

Ultrasonication Extraction - HPLC-VIS Fluorescence Method Validation for Trace Analysis of Oil and Grease in Water

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Abstract

A new method was developed to determine the oil and grease in water by HPLC-Vis fluorescence technique. Ultrasonication liquid-liquid extraction method was applied by using 1 ml of toluene to 100 ml of water. The analysis was carried out on a LC-10AT-VP chromatograph with a fluorescence RF. 10 a sykm detector equipped with a varian CN (250 × 4.6 µm) Column. The separation was preformed isocratically using a mixture of 90% solvent (n-Hexane) with 10% solvent (Toluene). Asphaltenic compounds were established to be the main fluorescence chromophores (excitation wave length at 420 nm and emission wave length at 500 nm). The correlation coefficient was (0.992), recovery ranged from 92% to 108% and the limit of detection was found to be 0.06 µg.L⁻¹. The method can be utilized successfully for determination of oil and grease in water samples.

Keywords: Crude oil; Oil; Grease; HPLC-Vis fluorescence; Method validation; Water environment

Introduction

Crude oil and grease are the constituents of produced water that receive the most attention in both onshore and offshore operations. Oil is an important discharge contaminant, because it can create potentially toxic effects near the discharge point. Dispersed oil consists of small droplets suspended in the aqueous phase [1].

Oil and grease (OG) is a very important parameter for water quality and safety. Directives and environmental regulations set limits to manage the amount of OG that could attach the water bodies through industrial discharges and additionally limit the amounts occur in drinking water. Decision Y2/2600 [2] that conforming with European Directive 98/83, has set a strict limit of 0.010 mg/L for drinking water. Decision 46399/1352 [3] additionally sets a limit of 0.2 mg/L for industrial discharges to surface waters related to human consumption.

International regulations including the 2000/2001 Oslo/Paris Convention (OSPAR) [4] and ISO 9377-2, the UK Dispersed Oil in Produced Water Trading Scheme [5]. All of these regulations now require off-shore oil platform monitor the O&G in their produced water before discharging to sea. OSPAR recommends that the discharged produced water should not exceed 30 mg/L.

The major compounds enclosed in oil and grease analyses are fats, soaps, fatty acids, hydrocarbons, waxes, and oils. The contribution of every of those substances will depend upon the source of the wastewater and the type of extracting solvent [6].

Most methods that used for the determination of oil. O&G in water include two steps: the first one is solvent extraction where a suitable solvent used for the extraction of the constituents of O&G from the aqueous phase and second step including the detection of extracted compounds by appropriate analytical technique. In general, two major types of compounds are measured by these methods: biogenic compounds and petroleum hydrocarbons. The attendance of those substances depends upon the source of waste water and the type of extracting solvent [7].

Three methods for the determination of OG in water were specified by Standard Methods for the Examination of Water and Wastewater (SMWW) [8]: Method (5520 B) a partition –gravimetric measurement, method (5520 C) a partition – infrared detection and method (5520 D) soxhlet extraction-gravimetric for determination of oil and grease, also environmental protection agency (EPA) legalizes method 1664

[9] as “N-hexane extractable material (HEM) and silica gel treated n-hexane extractable material (SGTHEM)” as “performance based”, therefore permitting the laboratories to introduce modifications in order to reduce interferences or lowering the cost, providing that all performance criteria are met. Determination the amount of O&G in water by gravimetric method is simple and inexpensive but this method has many disadvantages: low sensitivity (detection limits are 5-10 mg/L), lose the volatile components due to high temperature of evaporation process and the present of other compounds which are not O&G. Most oil in water analytical methods used in the fields make use of some type of electromagnetic spectra. For example, oil in produced water is defined by an infra-red absorption method. Constituents of the oil absorb the IR radiation in amounts proportional to the amount of oil present.

In the current study aims at validating a Chromatography-VIS fluorescence method for environmental trace analysis of oil and grease in water. Asphaltenes constituents were chosen to be the main chromophores in the validated Chromatography -VIS fluorescence method to determine the oil and grease. Asphaltenes are polyaromatic nuclei compounds linked by aliphatic chains or rings of various lengths to obtain a high molecular weight molecule [10]. Asphaltenes compounds appear to differ in molecules size, but with a statistically identical distribution of aromatic nuclei and linking units [11]. Asphaltenes are important compounds of crude oil that is colloiddally disperse in the oil phase with a mass fraction of 0 to 20% or above [12]. Liquid-liquid extraction enhanced by ultrasonication was used in this study to concentrate and simplify the extraction of analyte.

Ultrasonication assisted liquid-liquid extraction technique recently used in analytical chemistry laboratories this days as a result of their great advantages: working time is effectively reduced, increasing the yields and the quality of the extract [13-16].

