

Hydrocarbon Index Determination in Water and Soils by GC in 2 minutes (ISO 9377-2/H53 and ISO TR 11046 methods)

Thermo Fisher Scientific Inc., Milan, Italy

Key Words

- TRACE GC Ultra
- Hydrocarbon Index
- ISO 9377-2 / H53
- Mineral Oil in Water and Soils
- UltraFast GC

Introduction

Recent legislations for both drinking water suppliers and environmental protection institutes of many European 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, there are two standard methodologies that can be used as reference both mandating the analytical method to use for monitoring the maximum hydrocarbon content allowed. In these methods, the “Hydrocarbon Index” (H.I.) is conventionally used to express the level of pollution.

- ISO 9377-2/H53 is the official European standard method used for the determination of the H.I. in drinking water, by Gas Chromatographic technique.
- ISO TR11046 is a semi-official European standard method used for the determination of the H.I. in soils by GC or Infrared spectroscopy. In the past, the latter was considered the best performing technique because of its shorter run time (2 minutes compared to 20 minutes for GC); however, the very stringent European normatives regarding solvent toxicity make this technique, using CCl_4 as extraction solvent, quite unpopular and obsolete. For this reason, this method is referred to and catalogued only as a Technical Report and not ISO norm.

In this light, UltraFast GC emerges as the best alternative to replace the IR technique, being able to compete with it regarding analysis time, but without featuring any limitation in solvent types to be used for the extraction. Among the GC manufacturer leaders, only the Thermo Scientific TRACE GC Ultra™ can incorporate proprietary UltraFast technology, which allows for the completion of the analytical cycle (sum of sampling time, run time, and cooling time) in less than 5 minutes.

This note describes how the TRACE GC Ultra, when equipped with the UltraFast option, is able to maximize the sample throughput by significantly reducing the analysis time and increasing sensitivity without losing compliance with the official methods.

The comparison between UltraFast GC and conventional GC is reported, as well.

UltraFast GC Configuration

For this application, the TRACE GC Ultra is configured with a SSL injector, an UltraFast option (including the analytical column), and a Fast Flame Ionisation Detector (FFID) featuring 6 ms time constant and acquisition frequencies up to 300 Hz. Such a high speed is, in fact, a compulsory requirement for the correct acquisition (15-20 points/peak) of the extremely narrow peaks (approx. 100 ms $\text{PW}_{1/2\text{h}}$) typical for this type of chromatography.

The column module, connected to the split-splitless injector and the FID detector as a removable accessory, is completely and directly controlled by the instrument local user interface and electronics.

The same gas chromatograph was used to perform the same application in conventional mode, once the Ultra Fast accessory was removed.

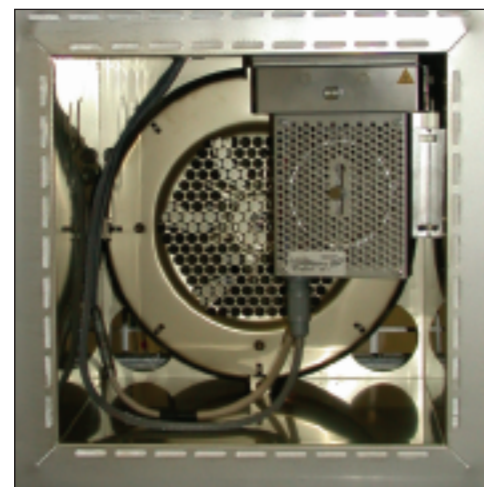


Figure 1: Thermo Scientific TRACE GC Ultra with UltraFast module

The analyses were performed using a Thermo Scientific AS3000 autosampler, designed to achieve maximum precision in automatic liquid injection in capillary GC. This automatic sampler allows the user to inject using two different techniques: cold needle and hot empty needle, both providing excellent performance in terms of data repeatability.

The selection of the injection technique can be accomplished in a fully automatic fashion, so that any possible lack of reproducibility due to the mixed vaporization modes is eliminated.

