Developing Improved Lab Analysis Methods to Detect Total Petroleum Hydrocarbons (TPH)

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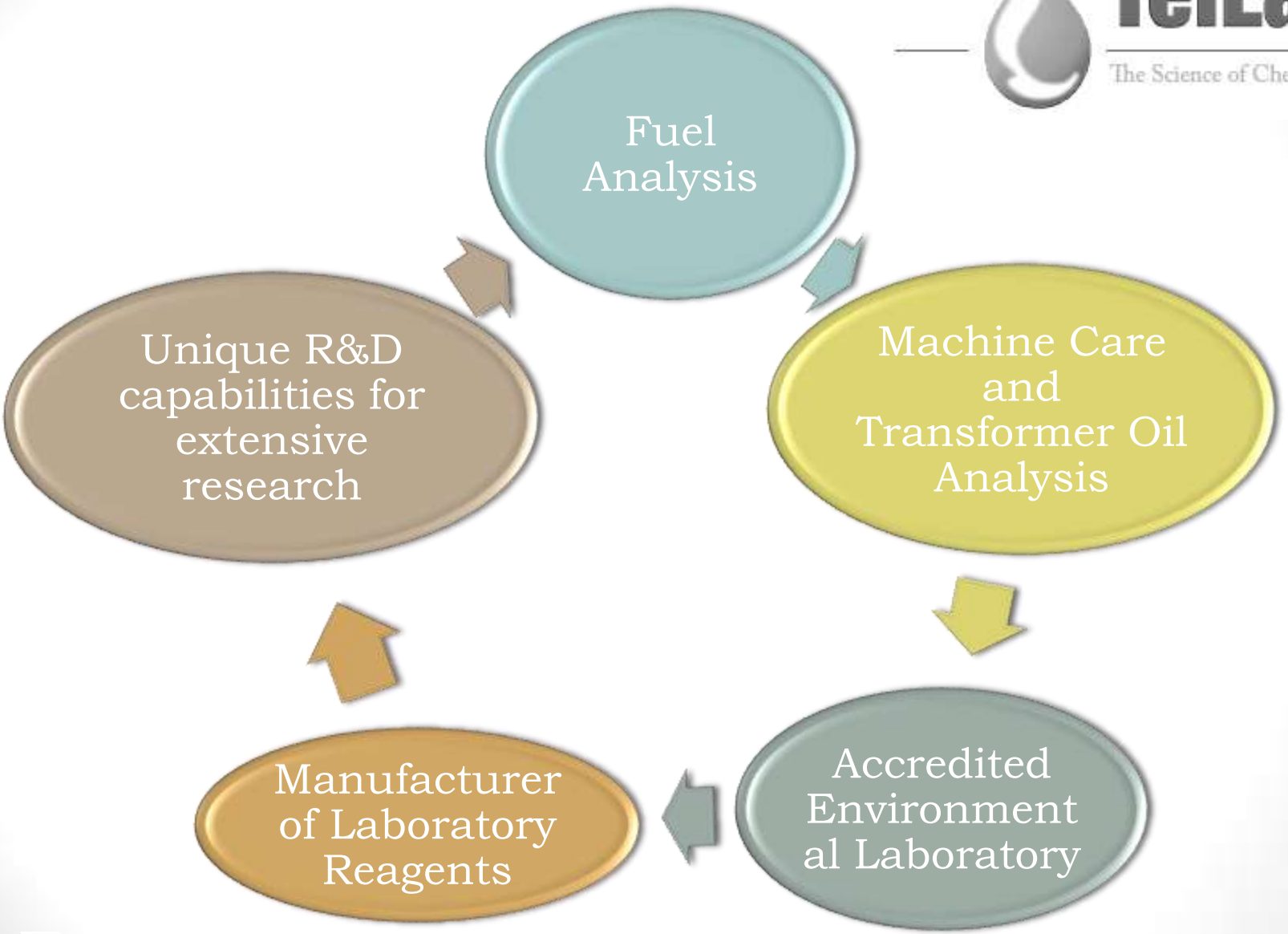
Topics of presentation

- Introduction
- Aim of the Project
- Project Outline
- Results and Discussion
- Conclusions

Company Overview

TelLab
The Science of Chemistry



R&D Department

TellLab
The Science of Chemistry

TelLab has an active Research & Development programme which covers projects in all areas of the company's activities.

