VALIDATION OF AN FT-IR METHOD FOR THE DETERMINATION OF OILS & GREASE IN WATER, WITH USE OF TETRACHLOROETHYLENE AS THE EXTRACTION SOLVENT.

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EXTENDED ABSTRACT

The term “Oil and Grease” (OG) encompasses a broad family of chemical compounds such as fatty material of biogenic origin, or petroleum hydrocarbon constituents. These compounds can cause environmental degradation and induce related public health risks when discharged in surface or ground waters. Consequently, OG is regulated by both European and National legislation for drinking water and wastewater. The development of methods for OG determination presents several difficulties and challenges for the analytical laboratory, since this parameter is method-defined, i.e. the method establishes the measurand. Moreover, the development of these methods usually follows a performance-based approach, allowing the laboratories to introduce modifications, as long as certain performance criteria are met. Among several alternative methods that have been proposed in the literature, FT-IR determination after liquid-liquid extraction is known to be an easy, low-cost alternative for monitoring of OG at the ppm level. However, established FT-IR methods are based on Freon 113 extraction, a solvent which has been banned as an ozone depleting agent. This paper presents the development and validation of an in-house FT-IR method for the determination of OG in water that uses tetrachloroethylene as a Freon 113 substitute. The method was developed in EYDAP’s laboratories for the monitoring and control of OG in surface and drinking waters. Results regarding the calibration, linearity, OG recovery, precision, detection - quantitation limits and robustness are presented and discussed. Tetrachloroethylene is proved to be a suitable alternative to Freon-113 and the method is appropriate for monitoring oil spills or discharges in surface waters or in the drinking water network, at levels >0.1 ppm.

Key words: Oil and Grease, Total Petroleum Hydrocarbons, FT-IR, Tetrachloroethylene.

1. INTRODUCTION

Oil and Grease (OG) is an important parameter for water quality and safety. Regulatory bodies worldwide set limits in order to control the amount of OG entering the water reservoirs or the sea through industrial discharges and also limit the amounts present in drinking water. With the aim of protecting public health from risks associated mainly with the consumption of petroleum constituents, Decision Y2/2600 [1], conforming to European Directive 98/83, has set a strict limit of 0.010 mg/L for drinking water. Decision 46399/1352 [2] also sets a limit of 0.2mg/L for surface waters intended for human consumption after conventional treatment. On the other hand, because OG can cause serious problems in the operation of wastewater treatment plants, Decision 179182/656/1979 [3] has set a limit of 40 mg/L total OG for industrial discharges in the sewer system of Athens that operates under the responsibility of EYDAP S.A..

Nevertheless, the above regulations do not include a definition of the term “Oil & Grease”. In fact, the definition of OG is closely related to the analytical methods and their results, i.e. it is the method that defines what is measured. Usually methods developed for determination of OG in water include a step where a suitable solvent is used for the extraction of the constituents of OG, which are then measured by an appropriate technique. The steps of extraction and measurement as well as the exact conditions of the analytical processes determine what is actually measured. In general, two major classes of compounds are quantified by these methods: biogenic compounds such as vegetable oils, animal fats or vegetative material and petroleum hydrocarbons. Depending on the exact method and treatment of the samples or extracts, the range of compounds or interferences that are quantified can considerably vary.

Standard Methods for the Examination of Water and Wastewater (SMWW) [4] specifies three alternative methods for the determination of OG in waters: a partition-gravimetric method (5520 B), a partition-infrared method (5520 C) and a soxhlet extraction-gravimetric method (5520 D). Method 5520 B uses n-hexane as the extraction solvent, which has replaced 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) for gravimetric procedures since the 20th edition. Thus, method 5220 B defines OG as any material recovered as a substance by n-hexane from an acidified sample. EPA specifies method 1664 [5] as “N-hexane extractable material (HEM) and silica gel treated n-hexane extractable material (SGT-HEM) by extraction and gravimetry”. The silica gel treatment allows for the separate determination of Total Petroleum Hydrocarbons (TPH). EPA states that method 1664 is “performance based”, therefore permitting the laboratories to introduce modifications in order to overcome interferences or lower the cost, provided that all performance criteria are met. Although gravimetric methods such as SMWW 5220 B and EPA 1664 are simple, quick and inexpensive, they present the disadvantages of low sensitivity (usually detection limits are 5-10mg/L), loss of constituents that volatilize at temperatures above those used for the evaporation of the solvent and inclusion of compounds which are not “oil and grease” but are extracted by the solvent and therefore contribute to the final weight.