Method

The H.I. is the cumulated amount of hydrocarbon compounds contained in water or soil samples, extracted with cyclohexane but not absorbed on Florisil®.

According to the official methods, this parameter can be measured by capillary gas chromatography, cumulating the total peak area of compounds eluted between n-Decane ($C_{10}H_{22}$) and n-Tetracontane ($C_{40}H_{82}$) used as internal standards.

The hydrocarbons contained in the sample are initially extracted with cyclohexane. Eventually extracted polar substances are then separated from the hydrocarbons by a clean-up step with Florisil (manganese silicate). At this point, the extract is concentrated, evaporating most of the solvent. An aliquot of the cleaned concentrated extract is finally analyzed by capillary chromatography using a non-polar column and FID detection.

Analysis

This injection is performed using the Liquid Band Formation technique. According to this technique, the needle penetrates only partially in the inlet with no pre- or post-dwell time, and the plunger is compressed at maximum speed, allowing it to carry out cold needle type injections. This can easily be exploited by setting needle penetration depth to “minimum” as on the AS 3000 automatic sampling system (Figure 2).

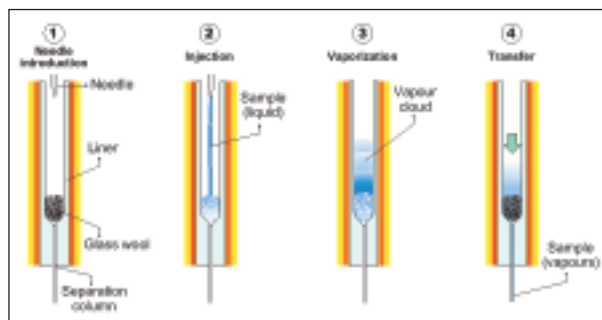


Figure 2: Cold Needle Injection

When using this approach, the solvent expelled from the needle tip forms a liquid band [1,2] 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 [3,4] have, in fact, shown that the sample leaves the wool only after complete vaporization.

The analytical column used for this application is a RTX®-1 column, 5 m long, 0.32 mm i.d., with 0.25 μ m film thickness.

The column temperature is programmed from 40 °C (18 sec) to 350 °C (30 sec) at a linear heating rate of 3.3 °C/sec. An initial isotherm is required to achieve the correct elution of the hydrocarbons with lower boiling points. The injection is performed in splitless mode using constant flow operating mode at 5 mL/min. The injector temperature is set at 300 °C, while the heated block temperature at 350 °C. The injected volume is 1 μ L.

Thermo Scientific data systems, such as ChromQuest™ or Chrom-Card 32 bit software, can be configured in a dedicated mode to automatically integrate the peaks as a group included between n-Decane and n-Tetracontane retention times. Quantification is performed using two external standards consisting of different types of oil diluted in cyclohexane.

System Evaluation and Results

As shown in Figure 3, a first analysis is performed on a solution of n-alkanes in order to verify the complete separation of C_9 from cyclohexane, which is easily observed.

A certified ASTM solution of n-alkanes from C_{16} to C_{44} , each at the same concentration, is then used to check for possible discrimination; under the analytical conditions indicated, the peak area ratio C_{40}/C_{20} is found to be > 0.9 , far higher than the minimum value (0.80) requested by the official method to consider the injector as non-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/ μ L.

The linearity of the system is tested successfully on a Quality Control mixture at different concentrations in the range 5-500 ng/ μ L, showing an excellent linear correlation coefficient.