Latest development of a range of different products

aqua monitrix™
Real time remote monitoring of water quality

Universal Absorbent for oil and chemicals

Pharma Test Kits
according to pharmacopoeia guidelines

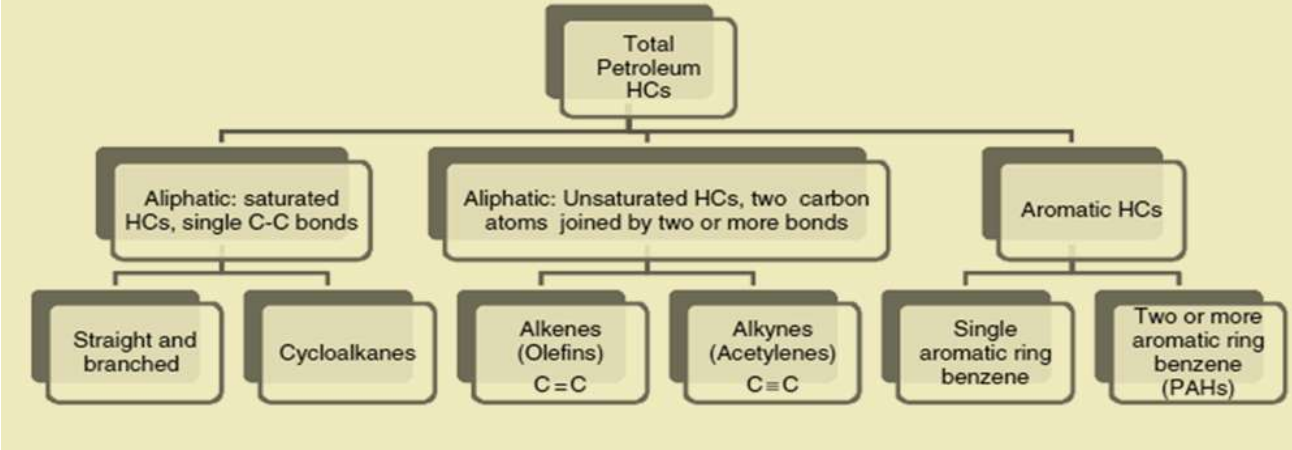
Global supplier

'Certificate in Excellence of Innovation' award in 2012 by InterTrade Ireland

What is Petroleum and how we can define Petroleum Hydrocarbons?

TPH: All Aromatic Hydrocarbon compounds which contain between 10 and 40 carbon atoms are associated with the release of a petroleum product to the environment

- C6 – C10 (volatile aromatic and aliphatic hydrocarbons)
- C8 – C30 (aliphatic and aromatic hydrocarbons including the 16 EPA PAHs)
- C10 – C40 (contains some of the lubricating oil fraction)



Current trends in TPH analysis

Various methods

- Gravimetric
- IR (Infrared spectroscopy)
- UVF (Ultraviolet fluorescence)
- GC/FID
- GC/MS

