

Determining the Hydrocarbon Oil Index in Water using Ultra Fast Gas Chromatography

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Recent European legislation for drinking water suppliers and environmental protection institutes has made the determination of the content of mineral oils and petroleum products in water and soils a compulsory requirement for quality certifications.

The Hydrocarbon Index (HI)

The current ISO 9377-2/H53 method mandates that the hydrocarbon content is determined by gas chromatography (GC). The hydrocarbon index (HI) is conventionally used to express the level of pollution. This article reviews the use of Ultra Fast GC (UFGC) as a viable method for determining the HI in water and soils.

ISO 9377-2/H53 is the official European standard method used to determine the HI in drinking water using solvent extraction and gas chromatography.

The HI is the total amount of hydrocarbon compounds contained in water and soil samples, extracted with cyclohexane but not absorbed on Florisil (manganese silicate). According to the ISO methods, this parameter can be measured by capillary gas chromatography using a non-polar capillary column by adding together the total peak area of compounds eluted between *n*-decane (C₁₀H₂₂) and *n*-tetracontane (C₄₀H₈₂), which are used as internal standards.

Ultra Fast Gas Chromatography

Ultra Fast gas chromatography (UFGC) is a widely used chromatographic technique for environmental analyses because it can separate closely related components in complex mixtures. When it comes to water and soil quality analyses, the main downfall of a gas chromatographic system is that it features long run times, needing at least 25 minutes to complete an analytical cycle. The simpler and most effective way to reduce long run times is the use of short narrow bore capillary columns that are able to grant the same system separation power, rapidly heated, at higher carrier gas velocity. Molecules are, therefore, moving inside the column at higher speed.

There are a wide range of column sizes available to speed up the chromatographic separation process, and according to the size and the achievable heating rate, several different degrees of speed can result. UFGC is characterized by the use of short (2–10 m) narrow bore capillary columns and temperature programming conditions faster than 1 °C/s. This leads to run times of 1 minute or less.



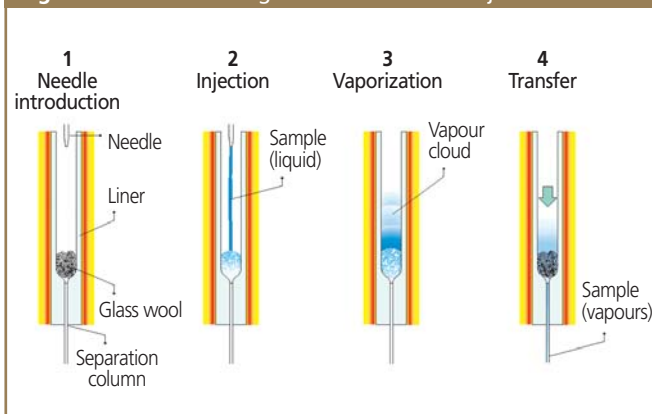
Theory

UFGC includes a directly resistive heated capillary column that is able to reach very high temperature programming rates and achieve very short cooling times. The fused silica capillary column is coiled along with a heating element and a temperature sensor, properly insulated and fixed in an easy to handle metal cage (column module), installed inside the standard gas chromatographic column oven. After the sample is injected through a conventional inlet, it is quickly eluted to the detector by heating the column at a maximum linear heating rate up to 1200 °C/min, thus dramatically decreasing sample run times and increasing laboratory productivity.

Advantages

UFGC can perform analyses up to 30 times faster than conventional GC over a wide volatility range of analytes, which is convenient for environmental samples. UFGC offers the

Figure 1: Schematic diagram of cold needle injection.



