



Fully automated platform for determining the hydrocarbon index according to the specifications provided by the UNI EN ISO 9377-2 method

Current environmental protection legislation requires, in various areas, the determination of the concentration of mineral oils. In particular, Legislative Decree 152/06 reports threshold values for this parameter for various aqueous matrices, such as:

- Emission limits in surface water (5.00 mg/l) and in sewerage (10.0 mg/l)
- Contamination threshold in underground water (0.350 mg/l)
- Maximum value for direct discharge into the sea in accordance with the methods established by the Minister of the Environment and Land Protection, with reference to the activities of prospecting, research and cultivation of liquid or gaseous hydrocarbons (40.0 mg/l)
- Quality characteristics in surface water intended for the production of drinking water (variable from 0.050 to 1.00 mg/l)

The currently most widespread method (UNI EN ISO 9377-2) consists of several steps, in particular:

- Extraction on 900 ml of sample
- Dehydration of the extract and purification on florisil®
- Concentration using a device Kuderna Danish
- Further concentration under nitrogen flow (optional)
- Injection into a suitable GC-FID system.

The method includes numerous controls aimed at ensuring the reliability of the analytical data, the most important of which are:

- Non-discrimination on the C10-C40 range
- Purification efficiency on florisil®
- Evaluation of recovery.

In this application note, the possibility of operating a scale-down has been **verified**, working on a few ml of sample and operating in Large Volume Injection (LVI) mode, so as to avoid any concentration step.



The proposed preparative platform is able to complete all the operations required by the method, including the preparation of the standards needed to build the calibration curve, maintaining performances in line with those required.

Thanks to the optimization of the preparative and injection parameters, it is possible to target a LOQ of 50 µg/l mg/l and a LOD of 35 µg/l, so as to reach the current regulatory requirements.

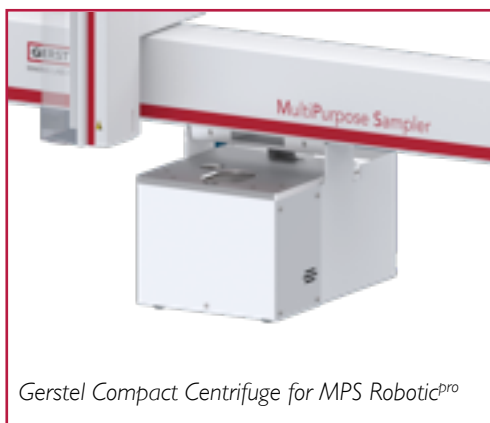
Method automation

The system is based on the **LVI injection technique on on-column**, made possible by the adoption of a valve capable of ventilating over 450 µl of solvent at the injection site. In this way, it is possible to reduce the volumes involved and eliminate the concentration step. The extraction is carried out on approximately 18 ml of sample using a **high efficiency oscillating shaker** (up to 4000 Hz). The drastic reduction in volumes allows the use of less than 2 ml of extracting mixture per sample.

The dehydration and purification phases on florisil® have also been optimized thanks to the use of dispersive SPE, also automated, which guarantees effective removal of water and polar substances in a few seconds.

This upgrade of the platform includes the implementation of a **centrifugation module**, which allows breaking any emulsions, and an **automatic decapper** to eliminate the problem of contamination by siloxanes.

Finally, the possibility of using syringes with different volumes and types on the two turrets allows the immediate injection of the final extract into GC and the processing of the volatile fraction via HS: a single platform allows the complete determination of the hydrocarbon index in accordance with the ISPRA guidelines (resolution of the Federal Council. Meeting of 17.12.2014. Doc. no. 46/14 CF).

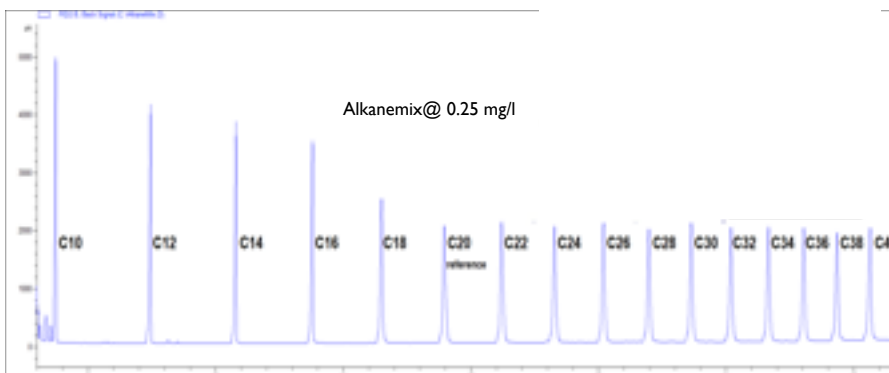


Instrumental performance

The verification of the specifications required by the official method must take into account the scale-down. In this regard, targeted tests were performed with solutions at appropriate concentrations.