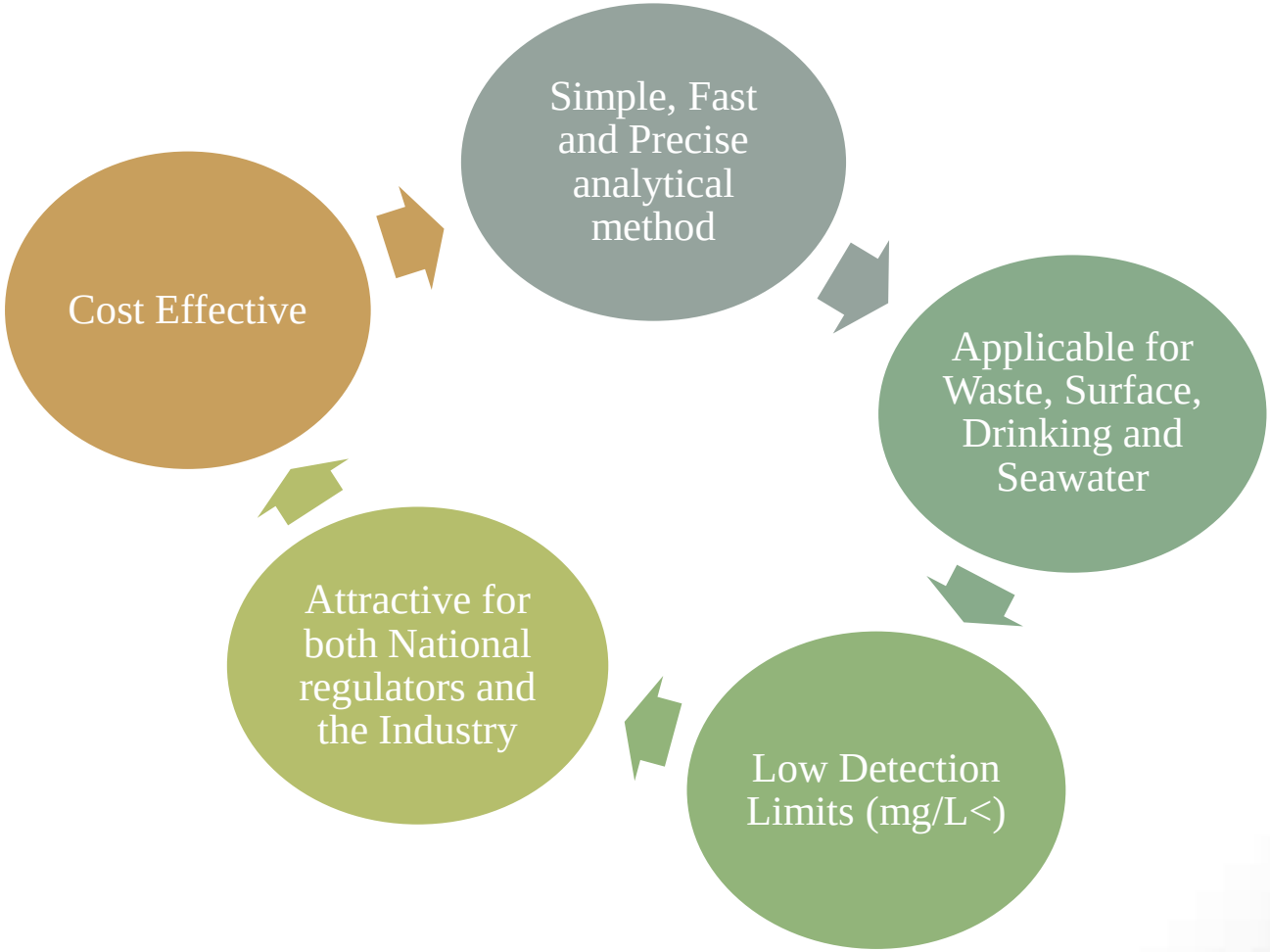
Limitations of the TPH analysis

- Lack of standardisation
- No comparable results between laboratories
- Limited scope of the existing methods
- Detection limits of the current methodologies don’t reach the national legislation limit

- Infrared and gravimetric methods are currently decreasing due to the nonspecificity of these methods and their inability to provide any information on TPH identification and potential risk.
- The primary advantage of GC-based methods is that they provide information about the type of petroleum in the sample in addition to measuring the amount.