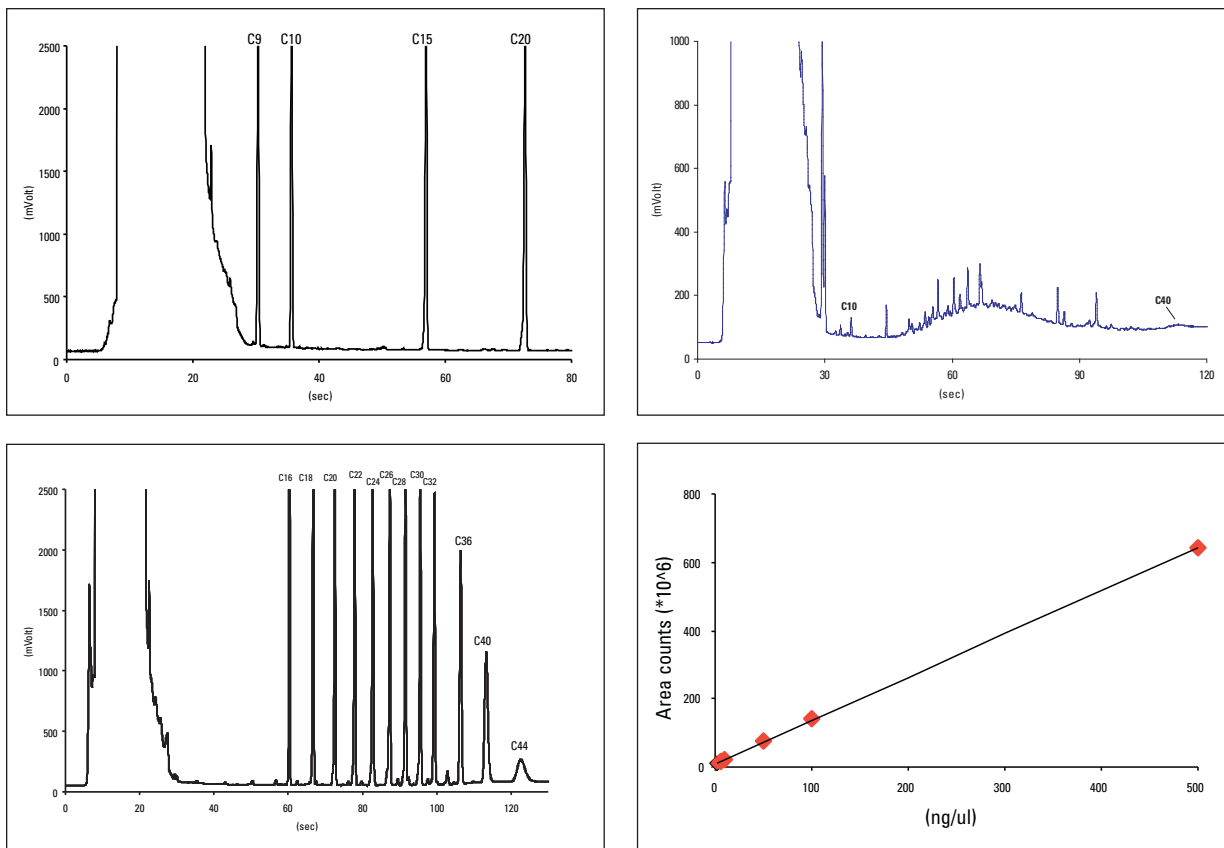


Figure 3: System Evaluation and Results

The system repeatability test is evaluated injecting a sequence of 3 real soil extracted samples and a Quality Control (50 ng/μL) mixture after each sample.

Excellent repeatability of the QC group peak areas is reported below. RSD% <1% is far lower than the compliance value (5%) indicated on the Technical Report.

PEAK	RSD%
C10	0.78
Group Peak	0.80
C40	0.79

To prove the system robustness, a large number of injections (about 100) are performed without replacing the liner, and no degradation of chromatographic performance is observed.

Conventional Gas Chromatography

To provide a significant evaluation, the QC sample at 50 ng/μL is analyzed with the same gas chromatograph in conventional Splitless-FID. The column used is an RTX-1, 30 m long, 0.32 mm i.d., 0.25 μm f.t., with an oven heating rate of 20 °C/min.

A direct comparison of the two chromatograms shows a significant gain in both speed and sensitivity.

Analytical time is shortened by a factor higher than 5, considering that a complete analytical cycle (sampling and cooling time included) takes place in less than 5 minutes, compared with 25 minutes of a conventional cycle.

Sensitivity is also considerably increased because of the strong peak compression effect, which maximizes the signal to noise ratio. This effect can be appreciated even from a visual comparison of the two chromatograms displaying the same signal scale (2250 mVolt).

