

Automated Clean-up for Mineral Oil (Hydrocarbon Oil Index) Analysis using the Agilent 7696A Sample Prep WorkBench

Application Note

Automated Sample Preparation

Authors

Frank David, Karine Jacq, and
Bart Tienpont
Research Institute for Chromatography,
President Kennedypark 26,
B-8500 Kortrijk, Belgium

Peter Mrozinski
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808,
USA

Abstract

Mineral oil (or Hydrocarbon oil) in water samples is determined by liquid-liquid extraction, followed by a clean-up step on Florisil, and GC-FID analysis. Using the Agilent 7696A Sample Prep WorkBench system, drying and clean-up of samples obtained after liquid-liquid extraction can be automated. High recoveries and excellent reproducibility are obtained for the mineral oil fraction, while the clean-up step is very efficient. The extracts are analysed by GC-FID. In combination with low thermal mass (LTM) – GC, an automated high throughput method is obtained.



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Introduction

Environmental contamination by hydrocarbon fractions, such as diesel or motor oil, is measured using GC-FID. This method, also called hydrocarbon oil index (HOI), mineral oil or total petroleum hydrocarbon (TPH) determination is one of the most important applications in environmental analysis. For water samples, liquid-liquid extraction (LLE) with an apolar (hydrocarbon) solvent with a boiling point between 36 °C and 69 °C (for example, hexane) is the first step in sample preparation. Next, the extract is dried over sodium sulphate and cleaned by passing over Florisil to remove more polar, co-extracted solutes such as lipids. The extract is then concentrated by N₂ blowdown (or Kuderna-Danish) and analyzed by GC-FID [1].

The sample clean-up procedure can be minimized using dispersive SPE instead of classical column chromatography or solid phase extraction. In d-SPE, a small amount of adsorbent is added to the sample. The matrix solutes (in this case: more polar solutes that are co-extracted in LLE) bind to the adsorbent and are removed from the solution. The purified extract is analyzed by GC-FID. For efficient clean-up, the extract needs to be dried on Florisil before d-SPE.

The mineral oil extract is then analyzed by GC-FID. Normally, a 10 – 30 m column with low film thickness is used. Typically the analysis time is about 30 min. Recently, it was demonstrated that sample throughput can be significantly increased by applying low thermal mass (LTM) technology [2].

In this application note, the automation of the drying and dispersive SPE steps of the hydrocarbon oil index method on the Agilent 7696 Sample Prep WorkBench is described. Prior to the WorkBench method, the extract obtained by LLE is concentrated (for example, by rotavapor or nitrogen blow-down) to about 1–1.5 mL. This fraction is then dried on sodium sulphate and cleaned on Florisil using autosampler vials, preloaded with the adsorbents. The final extract is analysed by fast GC-FID using LTM technology

Experimental

Chemicals and test solutions

A 1:1 mixture of diesel and motor oil (5,000 µg/mL each in cyclohexane) was used as mineral oil test sample. An alkane standard containing even numbered n-alkanes from C10 to C40 (50 µg/mL each in hexane) was used for repeatability testing and GC-FID calibration.

Stearyl stearate was used for checking the performance of the clean-up procedure, as described in ISO 9377 method. A stock solution of 2,000 µg/mL in acetone was prepared.

From these stock solutions, a calibration solution containing 5 ng/µL of each n-alkanes and 80 ng/µL stearyl stearate was prepared in hexane. Also, a calibration solution containing 400 ng/µL mineral oil and 80 ng/µL stearyl stearate was prepared in hexane. These solutions were used for direct injection.

Two spiking solutions were prepared in acetone. These solutions were then spiked into 900-mL water samples and extraction was performed with 50 mL hexane. The hexane fraction was concentrated under nitrogen using a Turbopap system to 10 mL. This extract was divided over several vials for repeatability testing of the 7696 WorkBench method. The first spiking solution contained 50 µg per n-alkane and 800 µg stearyl stearate. The second spiking solution contained 4,000 µg mineral oil and 800 µg stearyl stearate. Assuming 100% recovery in liquid-liquid extraction, the concentrations in the 10-mL hexane extract are identical to the calibration solutions.