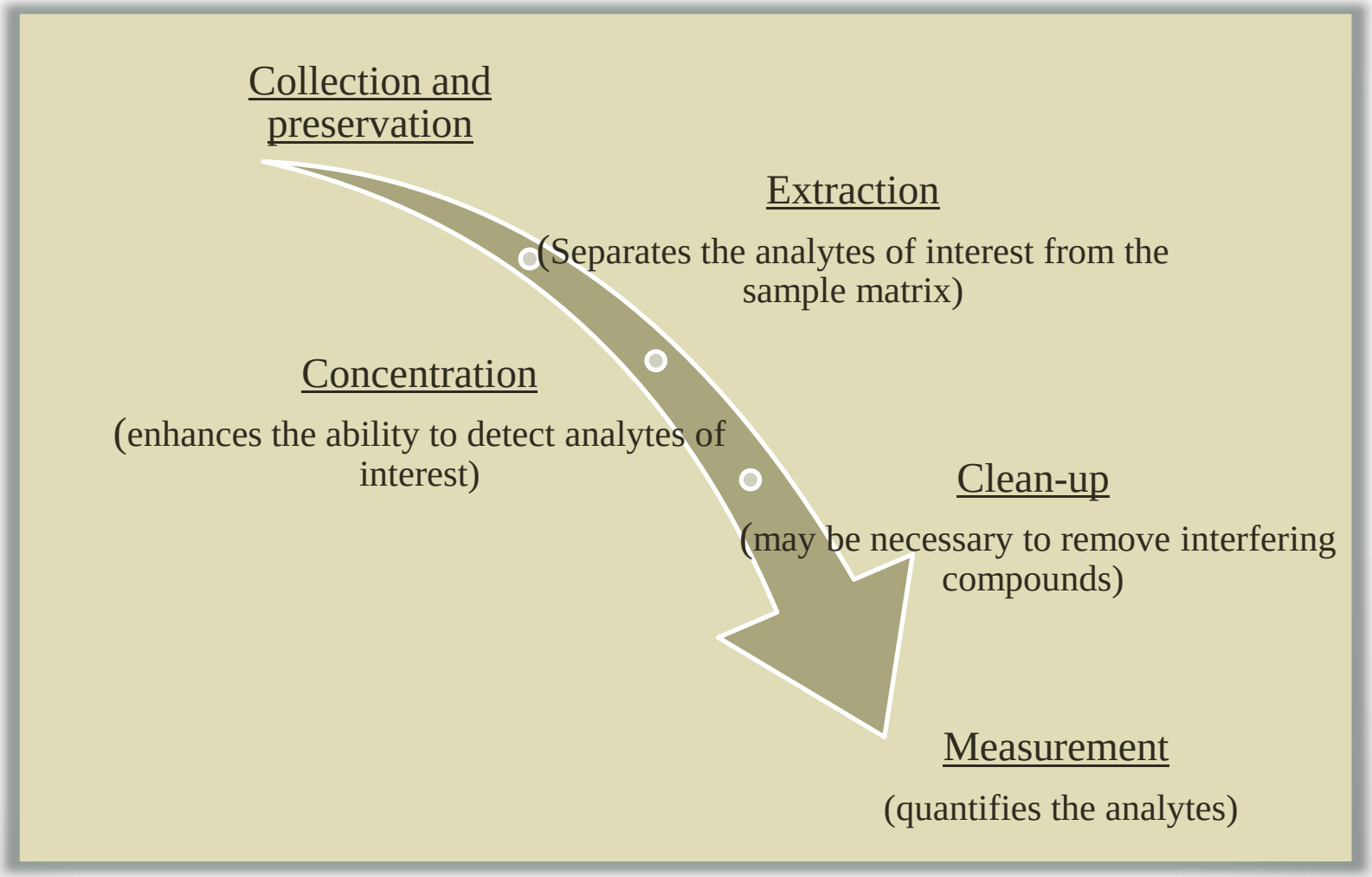
Objectives

Develop a Standard Method for TPH Analysis to be used in the Environmental Laboratories and Industry



Analytical plan

A typical analytical method proceeds with the following steps:



*Each step affects the final result, and a basic understanding of the steps is vital to data interpretation.

Project Summary

- Step 1. GC-FID optimization (capillary column selection, temperature program, use of pre-column, flow rate, injection volume, carryover)
