

# Ultra Fast GC Method for the Analysis of Total Petroleum Hydrocarbons (TPH) in Water and Soils, in Compliance with Texas TNRCC 1005

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## Key Words

- TRACE GC Ultra
- Texas TNRCC 1005
- Total Petroleum Hydrocarbons
- Ultra Fast GC
- Water and Soil Analysis



Figure 1: TRACE GC Ultra™ with TriPlus™ AS Autosampler

## Introduction

As attested by a US EPA survey, since over 20 years ago, hundreds of thousands of underground storage tanks (USTs) leaking petroleum have contaminated worldwide community drinking water supplies [1].

Recent regulations affecting both drinking water suppliers and environmental protection institutes of many European and US countries have made the determination of the content of mineral oils and petroleum products in water and soils a compulsory requirement for quality certifications.

Currently, the analytical techniques used to carry out this determination are Infra Red and Gas Chromatography. IR, although it has been extensively used in the past for its simplicity and high speed of analysis, implies the mandatory use of  $\text{CCl}_4$ , TTCE, or Freon as the extraction solvent, which is not favorable.  $\text{CCl}_4$  is currently banned due to its tremendous toxicity; Freon has been banned by the Montreal Protocol (1992), due to its ozone-depleting properties; TTCE has not been fully accepted, since the concern about its suspected carcinogenic effects.



In this light, GC-FID, being a robust technique and featuring no limitations in the solvent selection, emerges as the most valid alternative technique tolerated and supported by official norms for total petroleum hydrocarbons (TPH) applications. One of these norms, TNRCC 1005 from the Texas Commission on Environmental Quality (formerly Texas Natural Resource Conservation Commission) [2], has shown good correlation with IR-based method EPA 418.1, and is widely applied not only in Texas but throughout the United States.

This application is based on sample extraction with *n*-pentane and GC-FID monitoring of the hydrocarbon range from *n*C6 to *n*C36. This application shows the details of a new Ultra Fast GC method for TPH, able to comply with TNRCC 1005, and to compete with IR on analysis time; productivity is increased by a factor of 10 in comparison with conventional GC using a very simple and rugged hardware [6,7].

## Experimental

### Official norm and sample preparation

The TNRCC 1005 method consists of 2 consecutive steps:

- 1) in-vial extraction of the hydrocarbons from the sample matrix with *n*-pentane;
- 2) GC-FID analysis of the extract

About 10 mL of sample have to be extracted with 3 mL of *n*-pentane directly in a vial, and an aliquot of the extract will be analyzed by a GC unit, properly calibrated by means of diluted gasoil external standards ranging from 20 to 1000 ppm as a total hydrocarbons content. The TPH content will be calculated by integrating a group peak from *n*C6 to *n*C36, added as internal standards.

Re-concentration of the extract before the GC analysis through partial solvent evaporation is not admitted, and the GC system must be sensitive enough to directly analyze the extract content avoiding any solvent evaporation before the analysis. This allows for much faster and cheaper sample prep and prevents any risk of losing volatiles during the solvent evaporation step.

Sensitivity issue: the GC method must be able to quantify at least 5 ppm (mg/Kg) of TPH in the extract.

The official method reports that the GC analysis can be achieved using a non-polar column (25-30 m long, 0.25 mm as internal diameter, and film thickness ranging from 0.25 to 1  $\mu\text{m}$ ), oven temperature program from 30 to 325  $^{\circ}\text{C}$  operated at a heating rate of 15  $^{\circ}\text{C}/\text{min}$ , for a total analysis time around 30 minutes. But in the method text itself it is remarked that these parameters are only recommended; any changes to these method conditions can be made by the analyst in order to improve speed of analysis, sensitivity, separation, or to reduce the cost per analysis, providing that the new parameters will still provide compliance with the analytical goals.

