HYDROCARBON OIL INDEX:
SCALE DOWN APPROACH FOR AUTOMATION OF C10-C40 ANALYSIS ACCORDING TO UNI EN ISO 9377-2

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FOREWORD

The TPH quantitation in water sample is regulated in many EU State members. It involves the analysis of two hydrocarbon fraction: **VPH** (also called C<12) and **EPH** (also called C10-C40). Italian regulation asks for several water matrices an LOQ in the range of tenth ppb. The reference method for EPH (ISO 9377-2) requires one liter of sample and more than 50 ml of hexane, not to mention a high amount of Florisil® and sodium sulphate. Furthermore, the sample preparation requires lot of operator time, as well as carefully cleaned glassware. **The solution proposed by SRA, compared with the standard sample-prep, saves up to 90% of hexane, reduces up to 1/50 the sample volume, and requires less than 1/10 of Florisil®.** Furthermore, the whole sample prep is totally automated, with no evaporation step which can cause loss of volatile fraction. The operator is only asked to place samples on autosampler and start the process. In addition, the analytical platform is suitable to run both determinations (VPH and EPH) without any operator attendance.
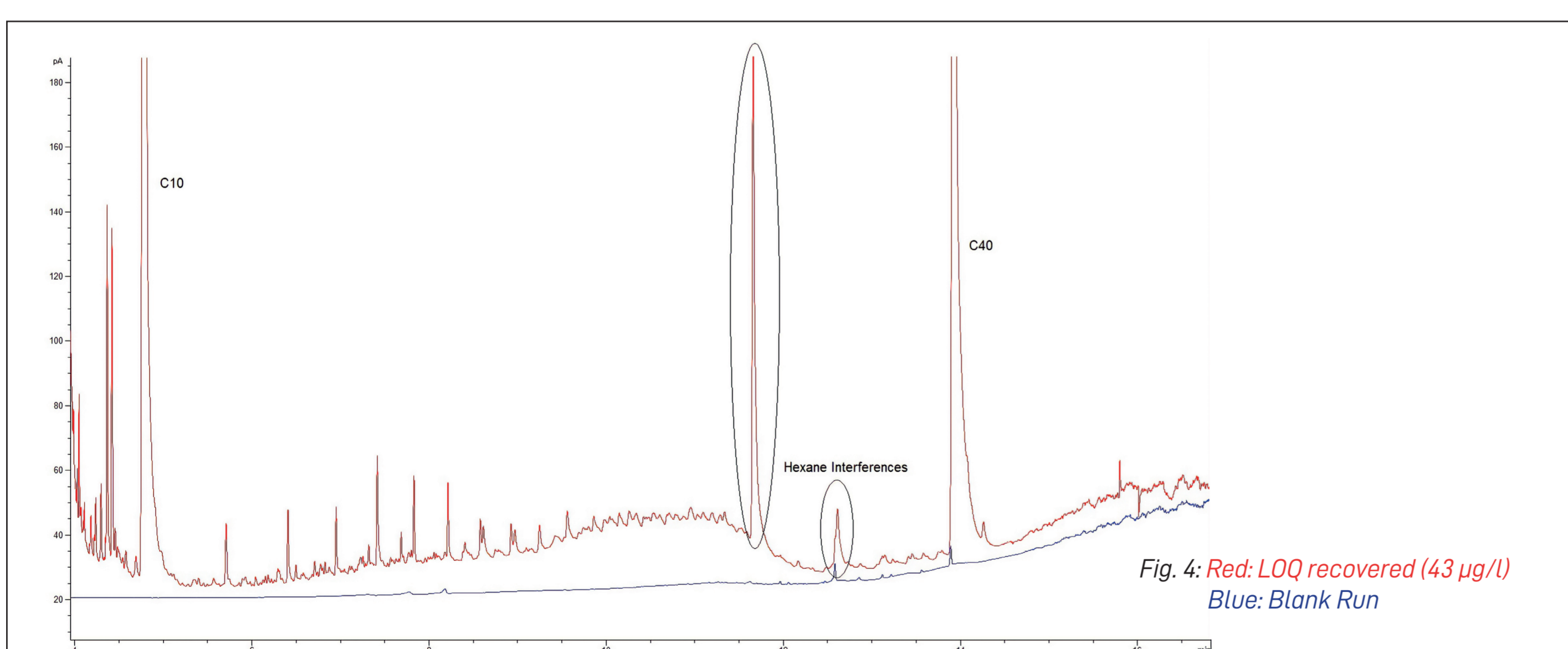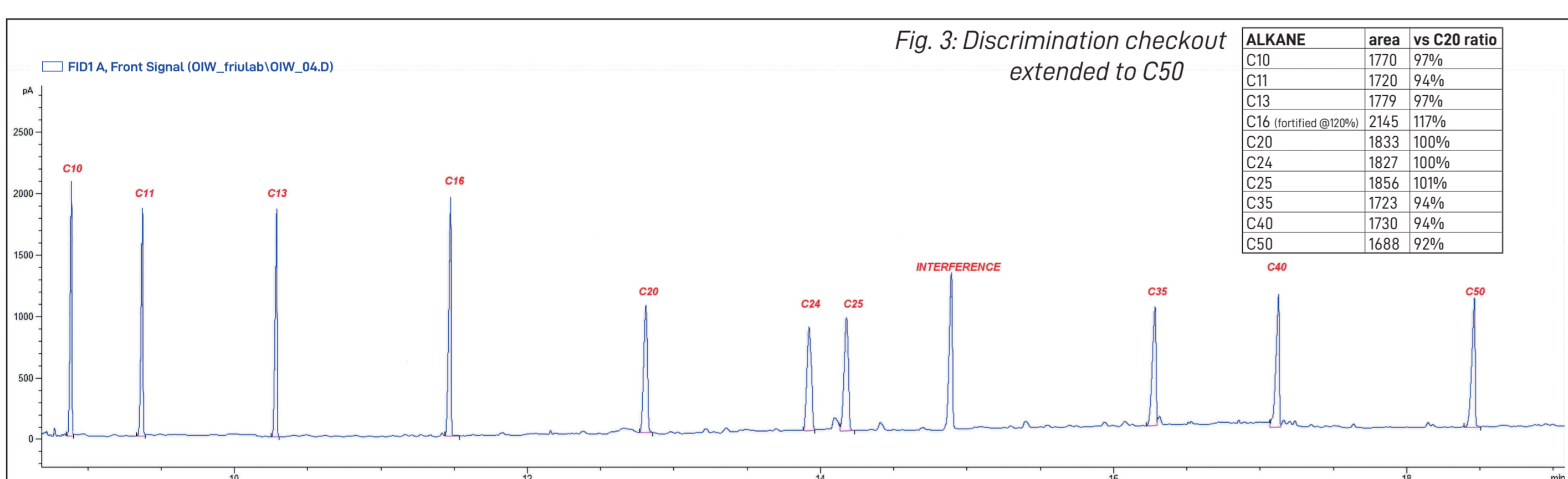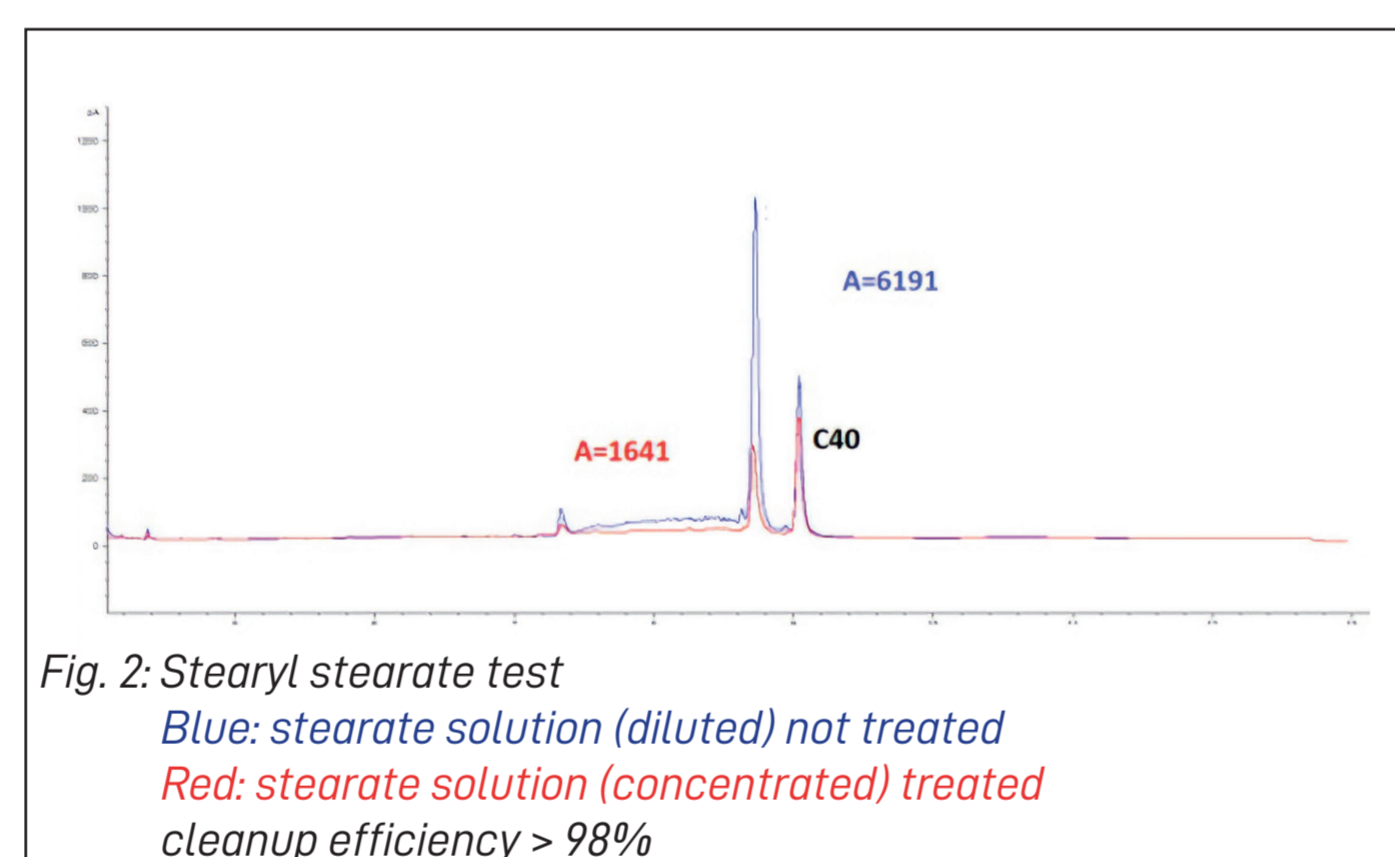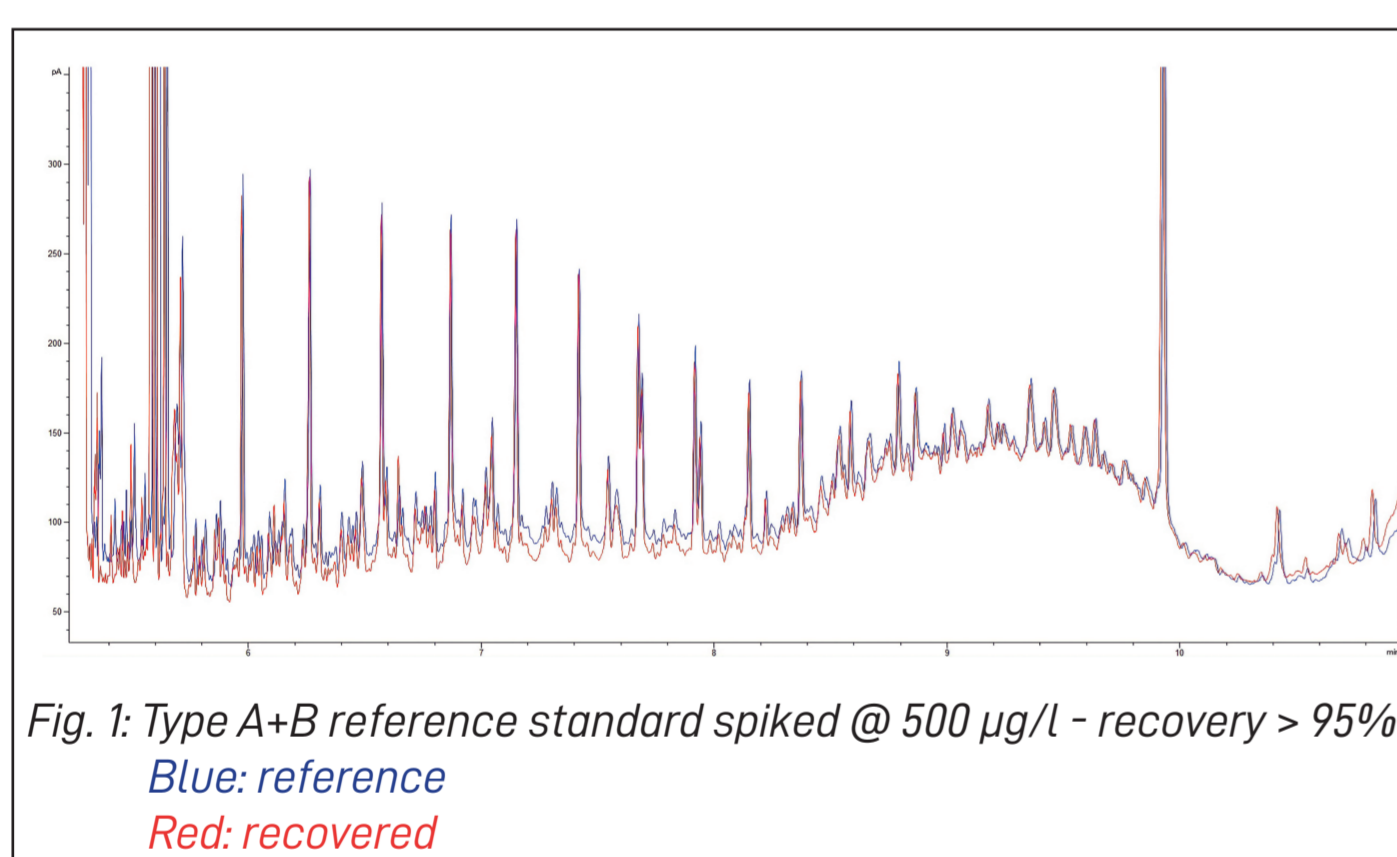
INTRODUCTION