Drying of the extract (in hexane) is done on anhydrous sodium sulphate. The clean-up adsorbent was Florisil. Both Na₂SO₄ and Florisil were first heated overnight at 140 °C.

First, 20 mg (± 2 mg) sodium sulphate was added to a series of 1.5-mL high recovery vials. These vials are labeled Dry. To a second series of 1.5-mL high recovery vials, 30 mg (± 2 mg) Florisil was added. These vials are labeled Clean-up. All vials were closed with screw caps to protect them from humidity.

Sample Preparation

The hexane extracts of water samples are placed in 1.5-mL high recovery vials (samples). A series of 1.5-mL high recovery vials containing 20 mg dried sodium sulphate (Dry) and 1.5-mL high recovery vials containing 30 mg Florisil (Clean-up) are also positioned in the racks, together with empty vials with a 200-µL insert (for final extract).

The front tower was configured with a 500 µL syringe, the back tower with a 250 µL syringe. Syringe rinsing is done with hexane.

An example of the resource lay-out of the 7696 WorkBench is shown in Figure 1.

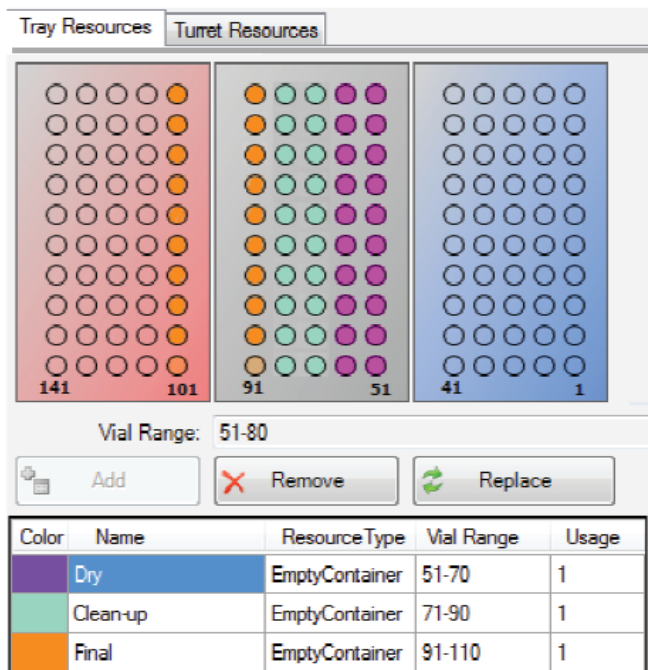


Figure 1. Resource lay-out for an Agilent 7696 Sample Prep WorkBench.

The Workbench method can be summarized as follows (command in bold, comment in italic):

1. **Add 500 μ L of Sample to Dry at Front Tower**
(Aliquot of extract is added to sodium sulphate)
2. **Mix Dry for 1 min (2,000 rpm, bidirectional, 4 s on, 1 s off)**
(Mixing allows good contact between sample and adsorbent, removal of water)
3. **Add 350 μ L of Dry to Clean-up at Back Tower**
(Aliquot of dried extract is added to Florisil)
4. **Mix Clean-up for 1 min (2,000 rpm, bidirectional, 4 s on, 1 s off)**
(Mixing allows good contact between sample and adsorbent, removal of polars)
5. **Add 150 μ L of Clean-up to Final at Back Tower**
(Transfer of cleaned extract to vial for further analysis by GC-FID)
6. **Flag Final as Result**

Instrumental Configuration

The analyses were performed on an Agilent 7890 GC system. The GC was equipped with a SSI inlet, an LTM II oven door and FID detection. Separation was done on a 0.32 mm \times 10 m, 0.10 μ m DB-5HT column (p/n 123-5701LTM).

The analytical conditions are summarized in Table 1 (see also [2]).

