# DEVELOPMENT OF A MINIATURE AND AIR-TRANSPORTABLE LIQUID CHROMATOGRAPH WITH UV DETECTOR: CRUDE OIL CHARACTERIZATION BY GPC-UV

## Introduction

The miniaturization and the strengthening of laboratory-based analytical instruments and methods to the field is a major consideration in instrument development. To reach this goal, researchers and companies from various fields have made significant progress within a variety of technologies. For some applications, the transportation of samples (unstable or difficult to ship) is a significant problem. For example, the shipping of petroleum samples from offshore facilities can be difficult and time consuming. In this case, it is necessary to transport the analytical module directly to the field. Several chromatographic techniques have been developed for the fractionation of complex petroleum samples according to various physico-chemical properties, such as molecular size, degree of aromaticity, or polarity. Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC) separates molecules based by both molecular weight and shape. GPC is widely used in the crude oil industry to characterize samples. The aim of our study is to develop a transportable GPC-UV system that can be transported by airplane as  standard luggage. Therefore, the system needs to weigh less than 23 kg, to withstand shocks and vibrations, and to be able to be carried by one person. Also, the system should be quick to start and stop and should fulfill all analytical requirements of laboratory-based instruments.

## Materials and methods

### Chemicals and Reagents

Toluene, Isopropanol (IPA) and Tetrahydrofuran (THF) were purchased from Merck & Co., Inc. All solvents were either HPLC or analytical grade. Crude oil samples were supplied by the TOTAL Research Center (Pau, France). Before analysis, crude oil samples were diluted using Tetrahydrofuran (50%/50%).

### Multiplexing and injection Module

The multiplexing module has 10 liquid ports: seven ports for the sample inlets, 2 ports for pure solvent inlets and 1 connected to a waste. The system has one common outlet linked to the injection module. 1ml of Isopropanol (IPA) and 1ml of Tetrahydrofuran (THF) are used to clean the multiplexing system and injection module between each measurement. The injection is performed automatically using four ports, a two-position valve and a 0.5 µl internal loop.

### Separation and Detection Modules

The THF flow is set to 200 µl/min (20 bars) and the cycle time is 40 minutes for this application. We use two columns PlGel 250 X 4.6 mm – 500A – 5 µm kept at 35 °C. We use a UV detector at 254 nm for quantification (wavelength can be adjusted for other applications).

*Figure 1: Picture of the transportable GPC-UV:*
*On the left, the analytical module and on the right the module with computer and electronic boards*

