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Challenges in the determination of petroleum hydrocarbons in water by gas chromatography (hydrocarbon index)

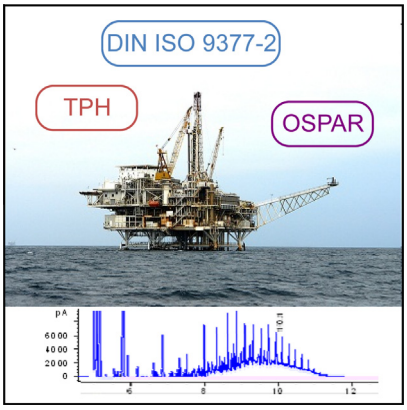
S. Drozdova [a], W. Ritter [b], B. Lendl [a,b], E. Rosenberg [a,*]

[a] Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164 AC, A-1060 Vienna, Austria
[b] QuantaRed Technologies GmbH, Columbusgasse 1-3/1/54, A-1100 Vienna, Austria

HIGHLIGHTS

- Comparison of quantitation of petroleum hydrocarbons by OSPAR and DIN ISO 9377-2 standard methods.
- Both methods show a significant, method- and sample specific bias.
- Neither of the two methods fully equivalent to the earlier 'total petroleum hydrocarbon' (TPH) method.

GRAPHICAL ABSTRACT



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ABSTRACT

Petroleum hydrocarbons inevitably are released into the environment and contaminate surface water bodies particularly near production or storage sites, but also escape accidentally during handling, transport or processing. Accurate measurement of dispersed oil in water is thus an important task which is usually done by gas chromatographic methods. The two standards that are typically followed in this respect are the DIN ISO 9377-2:2000 standard and the OSPAR (Oslo-Paris commission) method. In contrast to the DIN ISO method, the analytical method proposed by the OSPAR Analytical Method Committee is based on large volume injection (LVI) of the petroleum hydrocarbon extract in order to avoid any external preconcentration step, but still reach the stipulated detection limit. Although a standard method should provide a sufficient degree of robustness, we demonstrate here that the correctness and precision of results for the hydrocarbon index strongly depends on the proper choice of measurement parameters whose correct selection is left to the judgement of the analyst. Moreover, even under standardized conditions of measurement, the results will always show a sample-specific bias. In this work we discuss the influence of these parameters on the results, and what challenges the determination of petroleum hydrocarbons in water poses in general. The inadequacy of the two methods to provide a full equivalent to the earlier 'total petroleum hydrocarbon' (TPH) method is highlighted using a number of typical oil samples of different origin as example.

* Corresponding author. Tel.: +43 1 58801/15190; fax: +43 1 58801/15199.
E-mail address: erosen@mail.zserv.tuwien.ac.at (E. Rosenberg).

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1. Introduction

In order to interpret, evaluate the risk and make decisions about potential hazardous effects of petroleum hydrocarbons and ensure the appropriate protection of the environment, it is very important to have a sound understanding of the toxicology, analytical science, environmental fate and behaviour, risk and technological implications of petroleum hydrocarbons [1,2]. Oil contamination in the environment is primarily assessed by measuring the chemical concentrations of petroleum products in the affected environmental compartment (e.g. sediment, biota, water). The determination of total petroleum hydrocarbons or, alternatively, hydrocarbon index in water and soil is one of the important analytical tasks to assess levels of environmental pollution. It is well known [3,4], that petroleum and petroleum products are very complex mixtures that contain primarily aliphatic and aromatic hydrocarbons, heterocycles, salts, and relatively small concentrations of metals and organometallic compounds. The complexity of petroleum and petroleum products increases with carbon number of its constituents.

Produced water from offshore petroleum production, used to pressurize the crude oil reservoirs to enhance extraction, is a complex mixture of water and constituents from the crude petroleum and drilling fluids. The hydrocarbons isolated by the analytical methods for oil-in-water determination will include alkylated polyaromatic hydrocarbons, sulphur heterocycles like alkylated benzothiophenes and dibenzothiophenes, tetralins, and decalins. Polyaromatic hydrocarbons (PAHs) are potentially carcinogenic compounds and are therefore analysed separately and additionally. Apart from the nonpolar petroleum constituents analysed as oil in water, this complex mixture contains surface-active agents like phenol and alkylated phenols, organic acids, naphthenic acids and many inorganic compounds.