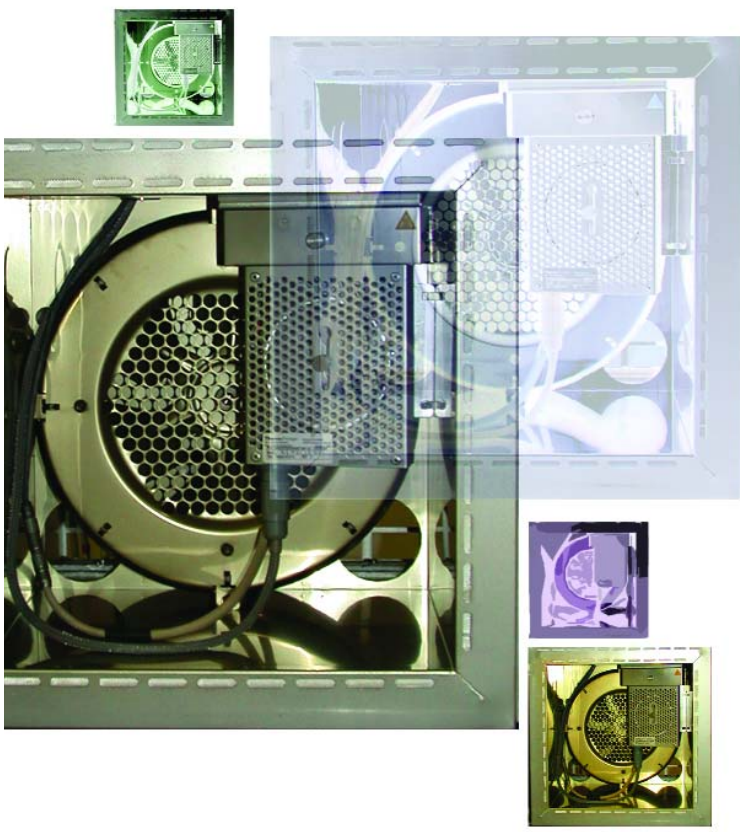
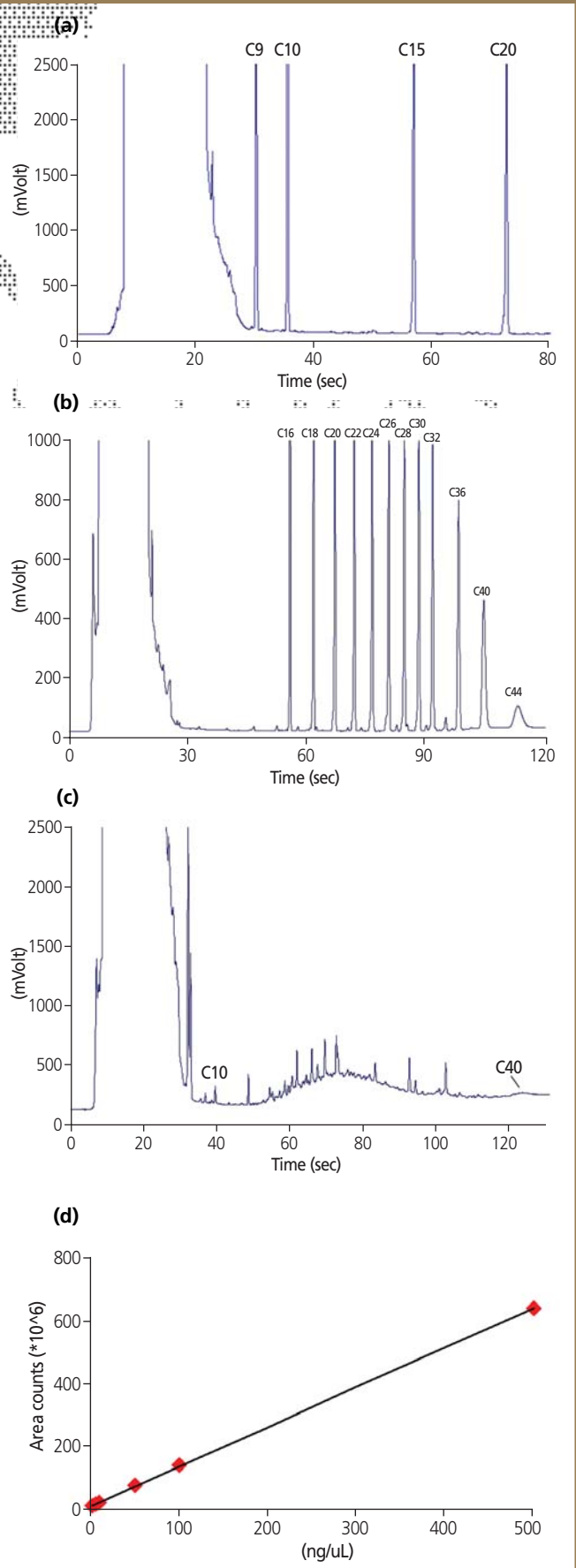


Figure 2: System evaluation and results (a) (b) (c) (d).



opportunity to reduce analysis costs by increasing productivity. The separation mechanism allows the introduction of samples at low split ratios, which increases sensitivity, making it suitable for trace level analysis.

Application

This section describes a method for the analysis of HI in water using UFGC to comply with the strict ISO guidelines.

Instrumentation

A gas chromatograph (TRACE™ GC Ultra, Thermo Electron) was configured with an SSL injector, an Ultra Fast column module (which includes the analytical column) and a fast flame ionization detector (FFID) featuring a 6 ms time constant and acquisition frequencies up to 300 Hz.

