

Determination of TPH in Water using SPE-DEX[®] and LVI-GC-FID

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Introduction

Commercial pressures placed upon environmental testing laboratories drives the industry towards increases in sample throughput capacity, shorter sample turnaround times and achieving more reproducible results, which more precisely indicate the level, if any, of contamination present. Concurrently, the usage of, and exposure to, organic solvents by laboratory personnel is being increasingly regulated. Technology that both expedites sample analysis and also reduces hazards to either the environment and/or health has yet to realise its full potential.

Determination of Total Petroleum Hydrocarbons (TPH) in aqueous samples is an analysis conducted in many environmental testing laboratories. Traditional methodologies typically involve manual liquid-liquid extraction (LLE) of the water samples with an immiscible solvent, such as n-hexane or dichloromethane; subsequently, the extract is dried using specially prepared anhydrous sodium sulphate, concentrated through an evaporation step, which may incorporate a solvent exchange, and analysed using conventional split/splitless GC-FID equipment. Within contemporary environmental testing laboratories the use of solid-phase extraction (SPE) technology, as an alternative to LLE, is not widespread.

Within this technical note, Anatune Ltd. presents a novel approach to the analysis of TPH in water that utilises a rational combination of newly-developed technology: automated SPE;

rapid extract drying using a Gore-Tex membrane; and analysis by LVI-GC-FID. The approach affords laboratories an immediate reduction in the amount of labour required for the extraction of samples and, depending upon the existing methodology being used, has the potential to decrease sample turnaround timescales considerably. Also, whilst automation of the extraction process minimises the amount of solvent handling and usage required within the laboratory, the combination described removes either the need for a chemical drying agent or apparatus for evaporation.

Horizon Technology SPE-DEX- 4790 units are programmable multipurpose automated SPE systems, capable of processing aqueous samples directly from their original containers. Once initiated, each 4790 unit sequentially delivers all the necessary solvents to precondition the sorbent material within the SPE disk, passes the water sample through the disk and, after a preset air-dry time, extracts the sorbed analytes from the disk into a collection vessel using the required amounts of solvents.

Introduction of a chemical drying agent to remove residual water from the hydrocarbon-containing extracts can have a deleterious effect upon subsequent quantitative analysis. The

solvent drying system (SDS-100) manufactured by Horizon

Technology, which incorporates a proprietary Gore-Tex hydrophobic membrane marketed as DryDisk[™], has been specifically designed to remove residual water from organic solvent extractions physically, not chemically. DryDisk[™] technology selectively excludes water and, being chemically inert, does not retain analytes. Removal of residual water in this way takes a fraction of the time that chemical drying can, and eliminates the great care that must be taken in the preparation, storage and handling of hygroscopic compounds, such as anhydrous sodium sulphate.

A versatile Optic 3 High Performance Injector is employed to introduce a large volume (50 µL) of the dried n-hexane extract into a Agilent 5890N GC-FID installed with a HP5 column. With the initial conditions set near to ambient temperature, hydrocarbons within the C₁₀₋₄₀ boiling-point range are quantifiable. This custom configured system has been used to quantitatively analyse a 1:1 mixture of diesel and mineral oil spiked into water at a TPH-concentration of 100-1000 µg/L; a summary of the results obtained is presented here.

Instrumentation

- Horizon Technology SPE-DEX- 4790
- BAKERBOND[™] Speedisk[®] C18 50 mm
- Horizon Technology SDS-100 & DryDisk[™]
- ATAS Optic 3 High Performance Injector
- Agilent 6890N Gas Chromatograph with FID

TPH Standard Mix:

A TPH Standard Mix (250 mg/mL), consisting of a 1:1 w:w mixture of neat Diesel and Mineral Oil (Thames Restek) in 95 % n-hexane (J. T. Baker, residue analysis grade), was prepared and 0.5-4 µL of this standard used to spike 1-L samples of tap water. The chromatogram Figure 1b shows a typical low-level spike recovery.