According to official method 9377-2, the sample prep required for EPH involves a tedious and solvent/time consuming process. The complete automation proposed by SRA Instruments is not only completely unattended, thus allowing laboratory technicians to dedicate themselves to other more productive and rewarding tasks; it has also a real "green-chemistry" approach. Following table compares the differences between 9377-2 approach and SRA Instruments' solution, listing the various improvements in terms of solvent, consumables and glassware saving (tab. 1).

	9377-2 method	SRA method	amount saved
sample volume	900 ml	< 20 ml	> 98%
solvent volume	< 50 ml	< 2.0 ml	> 95%
florisil amount	2.0 g	200 mg	90%
sodium sulphate amount	2.0 g	200 mg	90%
needed glassware	separating funnel test tube mearuring cylinder flask, funnel, etc.	none	no needs at all
laboratory additional devices	rotovapor nitrogen flow evaporator	none	no needs at all

METHOD PERFORMANCE

Obviously, the development of a new analytical approach must at least preserve, and hopefully improve, the performance of the reference method. To this end, every single requirement of 9377-2 has been verified, as highlighted in the following figures:

Fig. 1: Type A+B reference standard spiked @ 500 µg/l - recovery > 95%
Blue: reference
Red: recovered

Fig. 2: Stearyl stearate test
Blue: stearate solution (diluted) not treated
Red: stearate solution (concentrated) treated
cleanup efficiency > 98%

Fig. 3: Discrimination checkout extended to C50

ALKANE	area	vs C20 ratio
C10	1770	97%
C11	1720	94%
C13	1779	97%
C16 (fortified @20%)	2145	117%
C20	1833	100%
C24	1827	100%
C25	1856	101%
C35	1723	94%
C40	1730	94%
C50	1688	92%