Table 1. Analytical Conditions

Injection	1 μ L, splitless (0.4 min purge delay) 350 $^{\circ}$ C split/splitless liner (p/n 5183-4647)
Carrier	Helium, 9 mL/min constant flow
GC oven temp	340 $^{\circ}$ C isothermal
LTM	40 $^{\circ}$ C (0.5 min) – 200 $^{\circ}$ C/min – 240 $^{\circ}$ C – 100 $^{\circ}$ C/min – 340 $^{\circ}$ C (0.5 min) Analysis time: 3 min
FID	340 $^{\circ}$ C, 40 mL/min H_2 , 400 mL/min air

Results and Discussion

The first step in the determination of mineral oil in water samples is liquid-liquid extraction. Typically, a large sample (900 mL) is extracted with 50 mL solvent (hexane). This step cannot be automated and is still performed in a classical way. The obtained extract is concentrated (for example, under nitrogen using a Turbovap system, Zymark). The concentrated sample (1–2 mL) is transferred to a 2-mL autosampler vial and the remaining of the procedure is handled by the 7696 Sample Prep WorkBench.

The sample preparation procedure performed on the Agilent 7696 Sample Prep WorkBench is illustrated in Figure 2. In the first step, an aliquot of the hexane extract is dried over sodium sulphate. This step is important because traces of water reduce the performance of the next clean-up. An aliquot of the dried extract is then transferred to a vial containing Florisil. It was observed that the Florisil adsorbent needs to be activated at 140 $^{\circ}$ C to remove residual water. Also, tests were performed to verify the minimum quantity of Florisil needed. Clean-up performance was not sufficient when less than 20 mg material was used. An amount of 30 mg (\pm 2 mg) was considered as a safe margin.

After agitation of the extract with the Florisil, an aliquot can be transferred to an empty vial (with 200- μ L insert). This extract can be analysed by fast GC-FID. Since the vial contains 150 μ L extract, the same method could also be combined by large volume injection if needed.

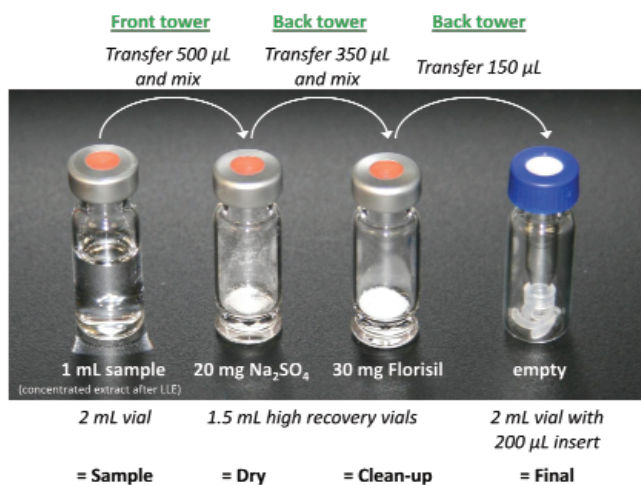


Figure 2. Picture of 2-mL vials during different clean-up steps on Work Bench
 1. Original water extract in hexane;
 2. After transfer of extract to Na_2SO_4 (drying);
 3. After transfer of extract to Florisil;
 4. Final extract.

A typical profile obtained for a mineral oil sample is shown in Figure 3. The upper trace shows the chromatogram obtained for a sample (400 $\mu\text{g}/\text{mL}$ in extract) without clean-up. To the mineral oil sample, an amount of stearyl stearate (80 $\mu\text{g}/\text{mL}$ in extract) was added. This compound (used as simulant for more polar interferences), elutes around C38.

The chromatogram obtained for the purified sample (theoretically same concentration as above) is shown in Figure 3, lower trace. It is clear that a similar profile is obtained for the mineral oil. The stearyl stearate is nearly quantitatively removed (peak area should be < 5% of peak area in non-purified sample).