- Step 2. Liquid-liquid and Solid-phase extraction optimization (selection criteria for solvents, pH effect, volume of extraction solvent, use of surrogate standards, clean-up (Silica gel, Alumina, Florisil, Sodium sulfate)
- Step 3. Interpretation of the results (matrix interference, weathering)

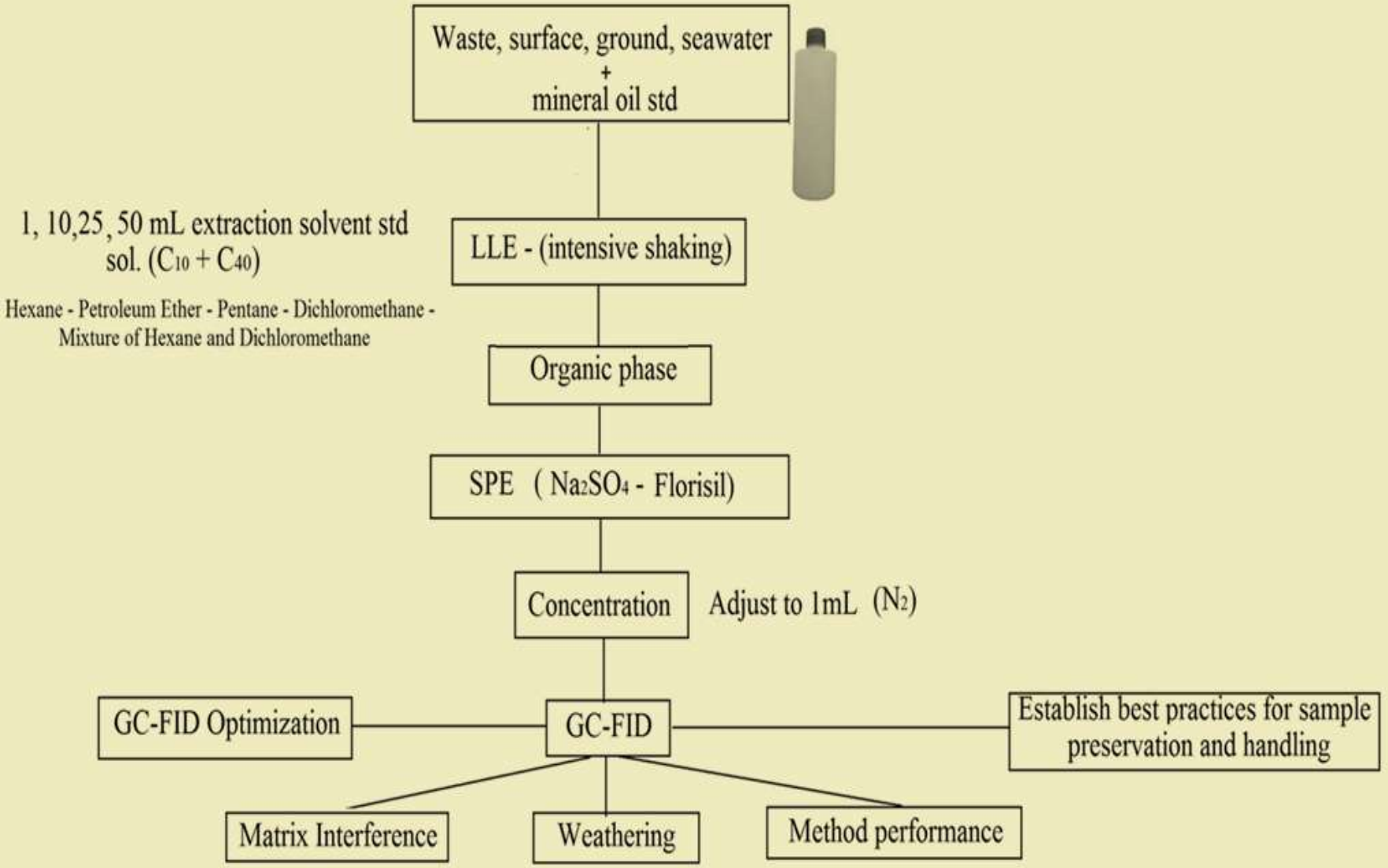
- Establish best practice guidelines for sample collection, preservation and handling
- Sampling strategy
- Application to real samples
- Identify environmental concentration levels for all types of water (waste, ground, surface and seawater)