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The most two techniques that used in the field of detection of O&G in water are Partition gravimetric method and partition infrared method the first one method is inexpensive and simple but it is only used for concentration that greater than 10 mg/L. The second method is more sensitive but it is impossible to get accurate calibration especially for samples of unknown hydrocarbon constituent [17]. The main purposes of this new method is to detect O&G in concentration that low than 0.01 mg/L which is required for drinking water standard and also to investigate the leakages of produced water from O&G fields into surface and ground water benefits from the advantage of high stability of asphaltene constituent.

Materials and Methods

Reagents

Toluene (99.9%) HPLC grade, hexane (95%) HPLC grade, 1-butanol (99.7%) HPLC grade and HCl (37%) ACS reagent all were purchased from SIGMA-ALDRICH.

Apparatus

LC- 10 AT-VP chromatograph with a fluorescence RF. 10 a sykm detector equipped with a varian CN (250'4.6 μ m) Column., Branson ultrasonic bath, Set a centrifuge, Analytical balance (Sartorius five-decimal analytical Balance), Pipette (Eppendorf).

Procedure

Crude oil samples

Three types of crude samples collected for the purposes of standard preparation:

- Fresh crude oil collected from shipping tank,
- Withered crude collected from evaporation pond in which the crude exposed to photo and bio.

Oxidation

Crude oil from viscosity breaking unit (crude exposed to temperature higher than 300°C).

Standards preparation

0.2021 gm of crude oil weighted and dissolved in 1 L of hexane: toluene (9:1) solvent. Then 100 μ L, 33 μ L, 20 μ L, 13 μ L and 10 μ L added to five 100 ml volumetric flasks within 5 ml 1-butanol and water as a solvent. The flasks sonicated (30 KHz) in ultrasonic bath for 20 min to prepare emulsified oil in water: 20 ng ml⁻¹, 6.5 ng ml⁻¹, 4 ng ml⁻¹, 2.5 ng ml⁻¹, 2 ng ml⁻¹ standard solutions.

Sample preparation

28 μ L from the stock solution added to 100 ml of stream water in order to get the same matrix of environmental samples then the solution emulsified in an ultrasonic bath (30 KHz) for 1 hour.

Extraction: ultrasonication liquid-liquid extraction method [18] were applied: 1 ml of toluene and 1 ml of hydrochloric acid (10%) added to 100 ml of water contaminated with oil and then the mixture sonicated (35 KHz) in an ultrasonic bath for 10 min. The unstable emulsified mixture separated by centrifugation force.

Measurement: From the toluene layer 20 μ L was carefully pipetted and injected into HPLC-Fluorescence system (LC-10AT-VP) equipped with 10 a sykm detector. The separation was performed on varian CN (250'4.6 μ m) column. using isocratic mixture of 90% solvent

A (Hexane) with 10% solvent B (Toluene) for 4 min at a flow rate of 2 ml /min.

The analytical method validation and quality control

- Study the linearity of calibration curve of the total analytical process by analyzing standards (through the ultrasonication liquid-liquid extraction) at levels between 2-20 ng.ml⁻¹.
- Accuracy which was determined by recovery studies.
- Precision that was determined in terms of repeatability.
- Calculation the limit of detection (LOD) and limit of quantification (LOQ).
- Study the stability of asphaltinic compounds fluorescence peaks.
- Robustness test.

Results and Discussion

Calibration-Linearity

The linearity of the analytical method was established by analyzing five fortified samples (after the extraction process) at levels from 2.0 to 20.0 ng.ml⁻¹. Results showed good correlation coefficient, r^2 was 0.992 as shown in Figure 1.

Recovery

A recovery study has been performed at 5.5 ng.ml⁻¹ concentration in three replicates. The results are summarized in Table 1.

Precision

Precision was established in terms of assay repeatability as shown in Table 1, the standard deviation (SD) was 0.45 and relative standard deviation (RSD) was 8%.

Limit of detection and limit of quantification

Limit of detection (LOD) and limit of quantification (LOQ) were calculated by the signal to noise (S/N) ratio, LOD was 0.06 ng.ml⁻¹ and LOQ was 0.22 ng.ml⁻¹.

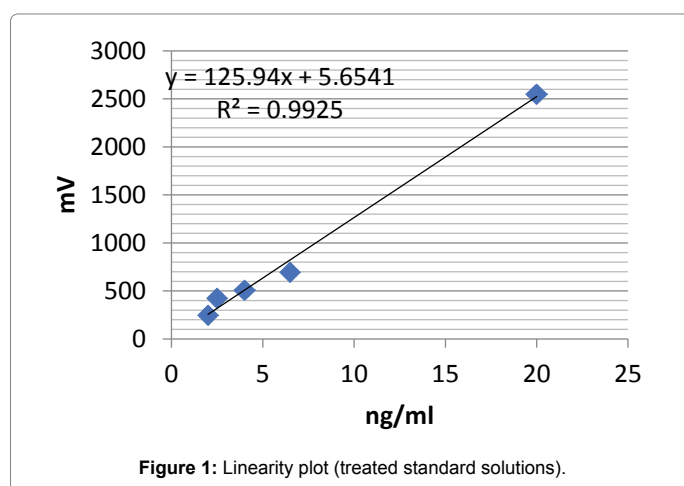


Figure 1: Linearity plot (treated standard solutions).