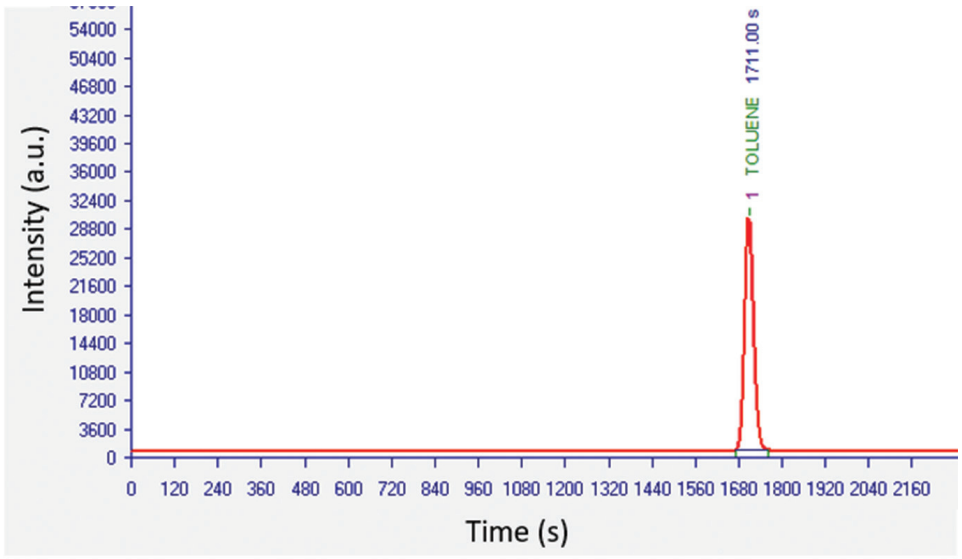


*Figure 2: Chromatogram of the analysis of Toluene sample*

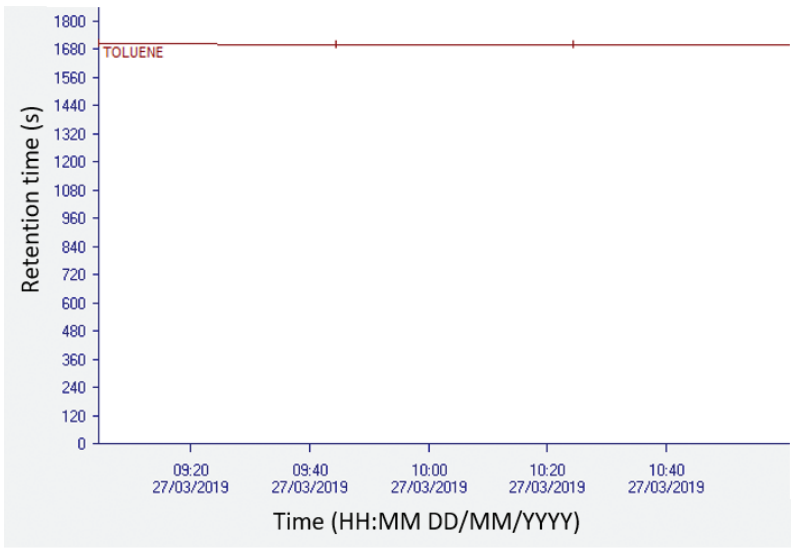


*Figure 3: Retention time stability obtained on Toluene for 4 injections*

### System Integration and Instrument Operation

As shown on Figure 1, the transportable GPC-UV system is comprised of two suitcases. In the first, all the analytical modules are installed: pump, multiplexing system, injection valve, columns and detectors. The computer and electronic boards that control the analytical module are installed in the second suitcase. The suitcases have been designed with a spring system to absorb shocks that occur during transport of the somewhat heavy internal components.

The analytical suitcase is 625 X 500 X 366 mm (L X W X H) and weighs 22 kg. The analytical module can be used in the suitcase or it can be removed and installed in an extractor hood for instance. The electronic module is 538 X 406 X 295 mm ((L X W X H) and weighs 18 kg. The whole system can be started within 15 minutes.

## Results and Discussion

Several experiments were conducted to characterize the performance of the GPC-UV system. We have focused on the following parameters: the shape of the peak and separation efficiency of Toluene, the repeatability of retention times as well as the repeatability of quantification and retention times of crude oil analysis.

### Column Performances

The system was first tested with injections of pure Toluene samples. The result can be seen in the chromatogram in Figure 2.

We obtained a gaussian peak with a width of 26s and 89s for half-height and 5 sigma, respectively. The theoretical plates on the transportable system are similar to laboratory liquid chromatographs (Table 1). This shows that dead volumes and tubing materials have been optimized to obtain very good performances.

### Repeatability on Toluene

The system repeatability was determined according to the following method: pure toluene samples were analyzed from four different vials installed in the multiplexing system. Each sample was injected once and we compared retention times for each injection.

Figure 3 shows the retention time stability obtained. The RT average and repeatability are shown in the Table 2. On four measurements, we obtained an average of 1704.7s, with a minimum value of 1703.6s and a maximum of 1705.4s. The relative standard deviation is 0.05 %. This indicates that the transportable GPC-UV system allows repeatable analysis on different sample vials.

To obtain stable results on the GPC system, we need the pump to deliver a very precise flow. The standard deviation is 0.775s which is equivalent to 2.6 µl with a THF flow of 200 µl/min. The results highlight the repeatability of the injection module, the pump and the column oven regulation.

### Crude Oil Analysis

When crude oil analysis needs to be performed, we need a sampling system that can handle highly viscous samples. Also, we need very efficient rinsing procedures between analyses of different samples in order to avoid memory effect when using the multiplexing system. The memory effects on the transportable GPC-UV were evaluated by performing the measurement of seven different samples. All samples were analyzed four times each, with a cycle time of 40 minutes. The whole experiment takes about 19 hours. Each crude oil sample was diluted with THF (50/50) in order to reduce the viscosity of the sample. The Toluene sample was the last substance to be injected. We can see that no memory effect of crude oil samples can be seen on the chromatogram because we have only one peak.

