

# Ultra Fast GC Method for the Analysis of Total Hydrocarbons in Water in Compliance with ISO 9377-2 (Mod.)

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## Key Words

- Oil in Produced Water
- ISO 9377-2 (Mod.)
- Hydrocarbons nC7-nC40
- BTEX
- Ultra Fast GC



## Introduction

Several million tons of water containing petroleum hydrocarbons are produced every year by offshore plants in the extraction process of oil and gas from undersea. The discharge of such produced water into the ocean is regulated by severe norms in order to protect the environment from pollution. The Oslo and Paris Commission (OSPAR) is responsible for the decisions and recommendations concerning marine issues in the North East Atlantic area, and sets the reference analytical methods for monitoring the pollutants content in produced water before discharge.

The OSPAR commission has recently confirmed that, starting from January 2007, a modification of the ISO 9377-2, indicated as ISO 9377-2 (Mod.) [1], will be the new reference method for the determination of oil in produced water.

This is a GC-based method, whose goal is to determine the level of pollution in water expressed with the "Hydrocarbon Index" (HI), corresponding to the cumulated amount of hydrocarbon compounds.

Stringent regulations regarding the use of toxic extraction solvents, such as CCl<sub>4</sub>, TTCE, or Freon make alternative Infra Red methods less favorable. Freon has been banned by the Montreal Protocol, due to its ozone depleting properties, and TTCE has not been fully accepted, due to its suspected carcinogenic effects.

In this application, Ultra Fast GC [3,4] is demonstrated as a reliable GC technique able to fulfill the strict requirements of the ISO 9377-2 (Mod.), featuring analysis time comparable to that of the IR methods. Productivity is increased by a factor of 10 in comparison with conventional GC, using a very simple and rugged hardware.



## Experimental

### Official norm and sample preparation

The ISO 9377-2 defines the HI as the cumulated amount of hydrocarbons included in the range between n-C10 and n-C40, to be analyzed in 4 different steps:

- a) extraction of the hydrocarbons from the sample matrix with an organic solvent;
- b) clean-up with Florisil® in order to remove the more polar substances;
- c) re-concentration of the extract through solvent evaporation;
- d) GC-FID analysis of the cleaned concentrated extract.

Some correlation data have clearly pointed out that ISO 9377-2 underestimates the dispersed oil content in water, compared with the IR reference method, and the main reason lies in the too narrow range of hydrocarbons investigated through this GC method [2].

For this reason the OSPAR commission basically decided to propose a few modifications to the ISO 9377-2, to generate the ISO 9377-2 (Mod.) as a new reference in replacement of IR based methods [1].

The new reference implies a broader range of investigation, from n-C7 to n-C40, and the use of n-pentane as extraction solvent. Since Toluene, Ethylbenzene and Xylenes do elute in this range, but are not considered part of the dispersed (aliphatic) oil in water, their content has to be calculated and subtracted from the hydrocarbons value.

Another important modification concerns the re-concentration step, that has to be completely by-passed: the GC system must be sensitive enough to directly analyze the extract content with no solvent evaporation before the analysis. This will allow for a faster sample prep, and will prevent any risk of losing volatiles during the solvent evaporation step.

Here is the summary of the main modifications reported in ISO 9377-2 (Mod.):

- use of n-pentane as extraction solvent;
- spike the sample with n-C7 and n-C40;
- integrate the group peak in the range nC7-nC40;
- integrate the TEX peaks and subtract their areas from the group peak, in order to calculate the dispersed oil content.

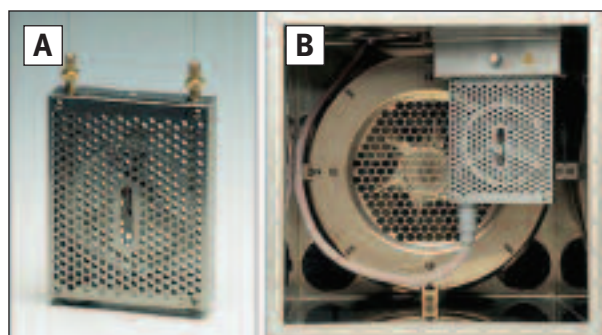
Sensitivity issue: the system has to allow the determination of 0.1 mg/L of hydrocarbons in the water sample, corresponding to about 2 mg/L in the water extract, avoiding any re-concentration step.