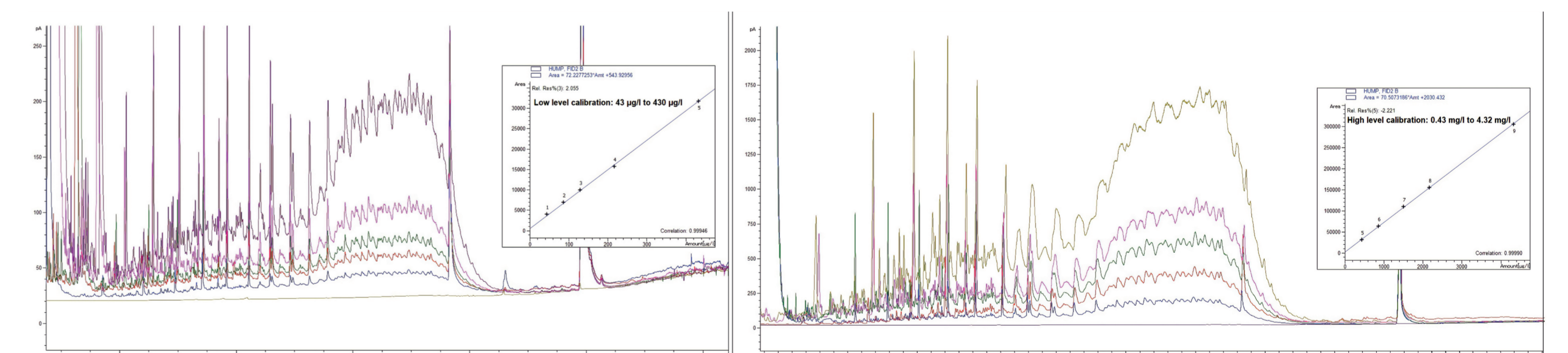Fig. 4: Red: LOQ recovered (43 µg/l)
Blue: Blank Run

SYSTEM FEATURES

The analytical platform includes several devices designed to avoid operational problems as syloxanes contamination (the automatic decapper ① allows to never pierce any vial septa), emulsions (4000 rpm centrifugation ② leads to a perfect phase separation), poor extractive power (the implementation of an high efficiency extractor – Gerstel QuickMIX ③ – assures great recovery in few minutes), and cross contamination (fast wash station ④ aimed to deliver rapidly and effectively the selected amount of fresh solvent). The prep-ahead function included in Maestro Software makes possible to overlap the analytical run and the preparation of the subsequent sample, leading to three EPH analyses per hour. If VPH quantitation is also needed, two hours are enough to get three samples completely processed without any attendance.

MATRIX CALIBRATION

Because of the efficiency of the entire process, the calibration was obtained directly in several matrices (tap water, surface water, groundwater), with excellent and comparable results. In following *Figure 5*, one of them is shown. The two calibration are coming from a unique sample-prep sequence, which is cut in two calibration intervals at low and high level.

COMPLETE HYDROCARBON OIL INDEX ANALYSIS

A second channel added to the Gas-chromatograph allows to perform, in the same sequence and without operator supervision, also the VPH analysis via HS. Whether the multistandard "VPH Atlantic" or "GRO" criterion is used, the system is able to comfortably reach 50 µg/l as LOQ.

SOIL SUITABILITY

By means of the implementation of a sonication device, the sample preparation becomes also suitable for soil analysis, maintaining the advantages of the "scale-down" approach, using less than 4 ml of solvent per sample and not requiring for any evaporation process.

CONCLUSIONS

The Oil In Water analyzer (OIW) proposed by SRA is a powerful platform aimed to eliminate any manual sample treatment, assuring at the same time high level of reliability in terms of productivity and data accuracy. The economic savings in terms of solvent (supply and disposal), consumables and time, necessary for the sample-prep itself and for the reconditioning of the glassware, is another point in favor of the transition to robotic automation.

REFERENCES

[1] ISO 9377-2:2000. Water quality — Determination of hydrocarbon oil index — Part 2: Method using solvent extraction and gas chromatography.

[2] Grob, K. (1987). On-column injection in capillary gas chromatography: Basic technique, retention gaps, solvent effects. Hüthig Verlag Heidelberg. ISBN 3-7785- 1551-9.

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