Absence of discrimination

The accurate setting of the injection conditions allows working in the absence of discrimination on the C10-C40 working range, as highlighted by the chromatogram below, figure 1.



#	RT	Compound	Area	C20 ratio
1	8.75	C10	3545	114%
2	9.49	C12	3410	110%
3	10.16	C14	3289	106%
4	10.76	C16	3208	103%
5	11.30	C18	3246	105%
6	11.79	C20_referece	3103	100%
7	12.24	C22	3293	106%
8	12.66	C24	3135	101%
9	13.04	C26	3213	104%
10	13.40	C28	3051	98%
11	13.73	C30	3267	105%
12	14.04	C32	3082	99%
13	14.33	C34	3115	100%
14	14.61	C36	3089	100%
15	14.87	C38	2882	93%
16	15.13	C40	3282	106%

Fig.1: Alkanemix @ 0.25 mg/l each (see method 9377-2 section 9.6)

Purification efficiency

A solution of stearyl stearate @ 300 mg/l was tested, treated in dispersive SPE mode using 300 mg of florisil®. Figure 2 shows a comparison between the purified solution (S_t) and the 1/20 dilution of the same (S_{nt}), with the relative S_t/S_{nt} value $\ll 1$ (see method 9377-2 section 9.6).

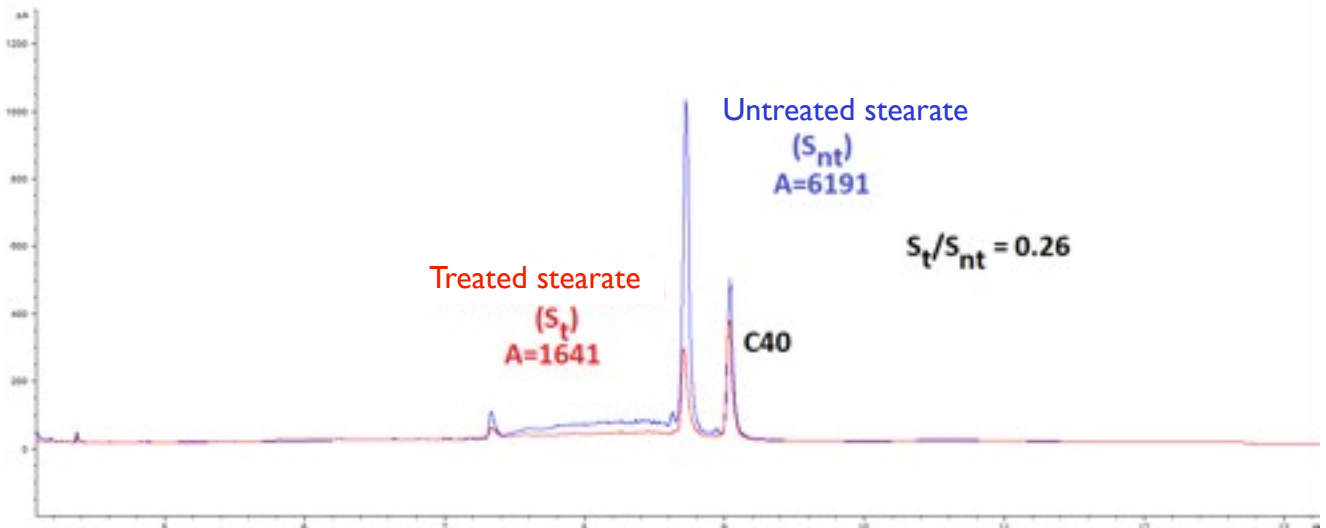


Fig.2: Verification of purification efficiency on florisil®

Recovery Evaluation

The method requires a percentage recovery between 80% and 110%; compliance with this requirement was verified for all the solutions used to construct the calibration curve, obtaining values between 88% and 104%. As an example, the calculations relating to the standard with a concentration of 0.216 mg/l are shown below.