### Instrumentation and Data System

A TRACE GC Ultra (Thermo Electron, Milan, Italy), 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 (Fig. 1) containing a capillary column combined with a heating element and a temperature sensor to ensure the direct resistive heating of the capillary column [3]. The assembly is held in an “easy to handle” metal cage and can achieve temperature programming rates as high as 1200 °C/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 longer average lifetime. The reason for this plus is that in Ultra Fast GC the column usually spends 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, 0.1 mm i.d., 0.1 µm film thickness UF-1 column (non-polar phase, Thermo Electron).

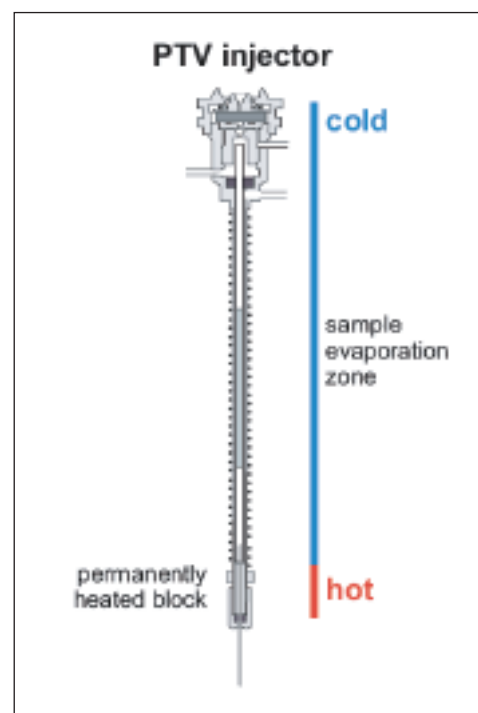


**Figure 1:** UFM column module (A) and its housing in a TRACE GC Ultra oven (B).

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 °C/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 (Fig. 2) to allow the coexistence of a cold-heated middle zone and a permanently heated one, within the same injector.

The relatively low thermal mass of this injector allows rapid cooling carried out through a dedicated fan. No external coolant other than ambient air is needed.



**Figure 2:** PTV inlet temperature profile.

Chrom-Card software (Thermo Electron) incorporates a dedicated function that allows the automatic integration of the portion of the chromatogram included between the retention times of n-Heptane (C7) and n-Tetracontane (C40), into a single group area, with the baseline reported at the signal level in front of the solvent peak. The integration of the individual TEX peaks is automated as well, so that one single analytical report includes both the group peak area and the TEX peak areas.

Standard mixtures for evaluating injection performances were prepared diluting n-alkanes, ranging from n-C7 to n-C40, in n-pentane at ppm levels. A Gasoil Reference Mix 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 this paragraph, the column temperature is programmed from 35 °C (0.8 min) to 350 °C (0.4 min) at 100 °C/min.

3 µL have been injected in split mode (split flow: 10 mL/min).

0.5 µL of MTBE has been injected as a Co-solvent in order to enhance the solvent effect and optimize the recovery of the more volatile compounds.

(In all the chromatograms shown, the position of nC7 and nC40, when not present in the samples, is reported in dotted lines).

### System compliance test

A solution of hydrocarbons has been analyzed in order to verify the baseline separation of C7 from n-pentane, which is easily observed (Fig. 3), and then to confirm the absence of any discrimination effect: under the analytical conditions indicated, the peak area ratio C40/C20 has been found to be > 0.9, far higher than the minimum value (0.80) requested by ISO 9377-2 (Mod.) to consider the injector as not discriminating.

This is one of the most demanding parameters for the injection system to obtain compliance with the official norm.

The same analysis demonstrates the ability of separating TEX components, even better shown in the analysis reported in Fig. 4.

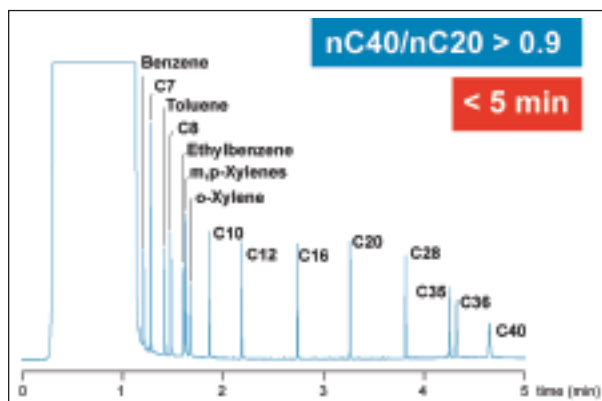


Figure 3: Standard chromatogram nC7-nC40.