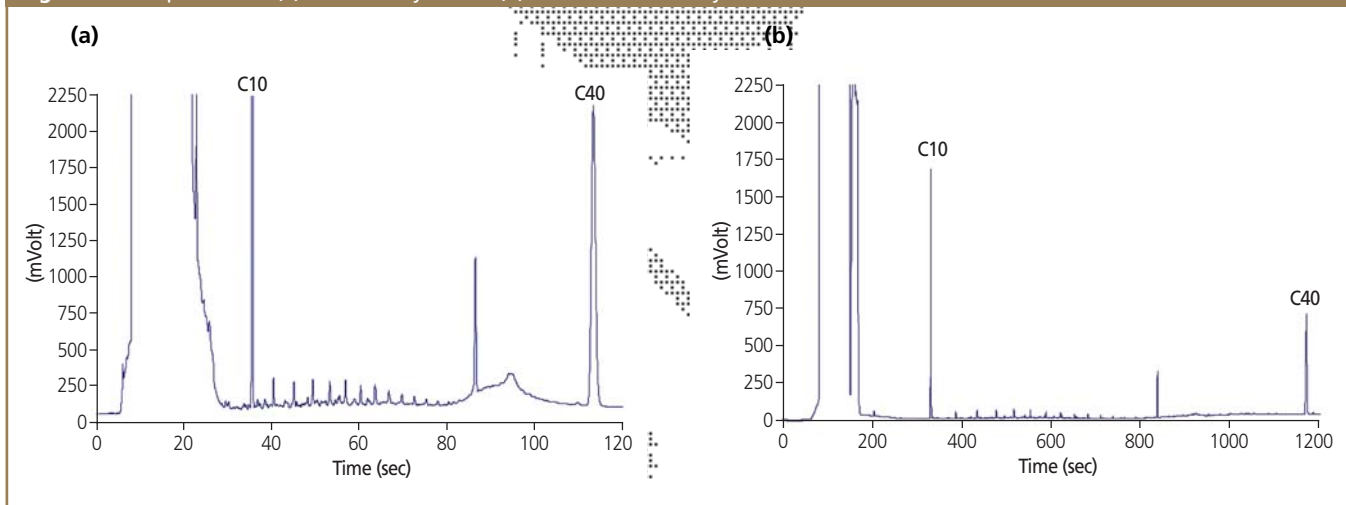
Such a high speed is a compulsory requirement for the correct acquisition (15–20 points/peak) of the extremely narrow peaks (approximately 100 ms $PW_{1/2}$) typical for this type of chromatography. The same gas chromatograph was used to perform the same application in conventional mode, once the Ultra Fast module was removed.

The analyses were performed using an AS 3000 autosampler while the analytical column used was an OV-1 column, 5 m long, 0.32 mm i.d., with 0.25 μ m film thickness (p/n UFM C00001070404). The column temperature was programmed from 40 °C (18 s) to 350 °C (30 s) at a linear heating rate of 3.3 °C/sec. The injection was performed in splitless mode using constant flow operating mode at 5 mL/min. The injector temperature was set at 300 °C, while the heated block temperature was set at 350 °C. The injected volume was 1 μ L.

Method

The hydrocarbons contained in the sample were initially extracted with cyclohexane. Eventually extracted polar

Figure 3: Comparison of (a) UFGC analysis and (b) conventional analysis.



substances were then separated from the hydrocarbons by a clean-up step with Florisil. At that point, the extract was concentrated, evaporating most of the solvent. An aliquot of the cleaned concentrated extract was finally analysed by capillary chromatography using a non-polar column and FID detection. When using this approach, the solvent expelled from the needle tip forms a liquid band (Figure 1) and is deposited at the bottom of the liner onto an inert glass wool packing, necessary to prevent the liquid from entering as such in the analytical column. Experiments conducted using a transparent SSL injector have, in fact, shown that the sample leaves the wool only after complete vaporization.

System Evaluation and Results

As shown in Figure 2, a solution of *n*-alkanes is first analysed in order to verify the complete separation of C₉ from cyclohexane, which is easily observed (a). A certified ASTM solution of *n*-alkanes from C₁₆ to C₄₄, each at the same concentration, is then used to check for possible discrimination (b); under the analytical conditions indicated, the peak area ratio C₄₀/C₂₀ is found to be > 0.9, far higher than the minimum value (0.80) requested by the official method to consider the injector as not discriminating. This parameter is considered to be the most important for system compliance with the standard methods. An analysis is then performed on a real soil extracted sample with a total hydrocarbons content of 50 ng/μL (c). The linearity of the system is tested successfully

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on a quality control mixture at different concentrations in the range 5–500 ng/μL, showing an excellent linear correlation coefficient (d). This method for the analysis of HI in water shortens analytical time by a fifth. The complete analytical cycle (sampling and cooling time included) takes place in less than five minutes compared with 25 minutes for the conventional cycle. Sensitivity is also increased because of the strong peak compression effect, which maximizes the signal to noise (SN) ratio.

Conventional Gas Chromatography

To provide a significant evaluation, the QC sample at 50 ng/μL was also analysed with the same gas chromatograph in conventional splitless-FID. The column used was an OV-1, 30 m long, 0.32mm i.d., 0.25 μm f.t. with an oven heating rate of 20 °C/min. A direct comparison of the two chromatograms showed a significant gain in both speed and sensitivity (Figure 3).

Conclusion

This technique is suitable to determine the HI in water and soil matrices and has a number of advantages over conventional GC technology. This method takes less than five minutes compared with 25 minutes required for conventional GC. Sensitivity is also considerably increased resulting in increased laboratory productivity and reduced analysis costs.

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