To test the reproducibility, the Agilent 7696 WorkBench method was applied to a series of 6 samples in hexane, containing alkanes (5 $\mu\text{g}/\text{mL}$) and stearyl stearate (80 $\mu\text{g}/\text{mL}$). In Table 2, the peak areas for 4 n-alkanes and stearyl stearate are given. Typically, the RSD % are around 1% (2.5 % for C40). The recovery (calculated as ratio of peak area in purified sample versus original sample) is higher than 80%. The recovery of stearyl stearate was 1.9% (average of $n=6$), so well below 5%.

Table 2. Repeatability ($n = 6$) of Peak Areas for n-alkanes and Stearyl Stearate and Recovery Versus Direct Liquid Injection of Nonpurified Sample

Compound	Average response	SD	RSD (%)	Recovery (%)
C10	58.1	0.542	0.93	99.6
C20	62.7	0.612	0.97	99.8
C30	60.4	0.656	1.09	101.1
Stearyl stearate	16.0	2.792	(17.5)	1.9
C40	50.5	1.293	2.56	86.4

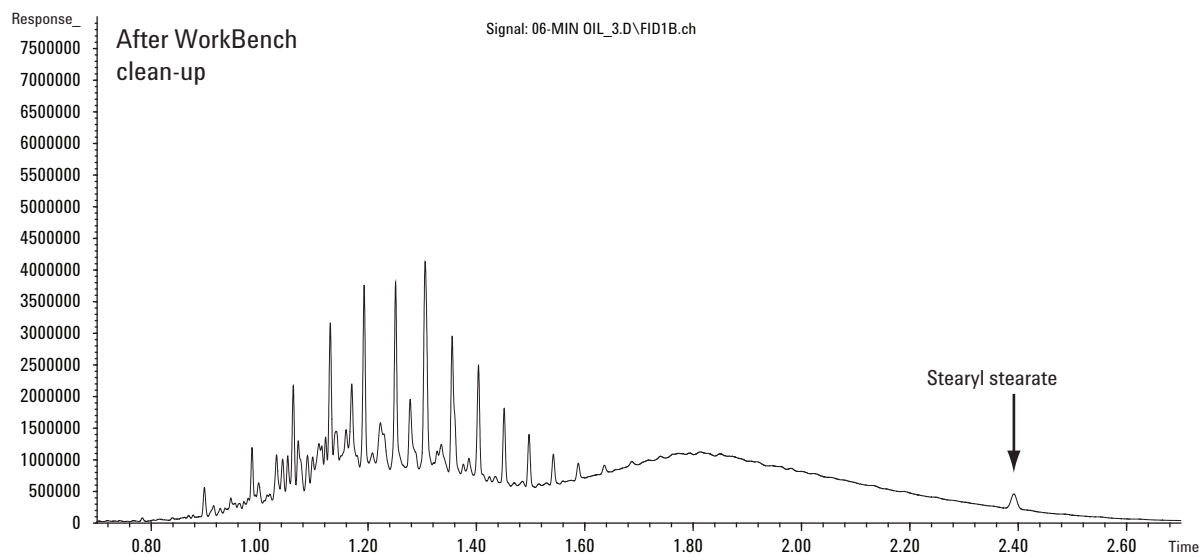
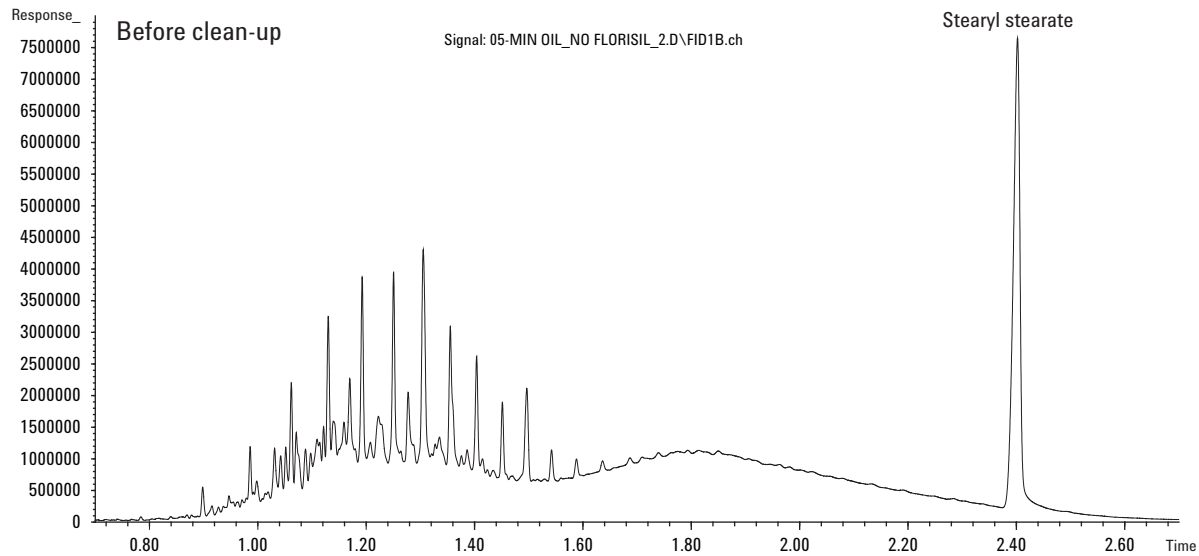