### Instrumentation and data system

A Thermo Scientific TRACE GC Ultra™ (Figure 1), equipped with the Ultra Fast Module (UFM) option, featuring a Programmable Temperature Vaporizing (PTV) inlet / FID configuration was used. Injections were performed with the TriPlus Autosampler (Thermo Electron). The UFM option consists of a column module (Figure 2) containing a capillary column combined with a heating element and a temperature sensor to ensure the direct resistive heating of the capillary column [3,4]. The assembly is held in an “easy to handle” metal cage and can achieve temperature programming rates as high as 1,200  $^{\circ}\text{C}/\text{min}$ .

The column module can be installed and removed from a standard GC oven as easily as a normal capillary column, offering the benefit of a 3-4 times higher average lifetime. The reason for this added longevity is that, in Ultra Fast GC, the column spends a far shorter time at the upper isothermal temperature in comparison with conventional temperature programs.

For this method, the Ultra Fast GC column module was equipped with a 5 m, 0.32 mm i.d., 0.5  $\mu\text{m}$  film thickness Thermo Scientific TRACE™ UFC-1 column (P/N UFMCO0001070907).

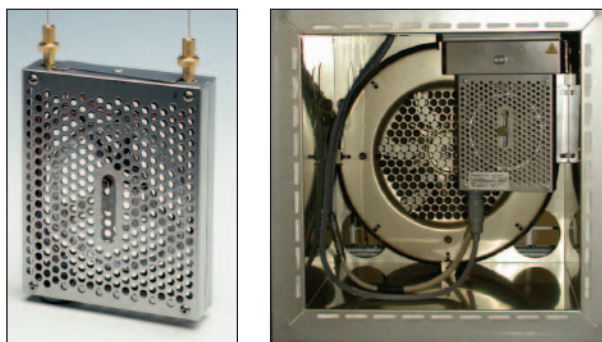


Figure 2: UFM column module<sup>(A)</sup> and its housing in a TRACE GC Ultra oven<sup>(B)</sup>.

The injector is a PTV, able to grant high recoveries for broad ranges of boiling points, avoiding any discrimination from the syringe needle during the injection phase. The sample is injected into the cold inlet as a liquid, and is then vaporized in the middle zone through the very fast heating of the injector body (at 14  $^{\circ}\text{C}/\text{sec}$ ) [5].

The sample vapors are then carried into the column module. The interface zone of the column is permanently heated through a metal block to prevent any risk of cold

spot formation. The inlet temperature profile has been properly optimized (Figure 3) to allow the coexistence of a cold-heated middle zone and a permanently heated zone, within the same injector.

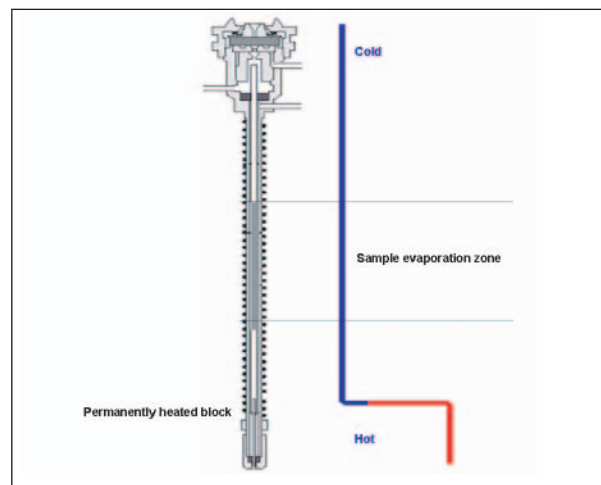


Figure 3: PTV inlet temperature profile

Thermo Scientific Chrom-Card software incorporates a dedicated function that allows for automatic integration as a single group area the portion of chromatogram included between the retention times of *n*-Hexane (nC6) and *n*-Hexatriacontane (nC36), with the baseline reported at the signal level in front of the solvent peak.