Clearly, different analytical methods used for the determination of the environmental concentration of petroleum and petroleum products will provide very different information. This is because they are designed to extract and measure slightly different subsets of petroleum hydrocarbons. No single method gives a precise and accurate measurement of the true *total* petroleum hydrocarbon (TPH) concentration for all types of contamination. The three most commonly used TPH testing methods include gas chromatography (GC) [5,6], infrared absorption (IR) [7] and gravimetric analysis [8,9].

GC-based methods are currently the preferred methods for petroleum hydrocarbon measurement because they detect a broad range of hydrocarbons, they provide both sensitivity and selectivity, and they can be used for petroleum hydrocarbon identification as well as quantification. Methods based on solvent extraction followed by quantitative infrared absorption measurement, have been widely used in the past for TPH measurement because they are simple, quick and inexpensive. However, the use of these methods in Europe is discontinued, since the sale and use of freons (required for the extraction of hydrocarbons from the sample) no longer is allowed, and freons are generally phased out world-wide due to their ozone-layer destructing potential. Moreover, IR-based methods do hardly provide any detailed information on the chemical composition of the oil, or the presence or absence of other relevant compounds (e.g., aromatics, or polyaromatic hydrocarbons). In contrast, they would even detect compounds that are not typically considered as TPH, such as surfactants which also may absorb IR radiation due to the presence of CH-bonds.

Gravimetric-based methods are also simple, quick, and inexpensive, but they as well do not offer any selectivity or information on the type of oil detected. Gravimetric-based methods may be useful for very oily sludges and wastewaters at high(er) concentrations, but are not suitable for measurement of light hydrocarbons which will be lost by evaporation.

Although most laboratories appear to employ GC based methods for petroleum hydrocarbon determination, however, a study of interlaboratory comparisons by Saari et al. [10] indicates that there is great variation in the GC operating settings which actually are applied in practice. The results show that the GC operating settings (especially injector settings) do have a significant influence on the performance of gas chromatographic systems for petroleum hydrocarbon determination.

Currently, there are two standard methodologies based on GC as substitutes for the former IR method that was abandoned due to the use of chlorofluorocarbons in the extraction, which can be used to monitor the maximum hydrocarbon content. To substitute for the defunct IR-based method, the DIN ISO 9377-2:2000 method has been developed and validated for the determination of hydrocarbon index in water by means of GC-FID as an official European standard method [5]. Due to systematic differences which became evident between the results from the DIN ISO method and the IR based method, the GC-based method was subsequently modified [11,12]. As a result, the modified version of DIN ISO 9377-2:2000 – the OSPAR (Oslo-Paris commission) reference method [6] for the determination of dispersed oil content in produced water – was published in 2005 and taken into force as a reference method in the field of petroleum production in January 2007.

Both methods are based on the extraction of water samples with a nonpolar (hydrocarbon) solvent, the removal of polar substances by clean-up with Florisil and capillary gas chromatography measurements using a nonpolar column and a flame ionisation detector (FID), cumulating the total peak area of compounds eluted between *n*-decane ($C_{10}H_{22}$) and *n*-tetracontane ($C_{40}H_{82}$) for the DIN ISO 9377-2:2000 standard method, see Fig. 1. The OSPAR method

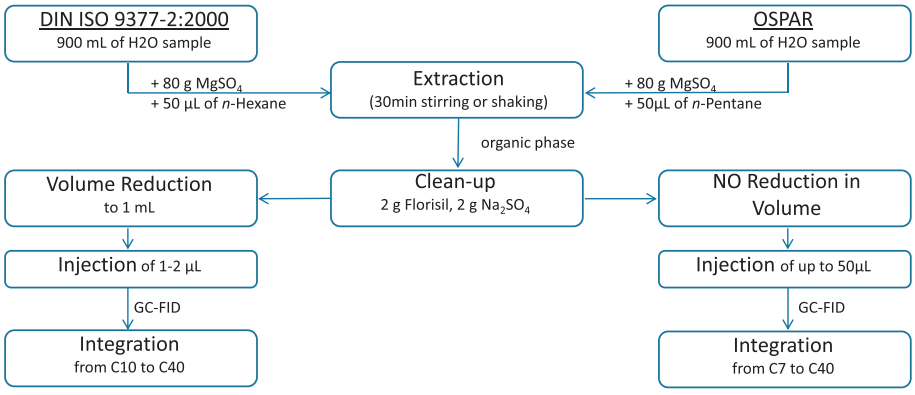

Fig. 1. Diagram of the analytical procedures proposed by the two standards DIN ISO 9377-2:2000 and the OSPAR (Oslo-Paris commission) method for the analysis of petroleum hydrocarbon contaminations in water.