Figure 3. GC-FID chromatograms from water extract containing 400 ng/ μ L of a petroleum based oil and 80 ng/ μ L stearyl stearate in hexane. Upper trace: direct injection without clean-up; Lower trace: after Agilent 7696 Sample Prep WorkBench system drying and clean-up procedure.

The same test was performed on a water sample extract containing hydrocarbon oil (400 µg/mL) and stearyl stearate (80 µg/mL). The results are summarized in Table 3.

These data clearly demonstrate that repeatability is excellent (RSD < 1%) on total area for mineral oil and that removal of stearyl stearate was also efficient in this test (recovery = 2.3% on average, so < 5%). The recovery of the mineral oil fraction was higher than 95% (criteria: 80% < recovery < 110%).

Table 3. Repeatability (n = 10) of Peak Areas for Mineral Oil and Stearyl Stearate and Recovery Versus Direct Liquid Injection of Nonpurified Sample

	Peak area		Recovery (%)	
	Mineral oil	Stearyl stearate	Mineral oil	Stearyl stearate
No clean-up	9342.0	895.4		
1	9760.9	20.6	104.5	2.3
2	9745.4	20.6	104.3	2.3
3	9602.1	19.7	102.8	2.2
4	9839.3	16.4	105.3	1.8
5	9841.8	23.0	105.3	2.6
6	9704.5	18.1	103.9	2.0
7	9800.4	16.6	104.9	1.8
8	9745.4	23.0	104.3	2.6
9	9735.6	19.6	104.2	2.2
10	9658.4	31.6	103.4	3.5
Average	9743.4	20.9	104.3	2.3
sd	75.4		0.8	
RSD (%)	0.77		0.77	

Conclusion

A miniaturized dispersive SPE clean-up method for the determination of mineral oil in water samples was automated on the Agilent 7696A Sample Prep WorkBench system. Hexane extracts from liquid-liquid extraction are dried and purified. The obtained extracts are analysed by GC-FID.

High recoveries and excellent reproducibility are obtained for the mineral oil fraction, while the clean-up step is very efficient. In combination with low thermal mass (LTM) –GC, a high throughput method is obtained.

References

1. International standard ISO 9377-2, Water Quality, Determination of hydrocarbon oil index, part 2: Method using solvent extraction and gas chromatography, 2000.
2. F. David, K. Jacq and R.L. Firor, High Throughput Mineral Oil Analysis by GC-FID Using the Agilent Low Thermal Mass (LTM II) System, 9/2011, Agilent Technologies publication 5990-9104EN

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