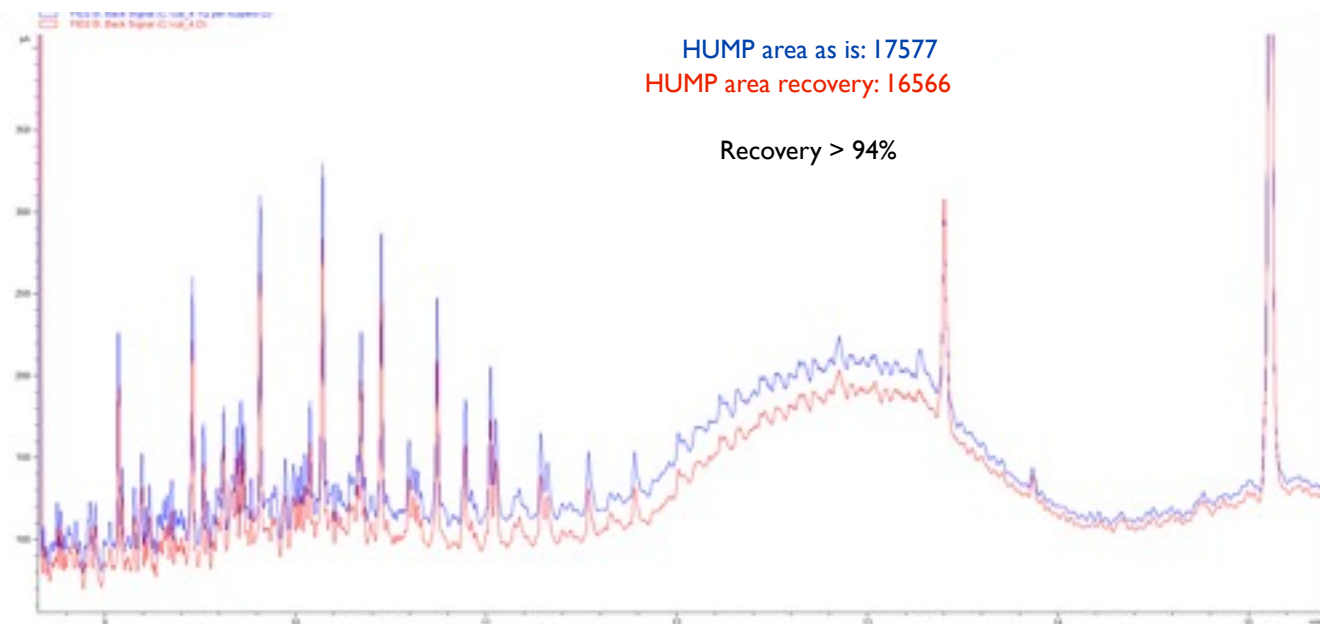


Fig.3: Recovery - calculations relating to the standard with a concentration of 0.216 mg/l

Linearity and Repeatability

The calibration obtained in the matrix, in complete automation, covers the range 43-1260 µg/l, as shown in figure 4. Accuracy and precision were evaluated on 6 repetitions of a spiked sample with a concentration of 500 µg/l, figure 5.