In Figure 4, the four repetitions of each different sample are very similar. This means that the injected quantities are always the same, we have no memory effects from previous samples and retention times are very stable.

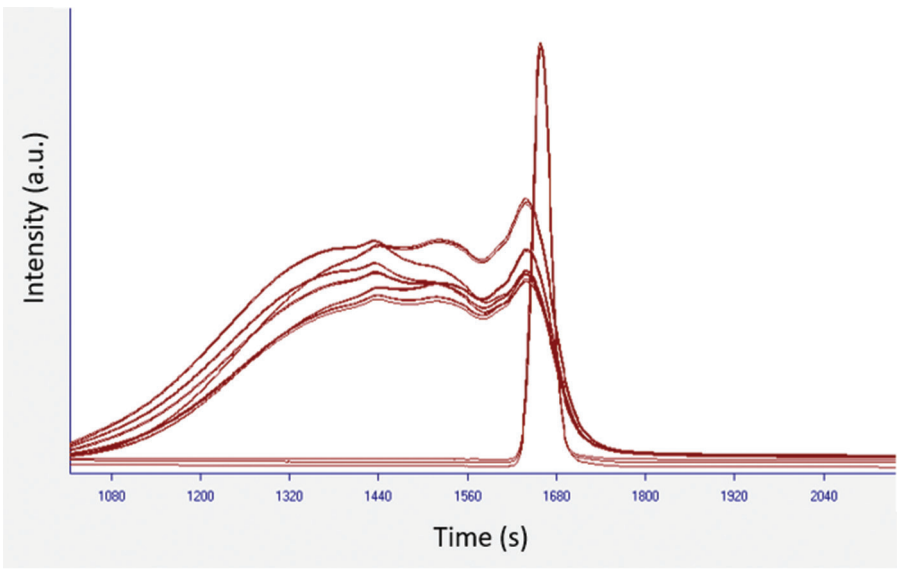


*Figure 4: Chromatograms obtained on 7 samples. Each Sample was analyzed 4 times.*

## Conclusion

In this work, a new and transportable GPC-UV that provides accurate analysis of seven samples is described. The transportable system operates in isocratic elution mode (200 µl/min and 20 bars) with columns heated to 35 °C. The system is standalone, robust and transportable on airplanes since its total weight is less than 20 kg (each suitcase). The liquid consumption for this application is only 200 µl/min. The system is fully controlled by custom electronics and software, which ensures data acquisitions, storage, processing and data transfer (Modbus, Profibus, 4-20 mA).

The transportable system offers the possibility of using different columns with pressure ranging from 10 to 400 bars and flow ranging from 0.50 to 10 ml/min. The temperature of the oven can be set up to 100 °C. In addition, different detectors can be added to the system for other applications.

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*Table 1: Results for the injection of Toluene sample*

| | Laboratory (200 µl/min) 2 columns (2 X 25 cm) | Transportable (200 µl/min) 2 columns (2 X 25 cm) |
|---|---|---|
| Elution time (s) | 1740.72 | 1711 |
| Width (1/2 heights; s) | 24.78 | 26 |
| Width (5 sigma; s) | 180 | 89 |
| Plates/m (1/2 height) | 54676 | 47984 |
| Plates/m (5 sigma) | 4676 | 18479 |

*Table 2: Retention time values obtained on Toluene*

| Retention Time | |
|---|---|
| Minimum (s) | 1703.6 |
| Maximum (s) | 1705.4 |
| Measurement number | 4 |
| Average (s) | 1704.7 |
| Standard deviation (s) | 0.775 |
| Rel. Std. Deviation (%) | 0.05 |

**Author Contact Details**

**Franck Amiet, Chromatotec** • 15 Rue d'Artiguelongue - Saint-Antoine 33240 VAL DE VIRVEE – France • Tel +33 (0)5 57 94 06 26 • **www.chromatotec.com**