproducible. Good retention time repeatability for the volatile compounds of BTEX was ensured by making certain that the column reached the starting temperature of 30 °C, and was held there for at least one minute.

Figure 7 shows the corresponding mass spectra of these compounds. The GC column exhibited good separation of xylene isomers, with *p*-xylene and *m*-xylene coming off the column at 8.134 minutes, and *o*-xylene seen at 8.518 minutes. To completely separate these isomers would require a much longer chromatographic run time. This was not appropriate given the goal of seeing the entire chromatogram of alkanes and their isomers present in the oily water samples from hydraulic fracturing.



**Figure 7.** A) Mass spectrum of benzene (RT 3.15 minutes) with the molecular ion peak at  $m/z$  78.0. B) Mass spectrum of toluene with the molecular ion peak at  $m/z$  92.1 and stable ion peak at  $m/z$  91.1. C) Mass spectrum of xylenes at 8.134 minutes with the molecular ion peak at  $m/z$  106.1 and stable ion peak at  $m/z$  91.0.

### Optimization parameters

The method was optimized to reduce the tailing on BTEX peaks. The column equilibration time was set at one minute, and purge flow to split vent to 100 mL/min at 0.25 minutes, as mentioned above. We mention this point a second time to re-iterate the importance of this parameter for good chromatographic repeatability for volatile compounds such as BTEX. Different temperature combinations were tested for the GC oven, MS source, and MS quad to achieve repeatability and resolution while maintaining good sensitivity of the MS. The source temperature was maintained at 230 °C, and the quad was set at 200 °C. For optimizing the performance of the Guard Chip, the GC was run under a manual temperature ramping program (as mentioned in Table 1) as well as track oven mode. However, there was no significant difference observed in relation to this parameter.

When the system was not in use, a sleep method was loaded with an oven temperature at 50 °C and the Guard Chip at 150 °C to prolong the life of GC components.

### Conclusion

The Intuvo 9000 GC coupled with the 5977B GC/MSD is an efficient, low-footprint, innovative solution especially for research laboratories in an academic environment. Its adaptability to perform well with different kinds of water samples, that is, groundwater, wastewater, produced waters from hydraulic fracturing, and so forth makes it the best choice for bench-scale chemical analysis with both targeted and nontargeted approaches. The retention time repeatability shown by

the instrument with hydraulic fracking samples loaded heavily with volatile and semivolatile compounds proves its potential to handle complex water samples. The rapid heating and cooling technology saves a lot of time between subsequent runs, while the Guard Chip increases the lifetime of the GC column. The ease-of-use of the software and rapid learning curve for multiple users, including those less experienced, were beneficial. The power of the MassHunter software was also used to find nontarget organic compounds when using a library program such as the NIST library.

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