- Linearity (Calibration equations, coefficients of correlation)
- Accuracy (recoveries at low, medium and high concentration levels)
- Limits of Detection (LOD)
- Limits of Quantitation (LOQ)
- Precision (Intra-day, Inter-day)
- Robustness
- Repeatability
- Reproducibility

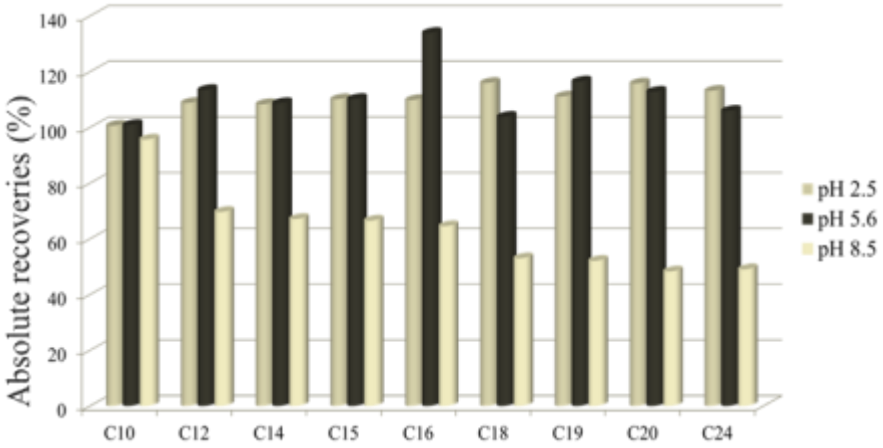
- Objective and Scope of the method
- Summary of methodology
- Detection limits
- Working range
- Description of the interferences

RESULTS AND DISCUSSION

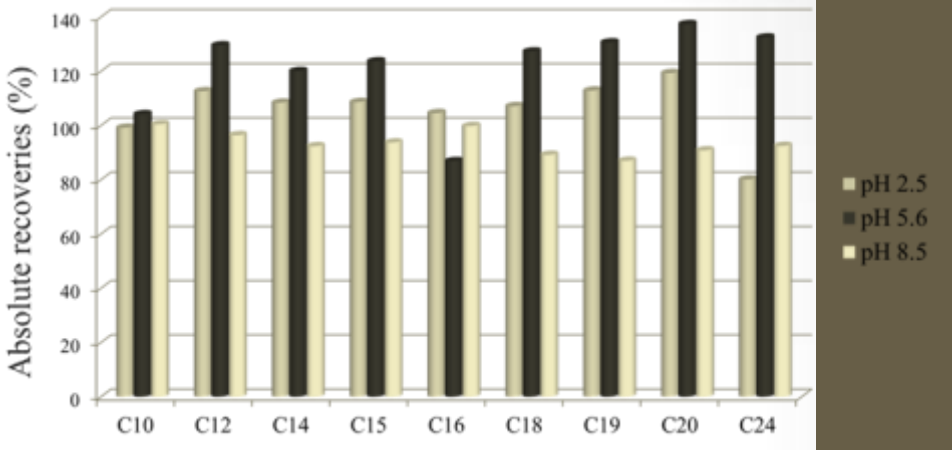
Method Development



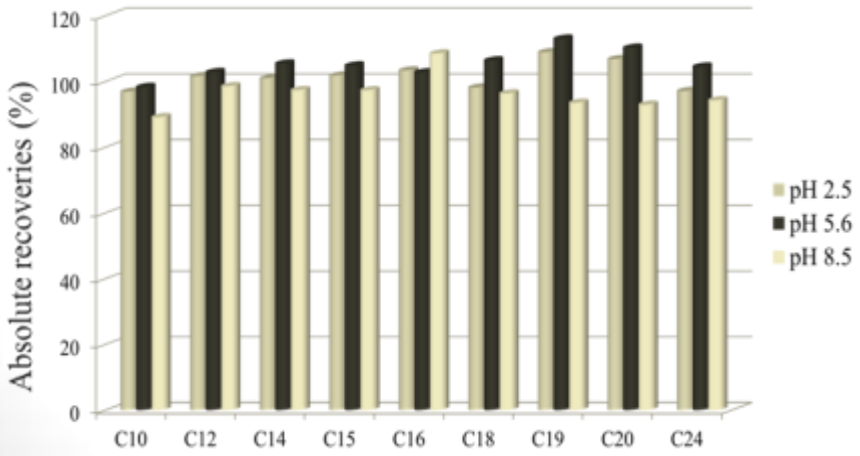
Extraction efficiency of different organic solvents at three pH levels