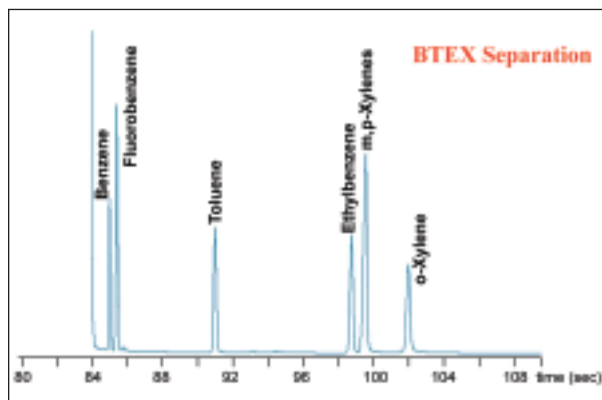


Figure 4: Standard chromatogram with TEX.

Fig. 5 shows the chromatogram of a Gasoil Reference Mix, 50 ppm of total hydrocarbons (high-lighted the separation C17-Pristane and C18-Phytane).

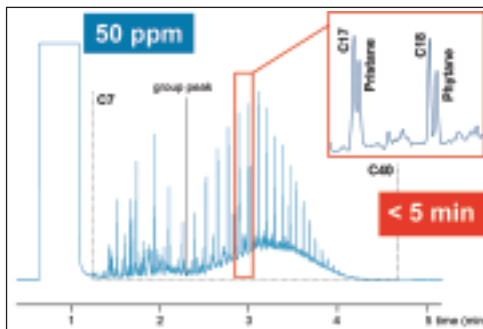


Figure 5: Gasoil Reference Mix, 50 ppm.

### Linearity and repeatability

Linearity has been tested by injecting the reference gasoil mixture at different concentrations (2-200 ppm), getting an excellent linear coefficient (Fig. 6).

The RSD % of the group peak, calculated over 10 consecutive repetitions of the reference at 50 ppm, is around 2 %.

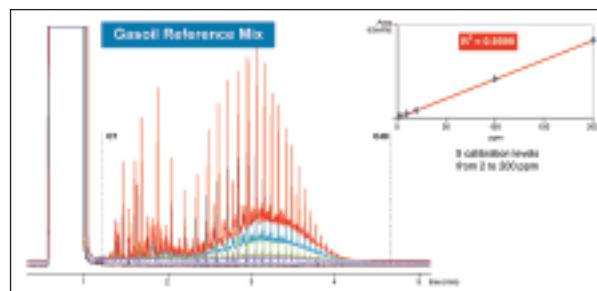


Figure 6: Linearity Test: 5 overlaid chromatograms and linear curve.

### Sensitivity test

Ultra Fast GC is able to produce a peak compression effect as a consequence of operating at high heating rates with short narrow-bore 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.

Fig. 7, reporting the chromatogram of the reference gasoil mix at 2 ppm, overlapped with that of the blank (n-pentane), proves that the system is as sensitive as requested by the method, with no need to inject more than 3 µL.

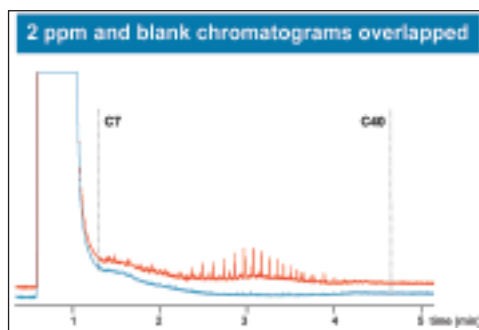


Figure 7: Sensitivity test.

## System robustness

A new liner model was used (Thermo Electron), pre-packed with a glass wool layer located on top of a glass restriction in order to prevent contamination of the column by non-volatile components (Fig. 8). The restriction keeps the wool in the same position in the liner, improving the repeatability of the results.