Standard mixtures for evaluating injection performances were prepared diluting *n*-alkanes, ranging from *n*-C6 to *n*-C40, in *n*-pentane at ppm levels. The Gasoil Reference D2887 diluted in *n*-pentane was analyzed at different concentrations to test linearity, repeatability, and sensitivity of the method. Several real water extracts have been analyzed to test the robustness of the described GC system.

### Ultra fast analysis: results and discussion

For all the ultra fast analyses discussed in the paragraph below, the column temperature is programmed from 5  $^{\circ}\text{C}$  (0.5 min) to 110  $^{\circ}\text{C}$  at 180  $^{\circ}\text{C}/\text{min}$ , then at 160  $^{\circ}\text{C}/\text{min}$  to 330  $^{\circ}\text{C}$  (0.3 min).

The initial temperature of 5  $^{\circ}\text{C}$  is obtained using a cryogenic coolant (Liquid N<sub>2</sub> or Liquid CO<sub>2</sub>) in the oven chamber. This allows for an enormous increase in the overall number of theoretical plates, thereby achieving the high resolution power needed to separate nC6 from *n*-pentane [6]. An injection of 1  $\mu\text{L}$  was made, using split mode, split ratio 1:4. All of the chromatograms presented have been obtained in less than 3 minutes.

### System compliance test

A first analysis of a solution of *n*-alkanes has been performed in order to verify the baseline separation of C6 from *n*-pentane, which is easily observed (Figure 4), and then to check for absence of any discrimination effects. Under the analytical conditions indicated, even nC40 is eluted with excellent recoveries (the actual limit indicated in TNRCC 1005 is nC36).

A different standard has been analyzed to demonstrate that the resolution is high enough to even separate TEX components, in case they are present (Figure 5). The position of n-C6 and n-C8 alkanes is reported with dotted lines.