Calibration standards, subsequently used to quantify the percentage recoveries obtained, were prepared volumetrically from the TPH Standard Mix solution. The top chromatogram in Figure 1a is that corresponding to a low-level standard.

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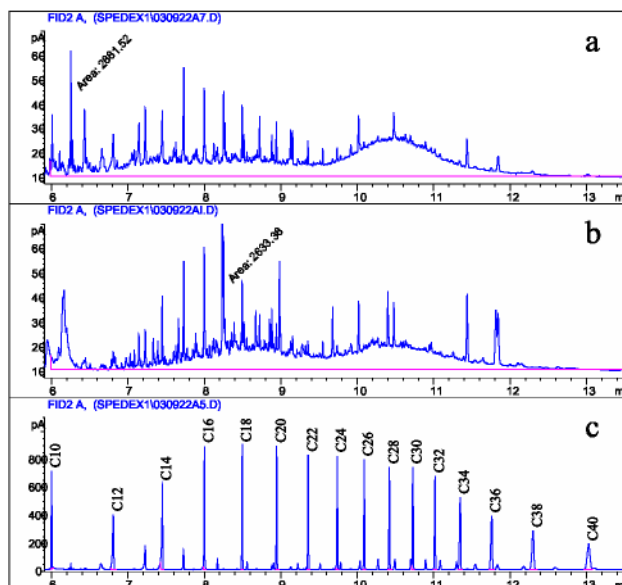


Figure 1: LVI-GC-FID chromatograms – (a) 5 µg/mL Standard; (b) 125 µg/L TPH extract; and (c) 1 µg/mL n-Alkane Florida Mix. The top pair of chromatograms has the same amount of TPH present in the 50-µL injection volumes analysed.

Florida Mix:

Retention-time drift and injector discrimination effects were monitored by the analysis of a Florida Mix Standard (1 µg/mL individual n-alkane concentration) prior to each batch of samples, which ensured that the LVI parameters remained unchanged. The bottommost chromatogram in Figure 1c is representative of those obtained under the LVI-GC-FID conditions described here.

Method

The stages involved in the determination of the total concentration of hydrocarbons within a water sample are summarised below: -

- Automated SPE-DEX controller unit programmed
- *Speedisk*® C18 preconditioned using a purge method
- Fully-automated solid-phase extraction of aqueous sample
- Water added to biphasic extracts to facilitate optimal solvent separation by DryDisk™
- Dried extracts quantitatively made up to 25 mL
- Large-volume injection used to introduce 50-µL aliquots of the extracts into the GC
- Quantification based upon external standard calibration

Automated Solid-Phase Extraction:

The automated solid-phase extraction units were operated in accordance with the manufacturer's instructions; hence, the SPE-DEX ~ controller was programmed with methods 1664.2 and 1664.9 prior to use. Each of the 2.5-L reservoir bottles was cleaned thoroughly and refilled with 500 mL of the appropriate analysis grade solvent. The extraction unit was fitted with an appropriate solid-phase extraction disk (BAKERBOND™

Speedisk® C18 50 mm) and, after being downloaded with method 1664.9 from the controller, purged in preparation for each extraction.

One-litre aliquots of tap water were spiked accurately with known amounts of the prepared TPH Standard Mix. Various spiked and blank samples were loaded onto the SPE-DEX ~4790 unit, reprogrammed with conditions for method 1664.2, and extracted. During the automated extraction process the system sequentially: pre-conditions the 50-mm hydrophobic disk, first with DCM and then methanol; subsequently, the sample is drawn through the sorbent material that is contained within the disk, facilitating the extraction of hydrocarbons from the aqueous matrix; and finally, after detecting the complete sample as having been extracted, analytes are eluted from the disk with a single acetone rinse and two rinses of n-hexane, the former being used to facilitate dissolution of the analytes from the solid-phase material by the latter.

