Chromatography Notes No AS2

The Anatune TPH-1 Analyser for the Automated Sample Preparation and Analysis of Total Petroleum Hydrocarbons in River and Waste Waters

John Fardon, National Laboratory Service, Environment Agency, Leeds, UK
Diane Nicholas, Anatune Ltd., Hardwick, Cambridgeshire, UK

Introduction

The current, widely used method for the sample preparation and analysis of Total Petroleum Hydrocarbons (TPHs) in surface waters and effluents involves the liquid-liquid extraction of a 1 L water sample with 25 mL carbon tetrachloride or other freons and analysis by FTIR. Carbon tetrachloride and freons are ozone-depleting chemicals, the use of which is banned from September 2001 in agreement with the Montreal protocol. The alternative and short-term solution to carbon tetrachloride, and other freons, is perchloroethylene. This reagent is toxic and has health risks, being a possible carcinogen and teratogen, but it also contains hydrocarbon impurities leading to an increase in background and hence raising the detection limits. There is a demand to reduce the use of chlorinated solvents. Therefore, a method is needed which uses a less harmful and purer extraction solvent, decreases the volume of solvent used per sample and if possible automates the sample preparation method.

An automated sample preparation and analysis method using the Focus robotic sample processor-LVI-GC-FID has been developed closely following the European standard method for the determination of hydrocarbon oil index in water, method ISO/DIS 9377-4. The main differences between that method and the Focus method is that the ISO/DIS method extracts 900 mL of sample with 50 mL of the extracting reagent and uses manual extraction, whereas the Focus method is automated and uses only 15 mL sample and 1.75 mL extracting reagent. Hence, any health hazards relating to the extracting reagent are greatly decreased through automation and the reduction in volume used per sample.

The method is suitable for the analysis of surface, waste water and water from sewage treatment plants and allows the determination of TPHs between n-decane and n-tetracontane down to 0.1 mg/L.

Instrumentation

Anatune TPH-1 Analyser comprising of:

- ATASGL Focus Robotic Sample Processor
- ATASGL Optic 2-200 Programmable Injector
- Agilent 6890 GC with FID
- Agilent ChemStation

The Focus is software controlled and uses magnets to transport the vials between the sample tray and the agitator. It prepares the next sample for analysis while the previous sample is being analysed by LVI-GC-FID, therefore the sample throughput is high with the combined sample preparation and analysis rate of more than two samples per hour and a sample tray with 25 positions, although this can be upgraded to 49 positions.

Method

The sample preparation method using the Focus is a multi-step method, as shown in Figure 1.

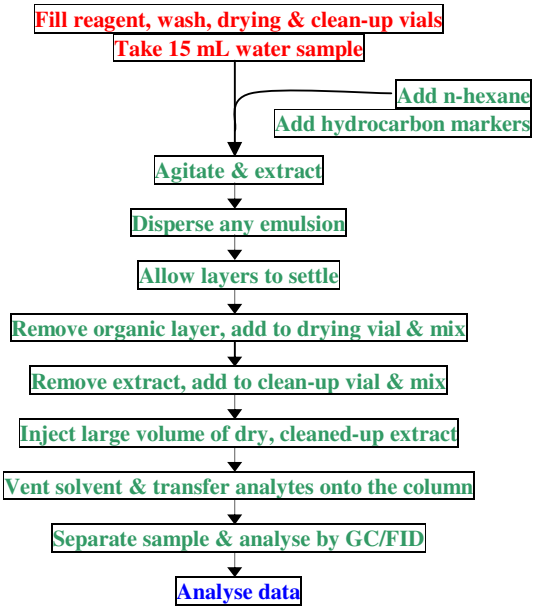

***Figure 1**: Overview of the TPH method*

The only manual part of the method is acidification of the water sample and the preparation of the reagents used. The Focus adds the extraction reagent containing the hydrocarbon markers, n-decane and n-tetracontane, to the sample vial. It places it in the agitator to perform the liquid-liquid extraction. After breaking any emulsion formed the Focus transfers a portion of the extract to the drying vial and mixes it to remove any water, then transfers a portion of this to the clean-up vial and mixes it to remove any polar compounds. Finally a large volume injection is made of the extract for analysis by GC/FID. Data is collected and analysed with the Agilent ChemStation.

A very important part of the method is the use of the correct liner, septa and reagents, these are all specified in the TPH manual. Also detailed are methods to reduce and break any emulsions formed, perform system suitability checks, reagent

checks, column compensation runs and guidelines for the set-up and maintenance of the whole TPH system.

