A robust method for the determination of mineral oil in water samples

(HYDROCARBON OIL INDEX)

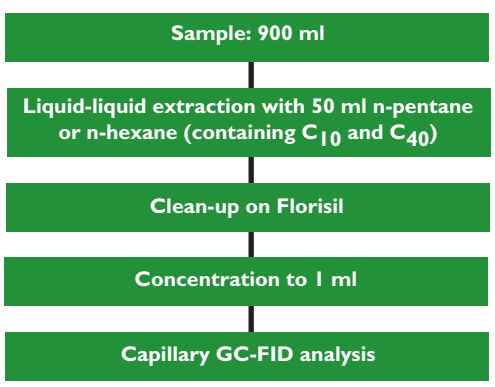
By Pat Sandra and Frank David

Introduction

Mineral oil is a complex mixture of semi-volatile hydrocarbons, including alkanes, alkenes and aromatics. These compounds can be determined in water samples by gas chromatography after liquid-liquid extraction. The hydrocarbons are not measured as individual solutes, but as a sum parameter, often called the hydrocarbon oil index (HOI). In the past, methods based on liquid-liquid extraction using a halogenated solvent followed by quantitative determination by Fourier Transform Infra-Red spectroscopy (FTIR) were used for the determination of mineral oil in water. These methods are currently being replaced by liquid-liquid extraction using a volatile hydrocarbon solvent, followed by clean-up on Florisil and capillary GC-FID analysis. All hydrocarbons are measured that are not retained on Florisil (non-polar fraction) and that elute on an apolar stationary phase between n-decane ($C_{10}H_{24}$, boiling point 174°C) and n-tetracontane ($C_{40}H_{82}$, boiling point 525°C). This fraction is defined as mineral oil. Typically concentrations between 0.1 mg/l and 1 mg/l are determined. This method complies with ISO 9377-2 and ISO 9377-4 [ISO 9377-2, *Water Quality, Determination of hydrocarbon oil index, Part 2: Method using solvent extraction and gas chromatography, reference number ISO 9377-2:2000, ISO, Geneva, Switzerland* (www.iso.ch)]. The method can be applied to drinking water, surface water, waste water and effluents from waste water treatment plants. The method is not applicable to the analysis of volatile hydrocarbons (boiling point < n-decane).

General procedure and analysis flow scheme

The water sample is extracted with an non-polar hydrocarbon solvent. Polar compounds that are co-extracted are removed by column chromatography over Florisil. The non-polar fraction, not retained on Florisil, is concentrated and analysed by capillary GC-FID. The total peak area between n-decane and n-tetracontane is measured and the hydrocarbon oil index is calculated using an external standard consisting of a mixture of two specific mineral oils.



Sample preparation method

Chemicals and solutions

- Extraction solvent: n-pentane, n-hexane or a technical mixture of hydrocarbons with boiling point range between 36°C and 69°C (e.g. petroleum ether)
- Extraction solution: solution containing 2 µl n-decane and 2 µg n-tetracontane per liter extraction solvent.
- Magnesium sulphate heptahydrate ($MgSO_4.7H_2O$)
- Standard stock solution: a mixture of equal amounts of two oils (A and B) is diluted in extraction solvent. Oil A is a diesel oil without additives, showing discrete peaks in the chromatogram. Oil B is a lubricant oil without additives with boiling point range between 325°C and 460°C, showing an unresolved hump in the chromatogram. Mixtures of these oils (1:1) can be purchased from different sources. A stock solution of the mixture is made in extraction solvent in a total hydrocarbon concentration of 10 mg/ml.
- Calibration solutions: From the standard stock solution, calibration solutions are prepared by dilution in extraction solvent. Typically total hydrocarbon concentrations of 0.2, 0.4, 0.6, 0.8 and 1 mg/ml are prepared.
- System performance test mixture: A standard mixture of n-alkanes with even carbon numbers from C_{10} to C_{40} (containing at least C_{10}, C_{20}, and C_{40}) is prepared in extraction solvent. The concentration should be around 50 µg/ml per individual hydrocarbon. This solution is used to verify the suitability of the gas chromatographic system (resolution and detector response) and to characterise the boiling point range of mineral oil in unknown samples.
- Clean-up column (15 cm l x 2 cm i.d.) packed with 2 g Florisil (60-100 mesh, 150-250 µm, heated for 16 h at 140°C, and stored in a desiccator) and covered with 2 g anhydrous sodium sulphate. Before use, the column is pre-rinsed with a few ml extraction solvent.