Extraction efficiency of Hexane



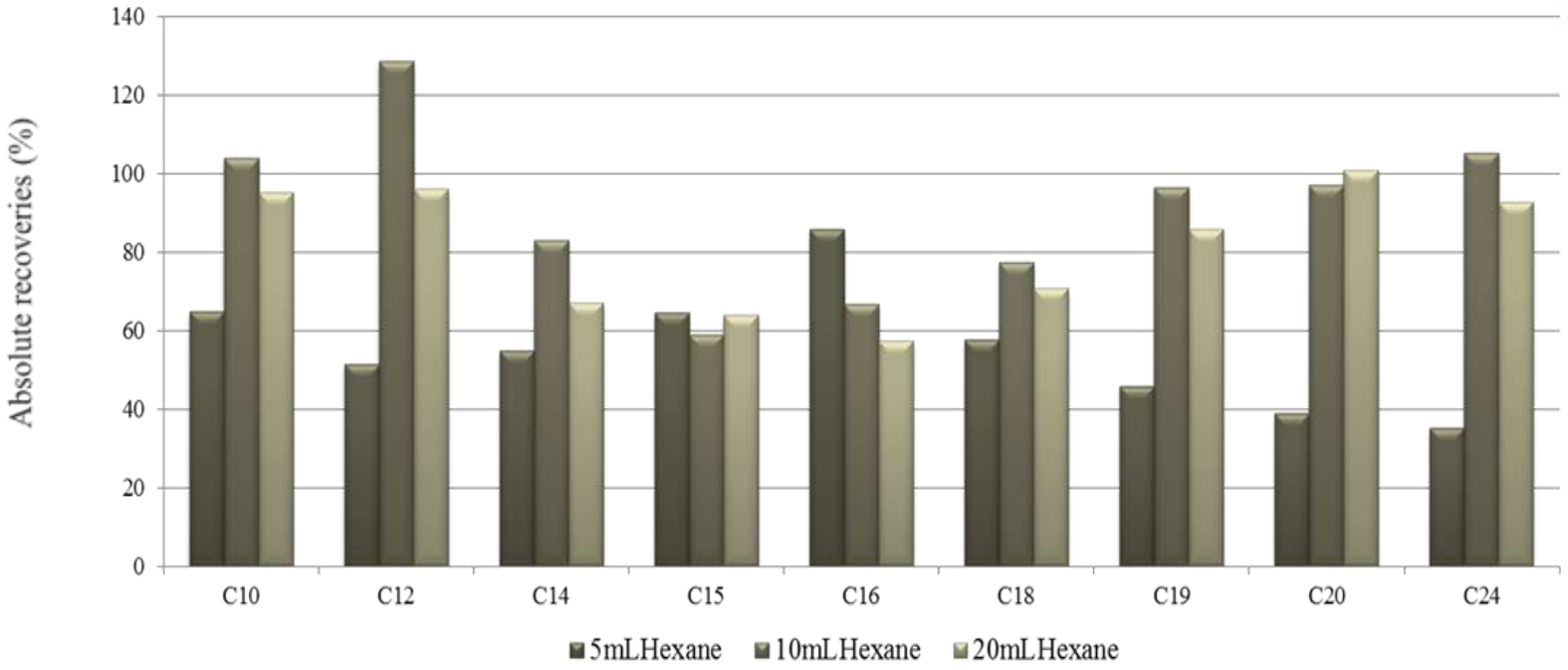
Extraction efficiency of Pentane



Extraction efficiency of Petroleum ether

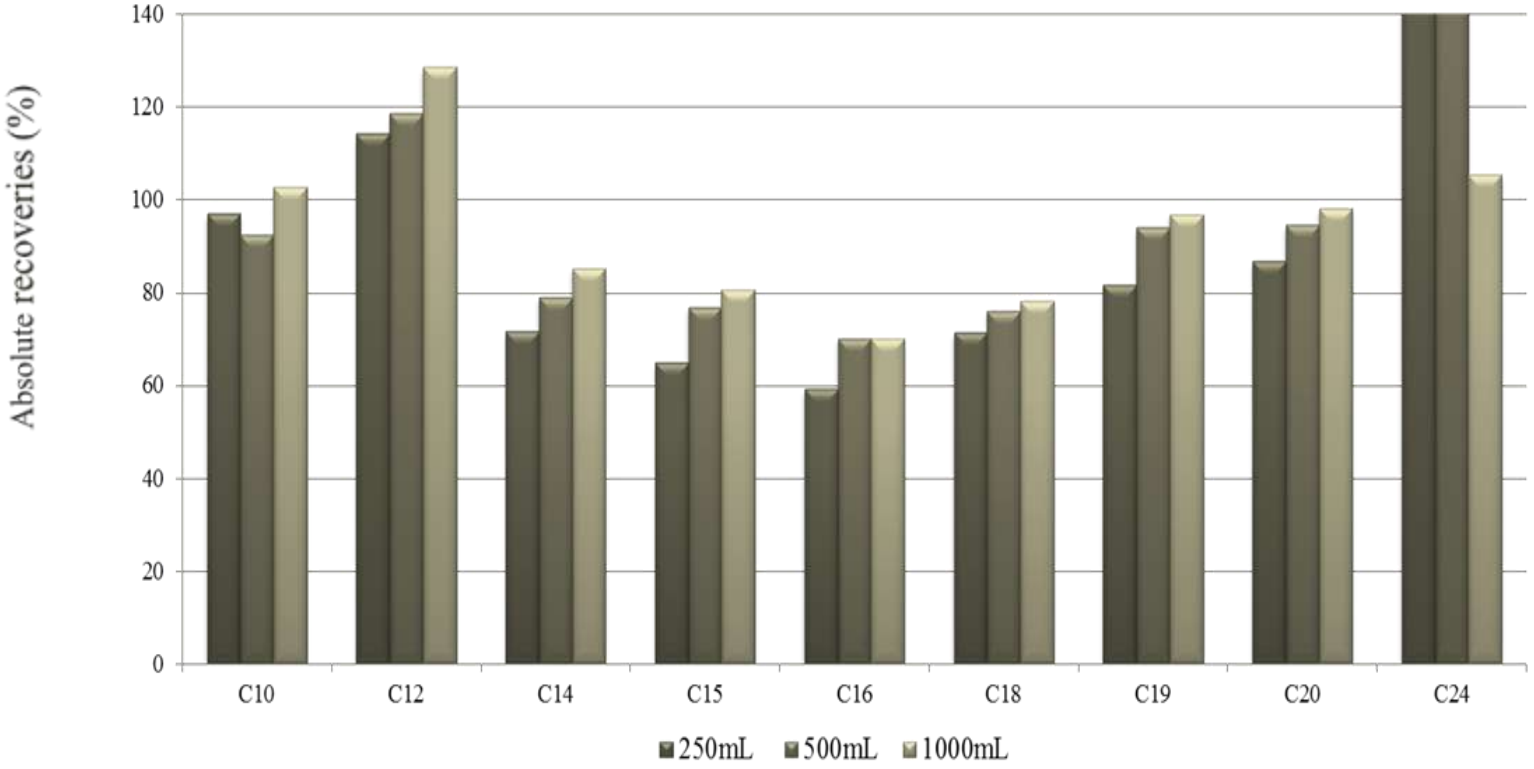
- Extraction with hexane at 8.5 pH level resulted in low absolute recoveries, which were ranged between 43 and 69%.
- Hexane resulted in sufficient RSDs (<6%) at pH 2.5 and taking into account its better chromatographic resolution, it was chosen for the isolation of the target compounds from water samples.