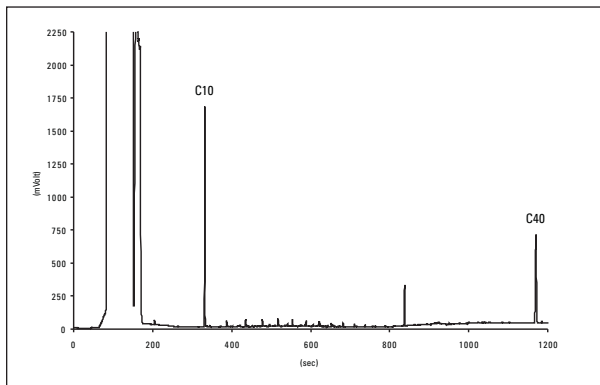
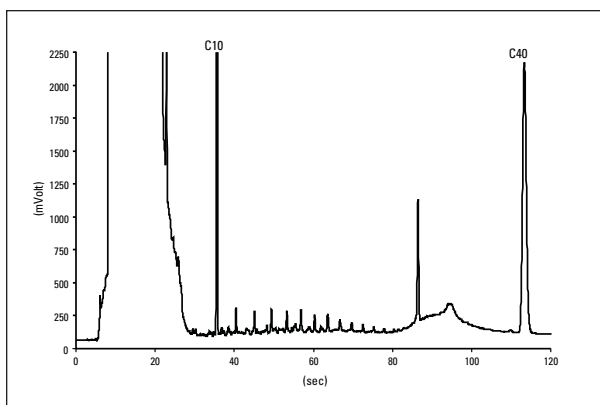


Figure 4: Comparison of UltraFast analysis (top) and conventional analysis (bottom)

Conclusions

The determination of the Hydrocarbon Index can be accomplished by the Thermo Scientific TRACE GC Ultra equipped with the UltraFast Module, in full compliance with the official methods. The injections can be best performed through the cold needle technique by the AS3000 liquid autosampler without any significant discrimination of the heavier compounds.

Analytical cycles can be reduced by a factor greater than 5 with respect to conventional GC, hence delivering impressive lab productivity. The UltraFast GC configuration is also able to provide higher sensitivity and is suitable for the analysis of samples at trace levels.

References

- [1] F. Munari, S. Trestianu Proc. 4th Int. Symp. Capillary Chromatography, Hindelang Germany, R. E. Kaiser (ed), Hüthig, Heidelberg, 1981, p. 349
- [2] K. Grob, M. Biedermann, J. Chromatogr. A, 2000, 897, 237-246
- [3] K. Grob, M. Biedermann, J. Chromatogr. A, 2000, 897, 247-258
- [4] K. Grob, Split and Splitless Injection for Quantitative Gas Chromatography, Wiley-VCH 2001, p. 84

Acknowledgement

Authors: Riccardo Facchetti, Andrea Cadoppi

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Australia
+61 2 8844 9500

Austria
+43 1 333 50340

Belgium
+32 2 482 30 30

Canada
+1 800 530 8447

China
+86 10 5850 3588

Denmark
+45 70 23 62 60

France
+33 1 60 92 48 00

Germany
+49 6103 408 1014

India
+91 22 6742 9434

Italy
+39 02 950 591

Japan
+81 45 453 9100

Latin America
+1 608 276 5659

Netherlands
+31 76 587 98 88

South Africa
+27 11 570 1840

Spain
+34 91 657 4930

Sweden/Norway/Finland
+46 8 556 468 00

Switzerland
+41 61 48784 00

UK
+44 1442 233555

USA
+1 800 532 4752

www.thermo.com

ISO 9001
DNV-CERT-00703-94-A0

Thermo Electron Italia S.p.A. is ISO certified.

©2007 Thermo Fisher Scientific Inc. All rights reserved. Rtx is a registered trademark of Restek Corp. Florisil is a registered trademark of U.S. Silica Company. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries.

Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

AN10025_E 10/07C