Results

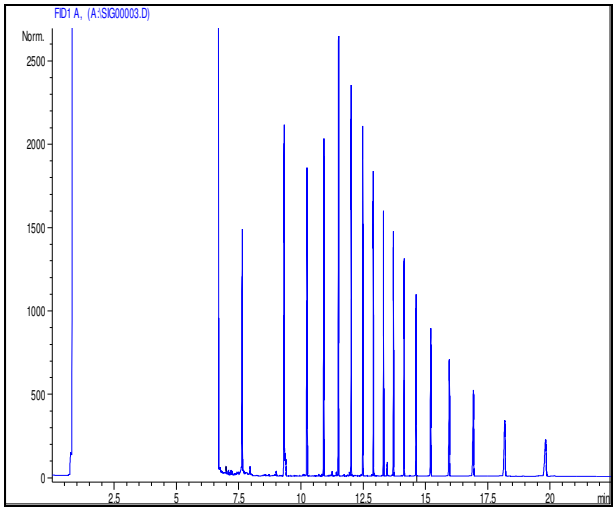

***Figure 2**: System suitability check: Large volume injection of 1 ppm Florida mix*

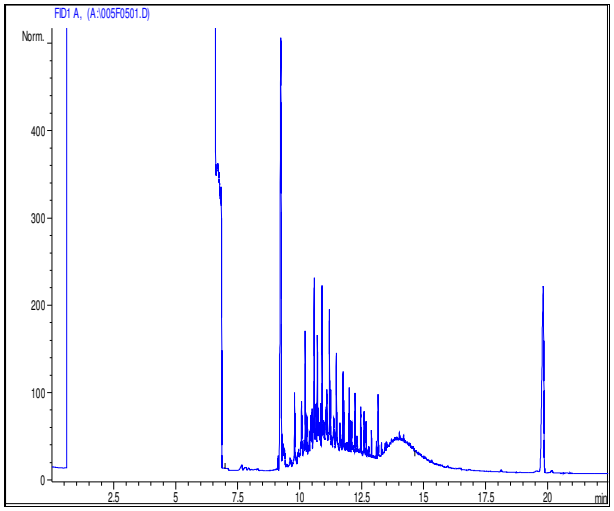

***Figure 3:** Extraction of a 2 ppm (high) standard of diesel + lubricating oil, showing n-decane and n-tetracontane hydrocarbon markers*

Performance Data

Table 1: Milli-Q Water

Spike level (mg/L):	**0.5**	**1.0**	**2.0**
%RSD:	12.72	13.4	9.3
LOD (mg/L):	0.0737		

Table 2: River Ouse Water

Spike level (mg/L):	**0.5**	**1.5**
%RSD:	14.3	7.66
% Rec:	104.36	99.88
LOD (mg/L):	0.1143	

Table 3: Final Effluent

Spike level (mg/L):	**0.5**	**1.5**
%RSD:	13.6	15.2
% Rec:	100.57	101.5
LOD (mg/L):	0.1215	

The relative standard deviation requirement for an organic method is 15%.

Calibration

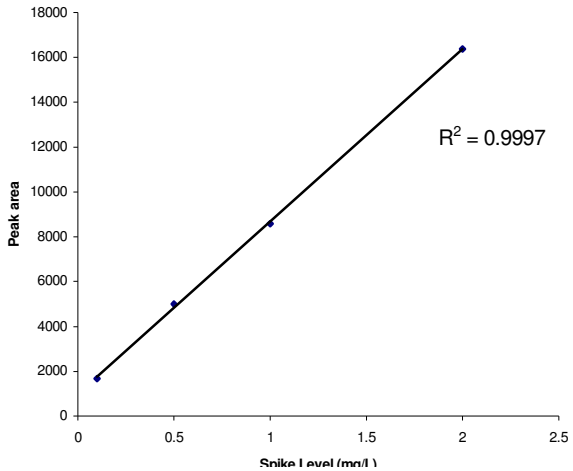

***Figure 4:** Calibration line of extracted diesel and lubricating oil*

Conclusions

The development of a combined system for sample preparation and analysis increases sample throughput and hence decreases the analysis cost per sample. The reduction in operator interaction as well as the reduction in volumes of reagents used per sample improves safety in the lab as well as reduces the costs of reagents and other consumables. The reduction in volume of the sample analysed reduces the sample size collected in the field and reduces costs in transportation to the lab for analysis.

The automated sample preparation and analysis of TPHs in river and waste-waters is a low cost, efficient method and simple to use, it is now commonly available as the Anatune TPH-1 Analyser.

Acknowledgements

We would like to thank Alan Wainright from the National Laboratory Service, EA Leeds for all the hard-work and effort in the development and implementation of this application, Tony Holland, TES Bretby for his support and encouragement and Gareth Roberts from Agilent Technologies for his advice.

Anatune Ltd, Broadway House, 149-151 St Neots Road, Hardwick, Cambridge, CB3 7QJ, UK
Tel: +44 (0) 1954 212909 Fax: +44 (0) 1954 212908 Email: info@anatune.co.uk Internet: www.anatune.co.uk