Method description

- The sampling bottle, containing approximately 900 ml water sample (known weight m_1) is cooled to 10°C (to prevent losses of extraction solution and solutes) and the pH is adjusted to pH 2 by adding hydrochloric acid.
- About 80 g magnesium sulphate is added to the sampling bottle. (If samples are known not to form emulsions, the addition of magnesium sulphate is not required)
- 50 ml extraction solution (containing n-decane and n-tetracontane) and a magnetic stir bar are added. The bottle is closed and the sample is vigorously stirred for 30 min on a magnetic stirrer.
- After separation of the phases, the organic layer is transferred to a clean-up column. This can be done by using a pipette or a microseparator [ISO 9377-2:2000]. Care should be taken not to transfer water to the clean-up column. If emulsions are obtained during extraction, centrifugation is required.
- The extract is eluted through the column, followed by an additional 10 ml extraction solvent (without C_{10} and C_{40}). The eluate is collected in a suitable recipient for concentration.
- The extract is concentrated to 1 ml. Concentration can be done by a rotavapor, Kuderna-Danish and/or under a flow of nitrogen (eventually automated using a Zymark TurboVap or equivalent system). Care should be taken that no solutes are lost during evaporation.
- The empty sample bottle is drained for 5 min, closed with the cap and the mass is determined (m_2). The sample mass (volume) is determined by $m_1 - m_2$.

Capillary GC-FID analysis

The analysis is performed by gas chromatography, using splitless injection and FID detection [Agilent Technologies Application Note 5988-0621E, 2000]. A low bleed apolar HP-1 column is used for boiling point separation. Column, liner, reference sample and GC-method, including a custom report template, are available as a solution kit (Agilent TechnologiesP/N G1530-60515).

Instrumental configuration:	
GC	Agilent 6890 or 6850
Inlet	Split/splitless
Detector	FID
Autosampler	Agilent 7683
Column (*)	15 m x 0.53 mm i.d. x 1.5 µm HP-1 (P/N 19095Z-221)
Inlet liner (*)	Split/splitless liner (P/N 5183-4647)
Chemstation/software (*)	GC version A.08.04 (with dedicated custom report template*)

(*) Column, inlet liner, custom report template are included in solution kit G 1530-60515

Operational conditions:	
Inlet mode	Splitless
Inlet temperature	350°C
Injection volume	1 µl (fast injection mode)
Carrier gas	7.4 ml/min helium, constant flow mode
Oven temperature – 350°C – 5 min	35°C (1.5 min) – 5°C/min – 60°C – 15°C/min
Detector temperature	350°C

- The analysis sequence is started by performing a number of blank runs. The baseline is monitored. Using the low bleed column, a horizontal flat baseline is obtained for the elution of hydrocarbons up to C_{40}. If some column bleed is observed but a reproducible baseline rise is obtained, the baseline can be stored and subtracted from the following runs by using the column compensation option in the signal function. Baseline subtraction is needed in cases when no horizontal baseline is obtained. A horizontal baseline is a prerequisite for correct peak area sum integration.
- The system performance test mixture is analysed. The retention times of n-decane and n-tetracontane are determined.
- Discrimination is checked. This can be done by comparing the peak areas for n-decane, n-eicosane and n-tetracontane. For all solutes, the response factor (area/concentration) should be similar. The response factor for n-tetracontane should be larger than 80 % of the response factor for n-eicosane (For identical concentrations, the peak area for C_{40} must be higher than 80% of the peak area for C_{20}). The calibration solution (mixture of oils) is integrated from C_{10} to C_{20} and from C_{10} to C_{40}. For both fractions, the response should similar (area C_{10}-C_{20} / area C_{20}-C_{40} i.e. between 0.8 and 1.2). Regarding discrimination, the choice of the injection method and the inlet liner are critical parameters and these are optimised in the GC configuration and GC parameters described above. Discrimination effects within the proposed analytical system were evaluated by making 25 sequential injections of a standard containing C_{10} and C_{40}. The data presented in Figure 1 demonstrate the robustness of the method. The analytical system clearly passes the discrimination test specified in the ISO standard.