Sample (ng.ml ⁻¹)	Replicates	Recovered (ng.ml ⁻¹)	Recovery%	Recovery% range	SD	RSD%
5.5	3	5.065	92.0%	92-108	0.45	8.14%
		5.960	108.4%			
		5.550	100.9%			

Table 1: Replicates study recovery and precision.

Study the satiability of asphaltic compounds

Samples of crude oil were collected from evaporation pond when crude oil is exposed to photo oxidation and bacteria degradation and another sample of crude is collected from viscosity breaking unit in which oil is exposed to high temperature above to (300°C), the stability of fluorescence peak was examined as shown in Figures 2-4.

Robustness

The robustness of the method was assessed by studying the effects of two factors, the addition of acid (0.5 ml, 1.0 ml and 1.5 ml) and the ultra-sonication extraction time (5 min, 10 min and 15 min).

A two factor-three-level-full factorial experimental design consisting of 9 runs was established. The two way anova analysis showed that there were no significant linear interactions. The result also showed that the best recoveries achieved by 10 min ultra-sonication extraction time and 1 ml of acid addition (Figure 5).

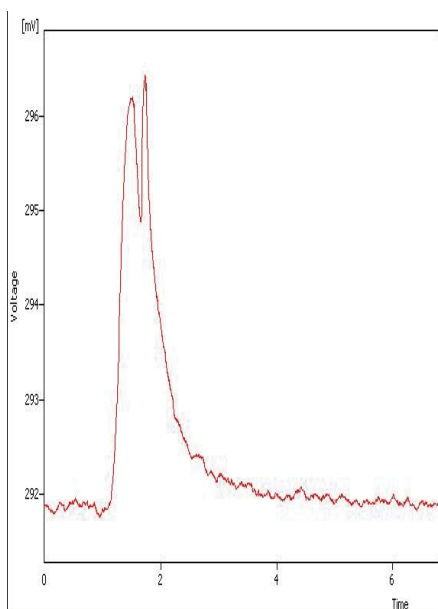


Figure 2: Fluorescence peaks of fresh crude oil.

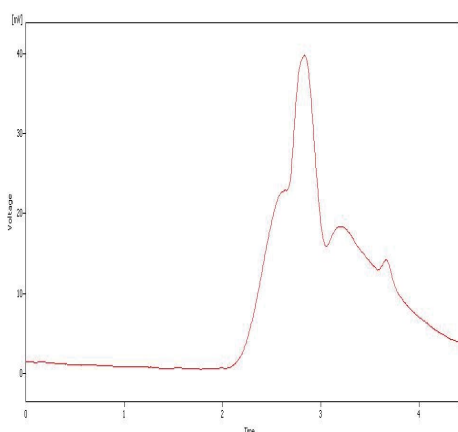


Figure 3: Fluorescence peaks of weathered crude oil.

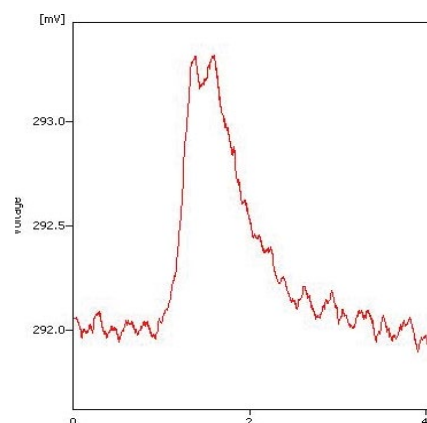


Figure 4: Fluorescence peaks of viscosity-broken crude oil.

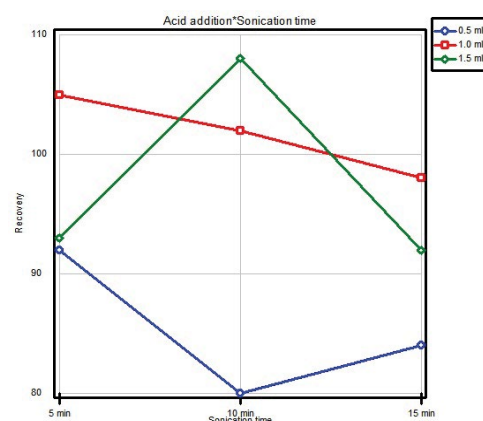


Figure 5: Acid addition (ml), Sonication time (min) Vs Recovery%.

Conclusion

Ultra-sonication pre-concentration and extraction of oil and grease from water followed by a Chromatography HPLC -VIS Fluorescence detection can be utilized successfully for determination of oil and grease in water samples as they show linearity with good correlation coefficient (0.992), good percentage recovery range (92% to 108%), good precision (SD=0.45; RSD%=8.14), LOD and LOQ 0.06 ng.ml⁻¹, 0.22 ng.ml⁻¹ respectively.

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