Solvent Drying System:

For a Gore-Tex membrane to be able to dry an extract the solvent must be immiscible with water, sufficient to phase separate, otherwise the water-containing solvent can permeate the hydrophobic membrane. The extracts obtained using method 1664.2 on the SPE-DEX 4790 units are inherently biphasic and, despite phase separation having occurred within the extract, the water-content of the denser acetone rinse layer is too low to be retained by the PTFE-membrane. Accordingly, as biphasic extracts were obtained even with Air-Dry times that were indeterminately long (>5 mins), the duration of this stage of the automated extraction process was set at 0 sec and an alternative, if at first sight somewhat surprising, method for facilitating removal of residual water from the extract was devised.

Addition of 15 ml HPLC-quality water to the biphasic extract results in the dilution of the water-containing acetone layer and facilitates its separation from the hexane phase. However, to ensure that the separation is wholly effective, the dilution must be made prior to the extract being poured into the SDS-100 assembly. Otherwise, the amount of acetone that is present in

the bottom-layer of the extract renders the Gore-Tex membrane permeable to water. Following the addition of water, the extract can be transferred to the solvent drying system and, after tilting the whole assembly such that the water-hexane interface makes contact with the surface of the DryDisk™, the dried hexane extract can be separated and drawn into the collection vessel.

Quantitative Analysis:

Especially in the absence of either internal and/or surrogate compounds, quantitative transfer of the extract from the collection vial taken off the SPE-DEX-4790 unit to the 25-mL volumetric flask was essential. After having been accurately made up to the fixed 25-mL volume, a portion of the extract was vialled up suitably for analysis by fully-automated LVI-GC-FID.

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Results

In order to achieve a linear calibration across an appropriate range of hydrocarbon concentrations, each of the calibration standard solutions was prepared using volumetric glassware and Hamilton syringes. To further minimise errors, a limit of two serial dilutions of the TPH Standard Mix (250 mg/mL) was performed in the preparation of each calibration level. With sufficient precision, calibration data has been confirmed as being linear at least upto 25 mg/L (Figure 2). However, chromatographic carryover, corresponding to hydrocarbons with boiling-points equal to or greater than docosane (n-C₂₂), was observed following the injection of standards with TPH concentrations exceeding 2.5 mg/L. Hence, in order to maintain the lowest limit-of-detection (LOD) and calibration linearity, analytical blanks were analysed following samples anticipated to exceed this threshold amount of mineral oils.

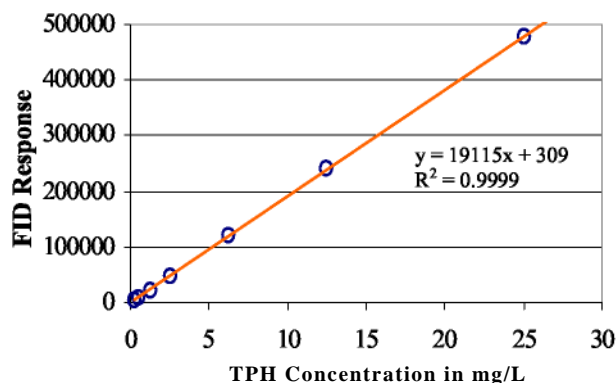


Figure 2: Linear calibration upto 25 mg/L – the TPH-concentration of the standards used were 0, 10, 20, 50, 100, 250, 500 & 1000 µg/mL, respectively.

Alternatively, Figure 3 shows a low-level calibration plot that covers the TPH-concentration range only as far as 1.25 mg/L. Comparison of the calculated slope with that obtained for the wider calibration range corroborates the need for care in using unweighted statistical processing, which does not take into account the greater variance that is associated with responses of larger magnitude. Unweighted linear regression analysis can adversely affect the balance that lies between lower detection limits and widening the linear dynamic range. After obtaining a linear calibration, Anatune Ltd. recommends that, rather than being solely reliant on the R²-value generated by the regression process, the quantification calculation be applied upon the responses of the standards used in its construct. This check ensures that concentrations encompassed by the working range are within industry-acceptable tolerances.