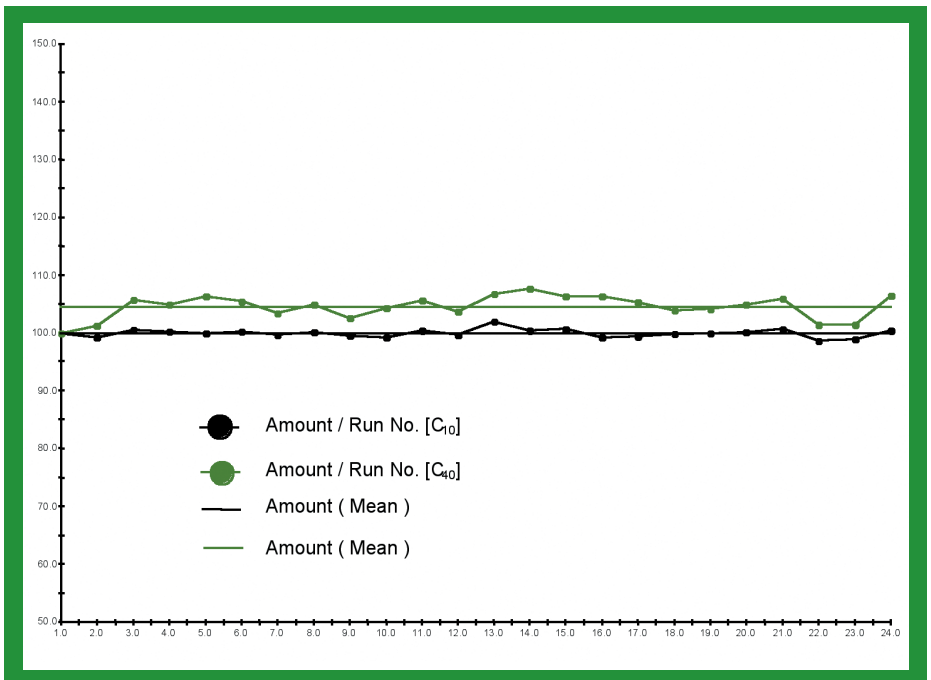


Figure 1. Discrimination test (25 injections)