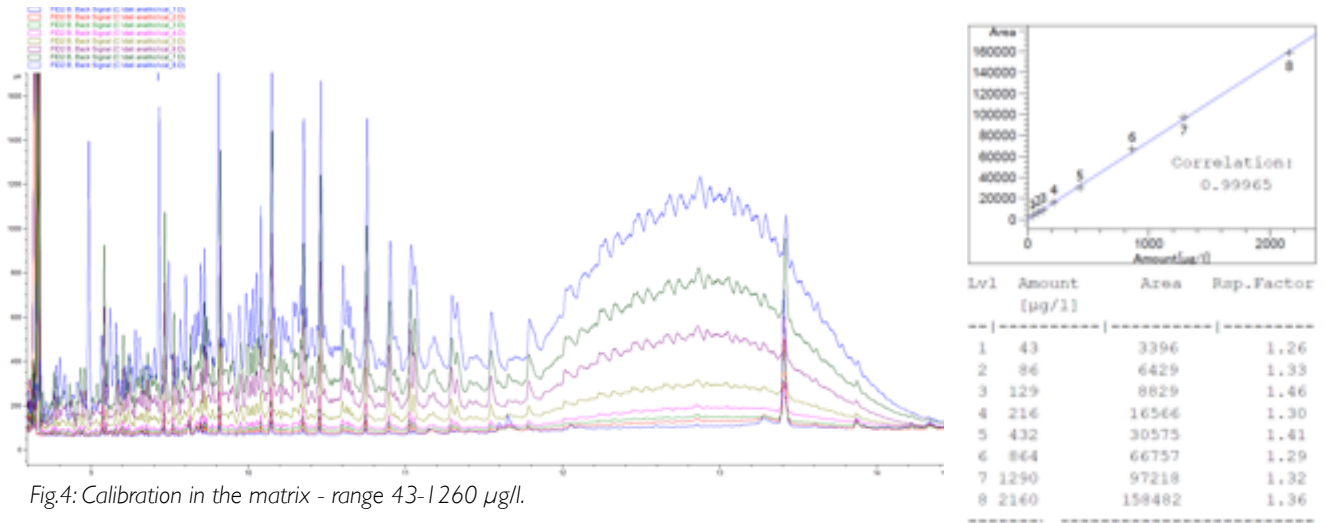


Fig.4: Calibration in the matrix - range 43-1260 µg/l.

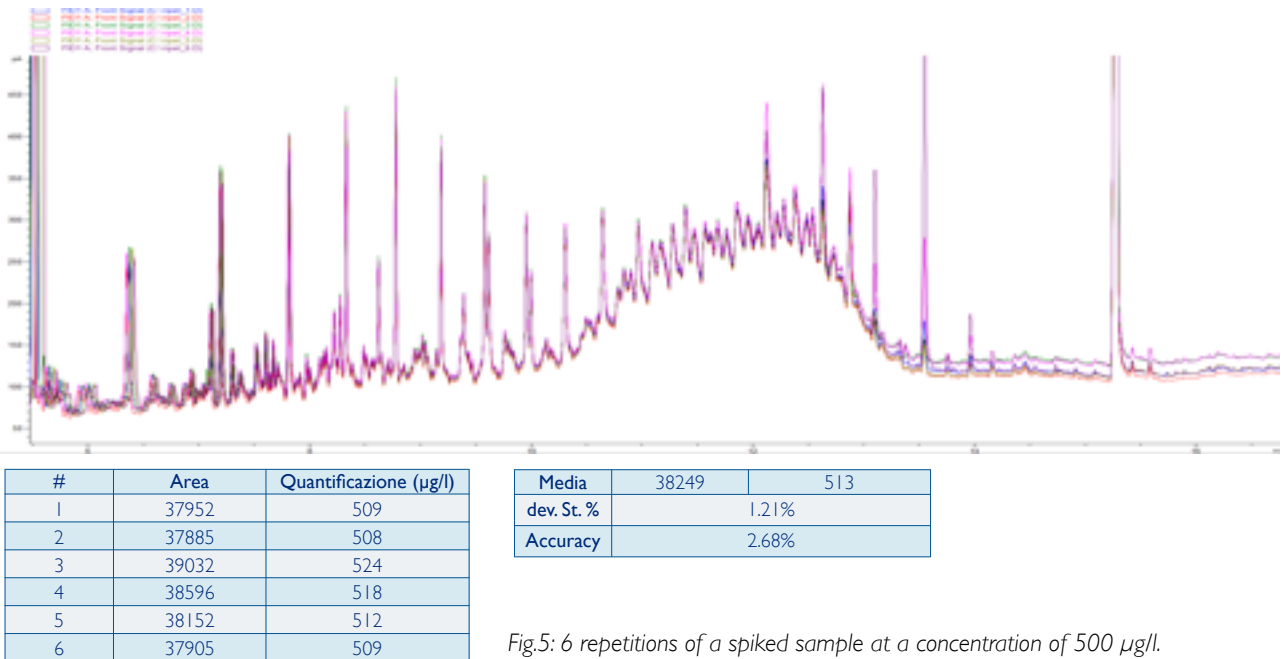


Fig.5: 6 repetitions of a spiked sample at a concentration of 500 µg/l.

Conclusions

The proposed preparatory station allows to:

- Reduce the amount of sample needed for the analysis by more than an order of magnitude
- Limit the solvent volume to less than 2 ml per sample
- Automate the entire process
- Avoid the evaporation phase
- Achieve excellent LOQ and LOD levels
- Meet the requirements of the official method

- Conduct the entire determination of the hydrocarbon index
- Eliminate siloxane contamination.

Thereby ensuring greater productivity and minimizing random errors resulting from a fully manual approach.

Through a minimal upgrade, the processing of soils and waste is also possible.