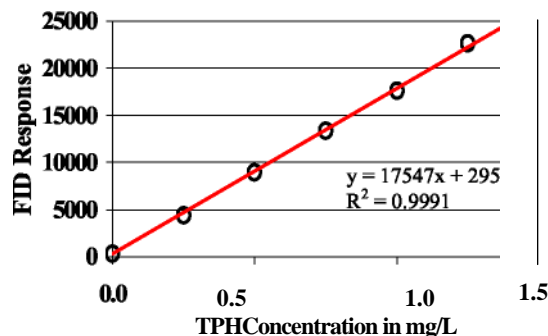


Figure 3: Low-level TPH calibration plot – standards with actual TPH-concentrations of 0, 10, 20, 30, 40 & 50 µg/mL were used to obtain this plot

Analysis of SPE n-hexane extracts obtained for TPH spikes in tap water was performed using a low-level calibration. The combination of BAKERBONDTM Speedisk[®] C18 and the SPE-DEX[®] 4790 extraction units was found to yield highly reproducible hydrocarbon recoveries. Percentage recoveries calculated for a series of ten 1-mg/L spikes are summarised in Table 1: -

Sample	Area	% Recovery
1	16997	95.15
2	15492	86.66
3	17822	99.80
4	15525	86.84
5	16498	92.33
6	17898	100.23
7	16131	90.26
8	16585	92.82
9	17391	97.37
10	13664	76.34
Mean (n = 10)	16400	91.78
Statistical Data	SD = 1282	RSD = 7.88

Table 1: Summary of the percentage recoveries obtained for tap water samples spiked to 1 mg/L TPH.

The middle chromatogram within Figure 1b is that of an extract spiked with a TPH-concentration of 0.125 mg/L, which shows quantitative recovery (>98 %) towards the lower end of the working range. Based upon preliminary data, not shown, an estimate of the TPH reporting limit for C₁₀₋₄₀ is 0.05 mg/L.

Conclusion

Extraction of aqueous samples using automated solid -phase extraction is an attractive alternative to conventional manual liquid-liquid extraction methodology. Once the reservoirs have been filled, the desired solvents are automatically dispensed by the SPE-DEX[®], thereby minimising the handling of these chemicals by laboratory technicians. As many as eight 4790 units, all of which can be operated from a single central controller module, can be simultaneously operated by one laboratory technician, which vastly increases the effective manpower of laboratory personnel.

Furthermore, the amount of benchspace required to accommodate a fully-functional eight-place extraction system manned by a single individual is considerably less than that required for four technicians conducting side-by-side LLE. Quantitative extraction by and subsequent recoveries of mineral oils from the *Speedisk*[®] was observed at TPH-concentrations as high as 5 mg/L without any further optimisation of method 1664.2, such as an additional n-hexane rinses or longer soak-times (data not shown).

Automation ensures a degree of extraction reproducibility that is unlikely to be obtainable manually, whether the existing methodology employed is LLE or SPE. The rapidity of analysis from sample to extract ensures that adaptation to an automated system is a highly cost effective solution for maintaining a high sample throughput. Moreover, sample turnaround time is shortened further by rapid residual water removal from the extract.

The water-containing sample extracts were dried using a Gore-Tex[™] membrane and not anhydrous sodium sulphate, which requires careful preparation and storage when used in the analysis of TPH; usage of the DryDisk[™] reduces the required usage of hazardous chemicals. Testing laboratories that utilise batch-manufactured compounds, such as drying agents, frequently monitor method blanks for background contributions attributable to contamination associated with the mechanical-processing of the chemical, which can adversely affect quantification of low-level concentrations of TPH. The solvent drying system, also developed by Horizon Technology and available through Anatune Ltd, is capable of rapid separation of macro- or trace-amounts of liquid-phase water from aqueous immiscible solvents. In this study the removal of water-containing acetone from the n-hexane extract was achieved through the addition of excess water to the biphasic extract.