Volume of extraction solvent tested



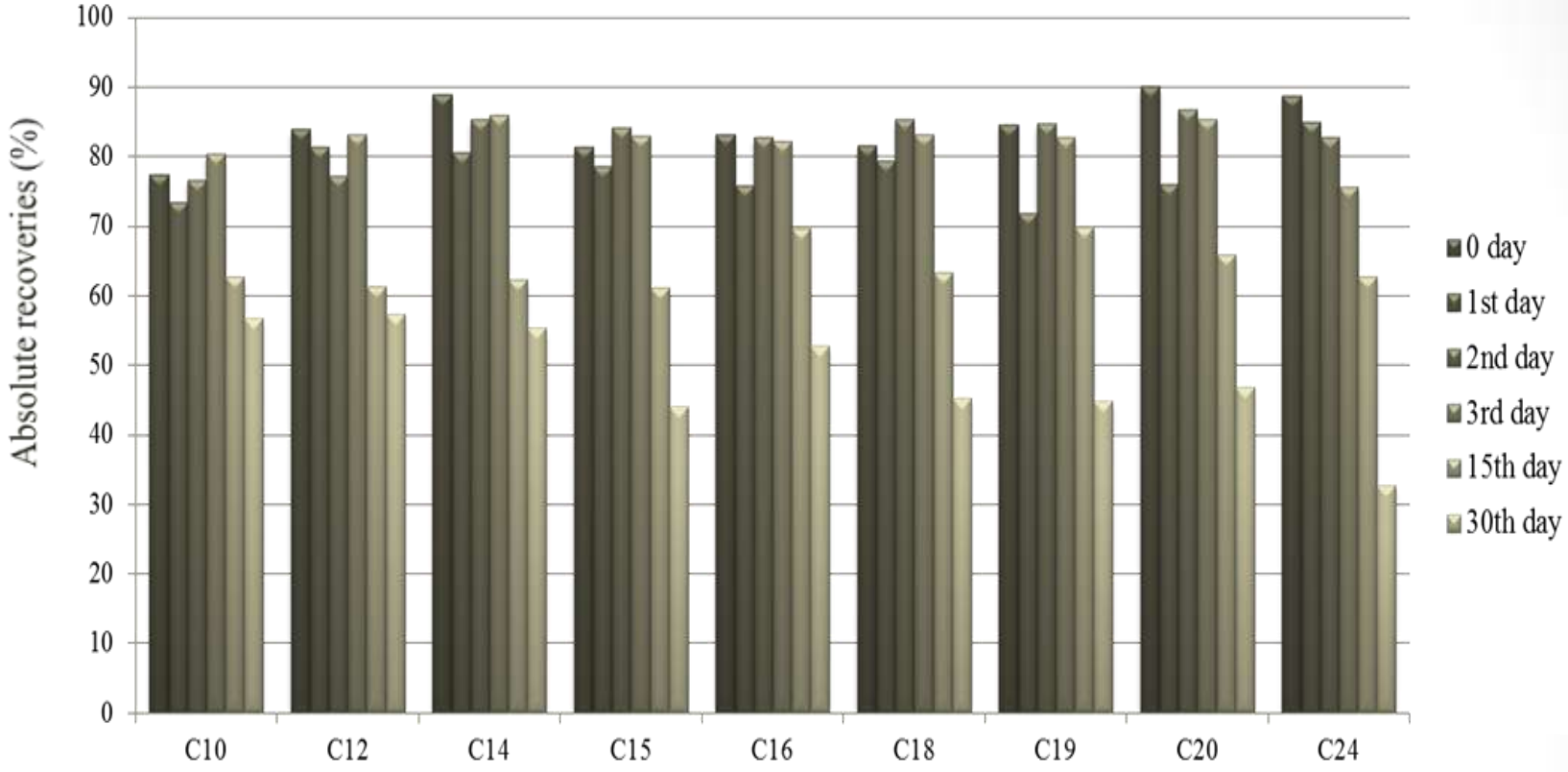
- Extraction of the target compounds from wastewater samples with 5 mL of hexane resulted in low absolute recoveries, which were ranged between 37 and 84%.
- Residual co-extracts caused a matrix induced chromatographic response effect when 1 mL of extraction solvent was used.
- 10 and 20 mL of the extraction solvent resulted in sufficient recoveries and RSDs (<14%).

Volume of water sample tested



- Lower LODs can be attained with a working water sample volume of 1000mL

Weathering and Matrix Interference



- Chemical composition of petroleum products is complex and may change over time following release into the environment.
- Hydrocarbon degradation was observed after 30 days of exposure in wastewater samples.
- Acidification of the samples (surface, sea, drinking and groundwater, wastewater) in the field is recommended according to the recoveries results to preserve the samples by killing bacteria which can degrade oil.

Validation of the developed method

Table. Calibration equations, coefficients of correlation (R_2), precision and recovery data of the developed analytical method for the determination of TPH in seawater, surface and drinking water

Matrix	Calibration equation	R_2	Mean Recoveries (%)	Intra-day precision RSD (%, n=3)	Inter-day precision RSD (%, n=3, k=3)
Seawater	y = 619410x + 2E+06	0.9929	95.4	2.7	8.3
Surface water	y = 444561x + 1E+06	0.9935	90.4	2.5	4.7
Drinking water	y = 1E+06x + 1E+06	0.9951	103.7	2.7	8

- The recoveries ranged from 95% to 103% for all water samples, indicating the good accuracy of the developed extraction method.
- The achieved LODs in the current study were lower to those previously obtained by other groups using other analytical techniques.

Table. Limits of detection (LOD) and Quantification (LOQ) of TPH in seawater, surface and drinking water

Matrix	LOD	LOQ
Seawater	0.32	1.08
Surface water	0.14	0.49
Drinking water	0.42	1.41

Summary

- The proposed analytical scheme based on LLE and GC-FID analysis proved to be effective for the extraction and enrichment of TPH in waste, surface, ground, drinking and seawater samples.
- The analytical method resulted in satisfactory recoveries, which ranged between 95% and 103% for all matrices.
- The developed method is currently applied to determine the levels of TPH in wastewater, surface and industrial effluent samples taken from different WWTPs operating in Ireland.

Thank you for your attention

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