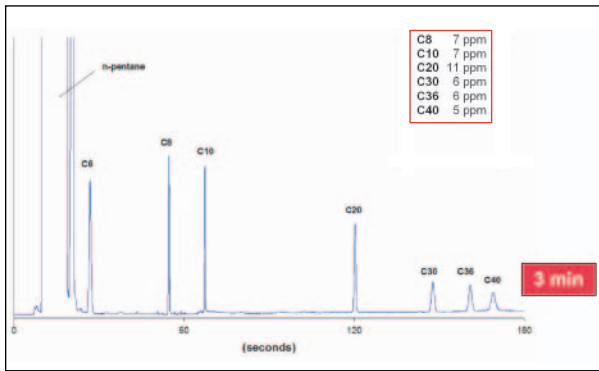


Figure 4: Standard chromatogram nC6-nC40

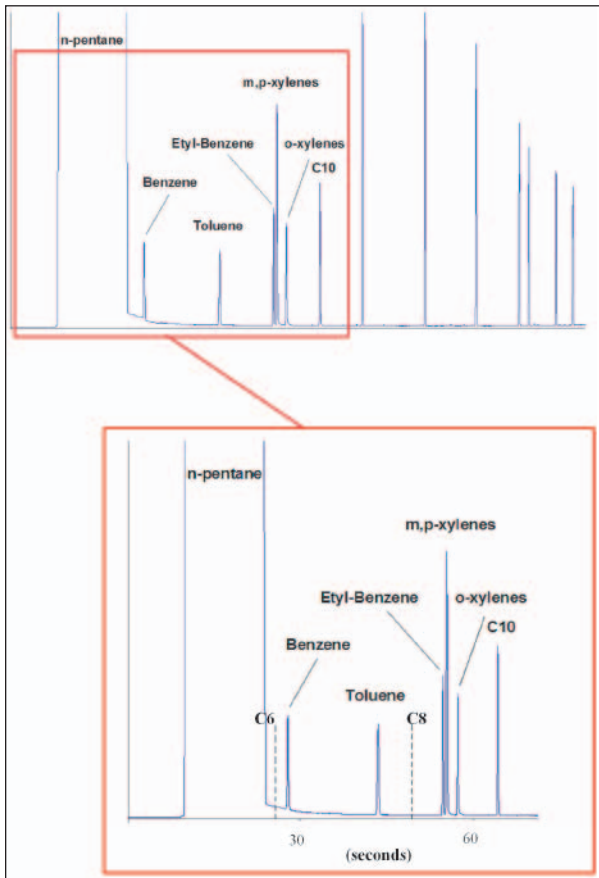


Figure 5: Standard chromatogram with TEX

#### Linearity and repeatability test

Linearity has been tested by injecting the Gasoil D2887 reference mixture at different concentrations (20-1000 ppm), getting an excellent linear coefficient (Figure 6). The %RSD of the group peak, calculated over 10 consecutive repetitions of the D2887 reference at 50 ppm (Figure 7), was 2.8%.

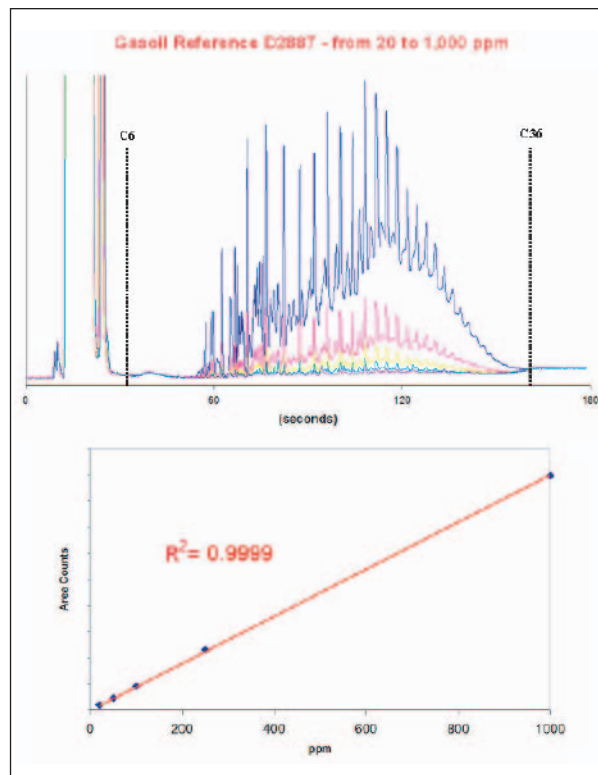


Figure 6: Linearity Test: 5 overlaid chromatograms and linear curve

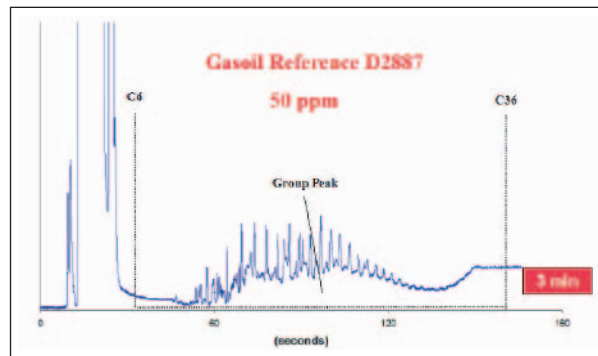


Figure 7: Gasoil Reference D2887 analysis

#### Sensitivity test

Ultra Fast GC is able to produce a peak compression effect as a consequence of operating at high heating rates with short columns. The signal-to-noise ratio is maximized, and the outcome is an increase in sensitivity over conventional GC by a factor that depends on the heating rate applied: the higher the heating rate, the higher the overall sensitivity delivered.

The system has proven to be as sensitive as requested by the norm, being able to quantify 5 ppm of total hydrocarbons in n-pentane with no need to inject more than 1 $\mu$ L.

In fact, the D2887 Reference diluted to 5 ppm in n-pentane was analyzed using the described parameters, and the ratio between the reference group peak area and the solvent (blank) area, analyzed under the same conditions, was 4.9. All the chromatograms are automatically baseline corrected by the data system.