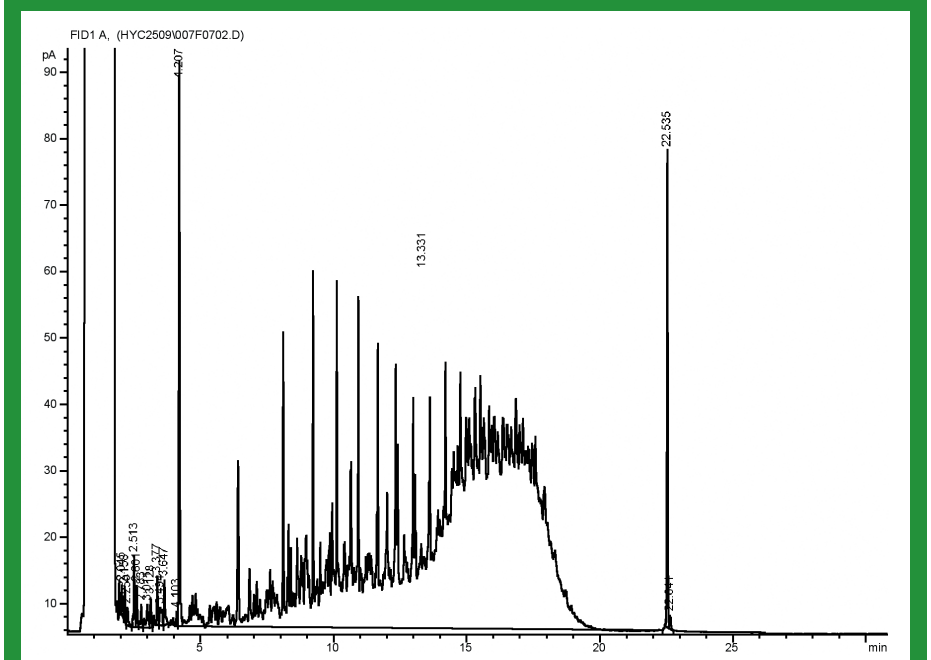


Figure 2. Mineral oil (standard) analysis (0.6 mg/ml) by capillary GC-FID

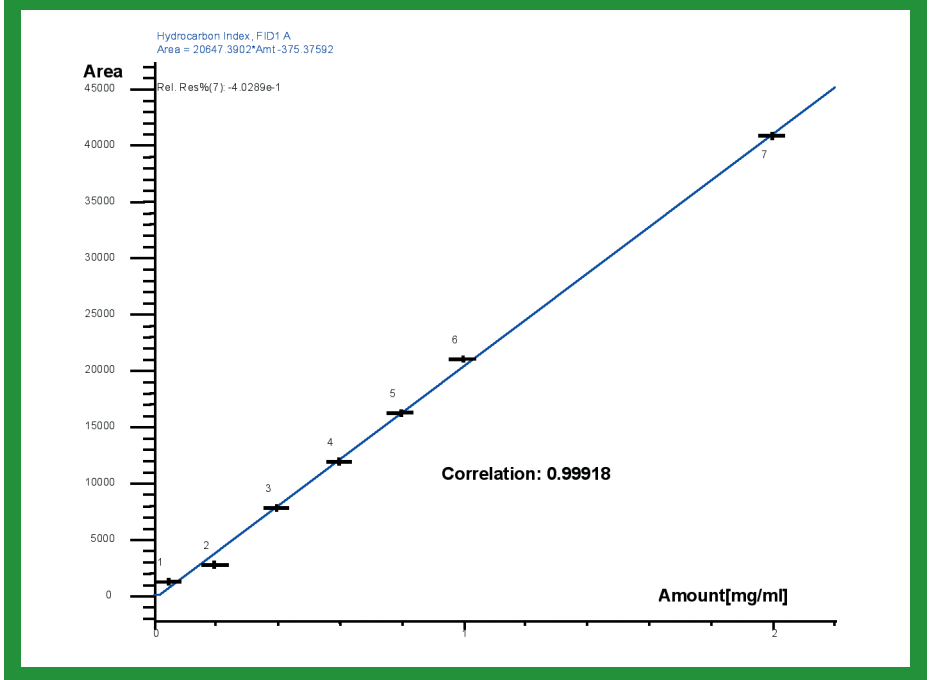


Figure 3. Seven point calibration curve

- The calibration solutions are analysed in order of increasing concentration. The peak area is summed from the retention time corresponding to the end of the n-decane peak to the retention time corresponding to the start of the n-tetracontane peak. The baseline level is maintained at the signal level corresponding to the signal level in front of the solvent peak. The peak area sum is plotted versus the concentration of total hydrocarbons in the calibration solutions (in mg/ml). According to ISO 9377, at least five calibration levels are required.
- A method blank sample is analysed. This method blank sample is prepared by extraction of a blank water sample (for instance bottled drinking water) using the extraction solution, followed by the clean-up and concentration procedure described above. In this extract, no peaks should be detected between C_{10} and C_{40}. This test is a control of purity of solvents and glassware.
- Finally the samples are analysed.

Results

The analysis of a standard mixture of mineral oil (0.6 mg/ml level) is shown in Figure 2 and a calibration curve in Figure 3. The peaks corresponding to n-decane and n-tetracontane are detected at respectively 4.207 and 22.535 min. The peak area is summed between these two peaks. The total peak area corresponds to the mineral oil.
From the chromatogram it is clear that two types of oil are present. Between 5 and 14 min, distinct peaks are detected corresponding to a typical diesel oil. Between 14 and 20 min, an unresolved hump is observed corresponding to a lubricant oil. The baseline level is maintained at the signal level corresponding to the signal level in front of the solvent peak (horizontal baseline).
The concentration of the hydrocarbons in the sample is calculated from the calibration curve (area = a x conc + b) or by the following formula:

$$HOI\ (mg/l) = \frac{(A_m - b)x\ F\ x V\ x\ w}{a\ x\ (m_1 - m_2)}$$

where HOI = hydrocarbon oil index (in mg/l).
A_m = peak area sum (C_{10}-C_{40}) measured for sample
a = slope of calibration curve (area y in function of concentration x in mg/l)
b = intercept of calibration curve
F = dilution factor (typically F=1 is no additional dilution is used)
V = final volume of extract in ml (typically 1 ml)
w = density of water sample in g/ml (w = 1.00 g/ml for fresh water)
m_1= mass of filled sampling bottle (in g)
m_2 = mass of empty sampling bottle (in g)

A custom report template is included with the HOI method and generates a report conforming to the ISO standard method.