To prove the system robustness, a large number of real water extract samples (about 100) was injected (Fig. 9) without replacing neither the liner nor the glass wool, and a reference mix was analyzed a few times before and after the long sequence: the high level of repeatability of these analyses (still around 2-3 %) and nice chromatograms shape prove (Fig. 10) that neither column contamination nor degradation of chromatographic performance occurred.

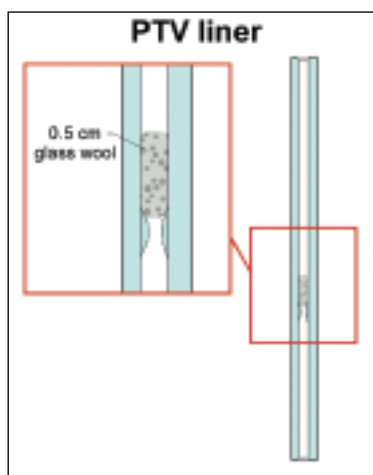


Figure 8: PTV liner model with glass wool.

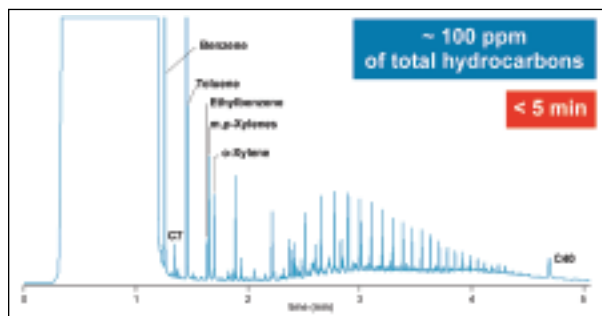


Figure 9: Real water extract chromatogram.

## 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 4.5 minutes, even the column cooling time is extremely fast, being around 2 minutes.

So, the resulting run-to-run time is about 8 minutes, which leads to a total productivity of about 60 samples per day, not including the runs that could be performed unattended overnight.

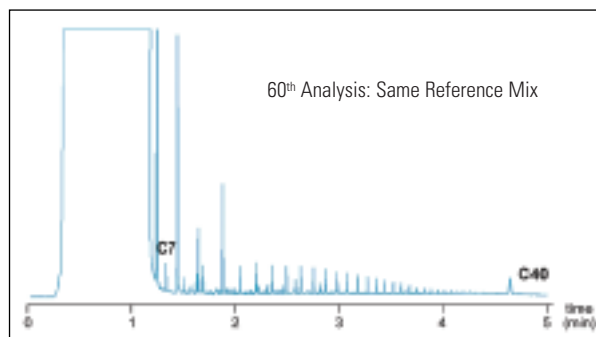
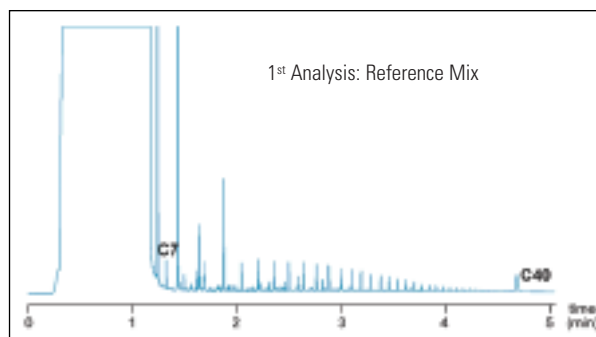


Figure 10: First and last analysis of a 1-day sequence.

## Conclusion

The OSPAR commission, that regulates the discharge of produced water in the North Sea, has confirmed that the ISO 9377-2 (Mod.) will be the new reference GC-based method for the determination of the Hydrocarbon Index, starting from January 2007, in replacement of the IR reference method.

The Ultra Fast option of the TRACE GC Ultra has proven to accomplish this determination in full compliance with the strict requirements of the new official norm, cutting the analytical time by a factor of 10 with respect to conventional GC.

Impressive lab productivity is delivered through a very simple and rugged hardware, quite suitable for the analyses of very dirty matrices usually requested in this field.

Low frequency of maintenance, extreme ease of use of the data system provided with a dedicated turn-key method, and high level of automation: these further features position the described technique as the ideal solution for quickly delivering hydrocarbons analysis in water according to ISO 9377-2 (Mod.).

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