## System robustness

A plug of glass wool was placed in the middle part of the liner in order to prevent contamination of the column by non-volatile components. To prove system robustness, a large number of real water extracted samples (approximately 100) were injected (see Figure 8) without replacing the liner or the glass wool, and at the end of the sequence the reference mix was analyzed several times. The high level of repeatability of these analyses (still around 2-3 %) proves that neither column contamination nor degradation of chromatographic performance occurred.

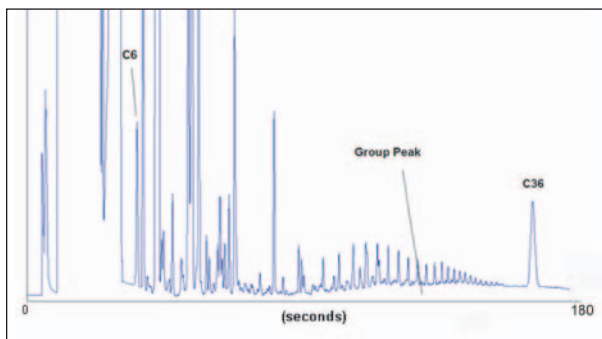


Figure 8: Real water extract chromatogram

## Overall productivity

The productivity of this Ultra Fast method can be easily calculated through the number of samples per day that can be potentially analyzed. Besides the run time, around 3 minutes, even the module cooling time is extremely fast, taking only 4 minutes to cover the temperature range from 330 °C (upper isothermal) to 5 °C (initial isothermal). This performance is even faster than a normal GC covering a normal range of temperatures from the upper isothermal to ambient.

The run-to-run time is about 7 minutes, which leads to a total productivity of about 70 samples per day, not including the runs that could be performed unattended overnight.

The sampling time, defined as the time needed by the autosampler to wash the syringe, is not considered, due to the capability of the TriPlus Autosampler of performing the syringe washing cycles during the previous analytical run in the sequence. This eliminates most of the dead times that usually exist between two consecutive runs.

The TriPlus AS has been conceived to boost productivity. The “clone” configuration (see Figure 9) allows for the installation of one autosampler to automate 2 adjacent GCs working simultaneously. In this way, one sampling turret works as two virtual autosamplers, even doubling the overall productivity.

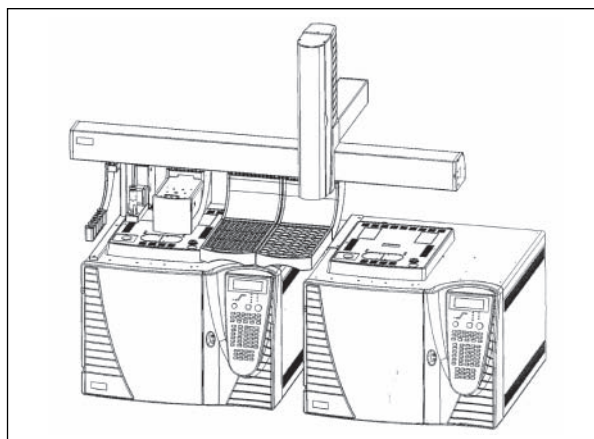


Figure 9: TriPlus AS automating 2 GCs working simultaneously

## Conclusions

The Ultra Fast option of the TRACE GC Ultra effectively accomplishes the determination of Total Petroleum Hydrocarbons in water and soil in compliance with the strict requirements of Texas TNRCC 1005, reducing analytical time by a factor of 10 with respect to conventional GC.

Impressive productivity is delivered through simple and rugged hardware, quite suitable for the analyses of dirty matrices usually requested in this field. Low frequency of maintenance, easy-to-use data system provided with a dedicated turn-key method, and high level of automation: these features position the described assembly as an ideal solution for quickly implementing Texas TNRCC 1005 in any environmental laboratory.

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