In conjunction with LVI-GC-FID, the extraction of hydrocarbons from aqueous samples using SPE-DEX[®] 4790 units (Horizon Technology) fitted with BAKERBOND[™] *Speedisk*[®] C18 50-mm extraction disks (J. T. Baker) has been evaluated for the purposes of TPH analysis. Using the aforementioned extraction method, quantitative recoveries and good reproducibility were readily obtained for laboratory-fortified blanks with a TPH-concentration of 1 mg/L. The lack of any in-house facility to accurately concentrate n-hexane extracts necessitated the requirement to dilute the extracts upto 25-mL volume prior to GC analysis, which prevented analysis of considerably more dilute extracts. However, whilst concentration of extracts prior to chromatographic analysis is routine, omitting this step doubtlessly kept background interference from extraction cross-contamination to a minimum. Although not used in this evaluation, the introduction of an internal and, if desired, a surrogate standard to the extract and water sample respectively would facilitate continuous monitoring of the extraction and analysis of samples by this novel approach.

The small but measurable positive intercept of the linear calibration arises from the inherent contribution of the solvent to the FID response and the integration parameters used to quantify the C₁₀₋₄₀ area sum, which corroborated the need to include an analytical blank within the calibration table. Chromatograms typical of standards used to comprise such a table are shown in Figure 4. Method blanks were found not to contain significant amounts of

hydrocarbon above the levels present in the analytical blank (data not shown). A lack of weighting parameters within linear calibration parameters can adversely affect the accuracy of the low-level concentration range of the calibration, which may not be immediately obvious from the linear regression fit data. The magnitude of the error associated with the preparation of standards of increasing concentration can cause more pronounced skewing of the calibration than the correlation coefficient (R^2) suggests. The data presented here satisfactorily show the calibration as being linear over a useable working range and provide evidence that this approach is capable of quantification down to the ever-lower levels required within the environmental testing industry.

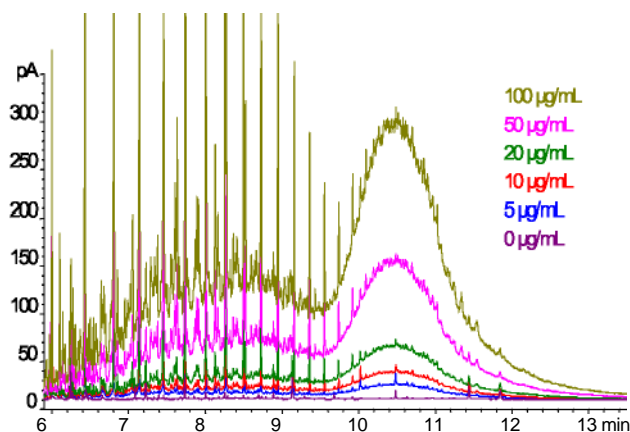


Figure 4: LVI-GC-FID chromatograms of standards – corresponding to 0.000, 0.125, 0.250, 0.500, 1.000 & 2.000 mg of TPH in 1-L water samples.

Consequently, the use of the SPE-DEX[®] and DryDisk[™] for the solid-phase extraction of hydrocarbons has been shown to be of use to commercially-competitive laboratories within the environmental testing industry. The combining of newly available technology to achieve faster and more reliable sample extraction that leads to better chromatography is demonstrated by the coupling of automated SPE with well-established LVI-GC-FID technology, such as that championed by Anatune Ltd.

Acknowledgements

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Related-Information & References

- Regression & Calibration, VAM Bulletin No. 18, Spring 1998, Pages 18-21
- Contact us for a list of related application notes