Remarks

- Sampling: Sampling is normally performed in 1000 ml glass bottles with a ground glass stopper or with a screw cap (PTFE lined). The sample bottles are filled to approximately 90%, closed and weighed (m1). The sample is stored at 4°C for maximum 4 days. For surface and ground water samples, it is advised to add hydrochloric acid to pH 2 for sample preservation.
- Method performance: The extraction recovery can be checked by spiking a 900 ml blank water sample with 1 ml of a 1 mg/ml solution of mineral oil in acetone. The standard stock solution (10 mg/ml in extraction solvent) is therefore diluted tenfold in acetone. The spiked sample is extracted and the extract is cleaned and concentrated as described above. The theoretical final concentration is 1 mg/ml. The recovery is calculated by comparing the peak area obtained for the extract with the 1 mg/ml calibration solution. Recovery should be between 80% and 110%.
- Performance verification of clean-up procedure: 10 ml of a 2 mg/ml solution of stearyl stearate solution in extraction solvent is eluted through a clean-up column. The column is rinsed with an extra 10 ml portion of extraction solvent. The eluent is diluted to 25 ml with extraction solution and an aliquot is analysed by GC using the same method as for the hydrocarbon oil index determination. The peak area of stearyl stearate is measured and compared to the peak area obtained for a direct analysis of a stearyl stearate standard solution of 40 µg/ml in extraction solution. The ratio of the peak area for stearyl stearate in the fraction eluted from the clean-up column versus the peak area for stearyl stearate in the 40 µg/ml standard solution should be less than 1. This corresponds to a clean-up efficiency of 95% (less than 5% breakthrough). If the concentration of stearylstearate in the eluate is higher, Florisil activation should be checked.
- Clean-up by matrix solid phase dispersion (MSPD): Alternatively, clean-up by matrix solid phase dispersion can be used. In this case, clean-up is not performed by column chromatography, but the adsorbent is added to the extract. After extraction, the organic fraction is transferred to a 50-100 ml vial or Erlenmeyer. 2 g anhydrous sodium sulphate is added and the recipient is shaken to dry the organic phase. After the drying step, 2 g activated Florisil is added and the recipient is placed a few minutes on a shaker. Polar co-extracted solutes bind on the Florisil material, while non-polar compounds remain in solution. After this adsorption step, the solution is filtered and the filtrate is concentrated as described above. Using the performance verification test for the clean-up procedure, this method can be compared to the column chromatography method. Similar results are obtained.
- In comparison to the FTIR method, data can be different. The halogenated solvent extraction – FTIR methods often do not include a clean-up procedure and there is no separation according to boiling point. Therefore, the low molecular weight fraction (< C_{10}) and the high molecular weight fraction (> C_{40}) are included in the determination and consequently higher concentrations are reported.
- The method based on GC-FID, gives also qualitative information on the sample. The boiling point discrimination can be used to identify the source(s) of contamination, e.g. diesel, paraffin oil, motor oil, etc.
- For samples with a high fat content (> 150 mg/l) or high amount of surfactants, lower recoveries have been noted or problems can occur with emulsion formation. Extra clean-up steps or modifications of extraction conditions (amount of extraction solvent) and clean-up conditions (larger Florisil column) are mandatory.

We thank Bernhard Wuest, Agilent Technologies, Waldbronn, Germany for his contribution

AUTHOR

Pat Sandra and Frank David
Research Institute for Chromatography, Kennedypark 20,
B-8500 Kortrijk, Belgium
Tel: 32-56-204031 Fax: 32-56-204859
E-mail: pat.sandra@richrom.com