Infrared-based methods are generally more sensitive with detection limits that are approximately 1mg/L. IR methods measure the absorbance of the C-H bond i.e. the stretching of aliphatic CH_2 groups at 2930 cm^{-1}, of CH_3 groups at 2960 cm^{-1} and of aromatic C-H bonds at 2900 – 3000 cm^{-1}. It is self-evident that IR methods can only use solvents without C-H bonds, but since no evaporation of the solvent is needed, there are no losses of volatile components. Three well-known IR methods for OG determinations are SMWW 5520 C [4], EPA 418.1 [6] and ASTM D 3921-96 [7]. All these methods use Freon 113 as the extraction solvent. However, since the Montreal Protocol banned the production of Freon 113, there is a need to find a suitable replacement solvent for measuring OG with IR-based methods. Carbon tetrachloride has been used already from the early studies on IR determination of OG in waters [8], but due to its toxicological effects it is not an attractive alternative. ASTM D 3921-96 allows the use of alternate solvents, suggesting tetrachloroethylene (perchloroethylene) as an alternative solvent [7]. Tetrachloroethylene (C_2Cl_4) is a rather non-volatile (b.p. 121°C) non-hydrocarbon solvent with infrared transparency that makes it suitable for IR measurements in the region of C-H bonds absorption. Horiba's proprietary S-316 solvent is also proposed as a substitute to Freon 113 [8]. This solvent, claimed to be environmentally safe, is used in a new ASTM Standard Test Method D 7066-04. Hydrocarbon solvents like hexane or pentane can be used in IR methods only after evaporation and as a result have the disadvantages of volatile constituent losses and possible contamination with solvent. DuPont's Vertrel MCA [9], a solvent used primarily as a degreasing agent, is accepted by EPA as a substitute for Freon, but since it is actually a mixture of hydrofluorocarbon with dichloroethylene, it has to be evaporated prior to IR measurement. Because of its very low boiling point (39°C), Vertrel MCA is considered better than hexane when fewer losses of volatiles are considered necessary.

Apart from liquid-liquid extraction (LLE) methods, solid phase extraction (SPE) methods have been developed that are combined with IR [10] or gravimetric determination [11,12]. These methods may offer several advantages over conventional LLE methods, such as less solvent use and high throughput, but their performance needs to be thoroughly evaluated against the standards mentioned above. Other methods include GC/FID, GC/MS, HPLC and immunoassay techniques that are primarily developed for monitoring of petroleum hydrocarbon constituents [13]. These methods have the advantage of providing identification or even fingerprinting capabilities, but it is often difficult to extrapolate their results in order to obtain "total OG" values.

Laboratories that want to implement OG in water monitoring programs have to carefully consider the above alternative methods with their advantages, limitations and implications. Especially laboratories that want to continue using IR methods for enhanced sensitivity relative to gravimetry, have to consider using a suitable solvent as a substitute to Freon-113 and validate the modified methods. Although tetrachloroethylene, as mentioned above, is proposed as an alternative solvent in ASTM D 3921-96, to the authors' knowledge there are no detailed published validation data with the use of this solvent. The aim of this paper is to present the development and validation data of an FT-IR method for measurement of OG in waters, that uses tetrachloroethylene as the extraction solvent. This in-house method was developed in EYDAP's Organic Micropollutants Laboratory, in order to be applied for monitoring of oil spills or discharges in lakes and in the drinking water supply network.

2. MATERIALS AND METHODS

Methods SMWW 5520 C [4], EPA 418.1 [6] and ASTM D 3921-96 [7] were used as guidance for the analytical process, which consists of the following steps:

a. Acidification of the sample with 5ml 1:1 sulfuric acid per liter.
b. Extraction of 1l sample with 30 ml tetrachloroethylene (x 3 times).
c. Filtration of the extracts through 10g sodium sulfate.
d. Measurement of absorbance at the maximum near 2930 cm^{-1}.

Tetrachloroethylene 99.9% IR-PAI grade was purchased from Panreac Quimica SA.. Anhydrous granulated sodium sulfate 99.0% was purchased from Fluka Chemie GmbH. Whatman 40 125mm filter paper was used for the filtrations.

A Perkin Elmer Spectrum BX FT-IR spectrometer equipped with DTGS detector and a single-beam sample compartment was used for absorbance measurements under the following operation parameters: *Cells: Quartz / Matched pair 50mm, Resolution: 4* cm^{-1}, *Number of scans: 20, Scan range: 3200-2700* cm^{-1}, *Vibration of interest: Bond C-H in the* *maximum of the area 2926-2930 cm^{-1}, Background spectra: Each time indicated from the analysis, Measurement mode: Ratio, Lab temperature: 25 ±2 °C.*

3. RESULTS AND DISCUSSION

Calibration - Linearity

Calibration lines were prepared by using different volumes of a stock calibration solution prepared by mixing equal volumes of Isooctane and n-Hexadecane, as proposed in [7]. The linearity of the instrumental technique was established by analyzing ten standard solutions at levels between 0.6 to 50 mg/L (Figure 1) using pure solvent as background spectra. The linearity of the analytical method was established by analyzing seven fortified samples (after the extraction process) at levels between 1.6 to 50 mg/L using treated reagent water (method blank) as background spectra.

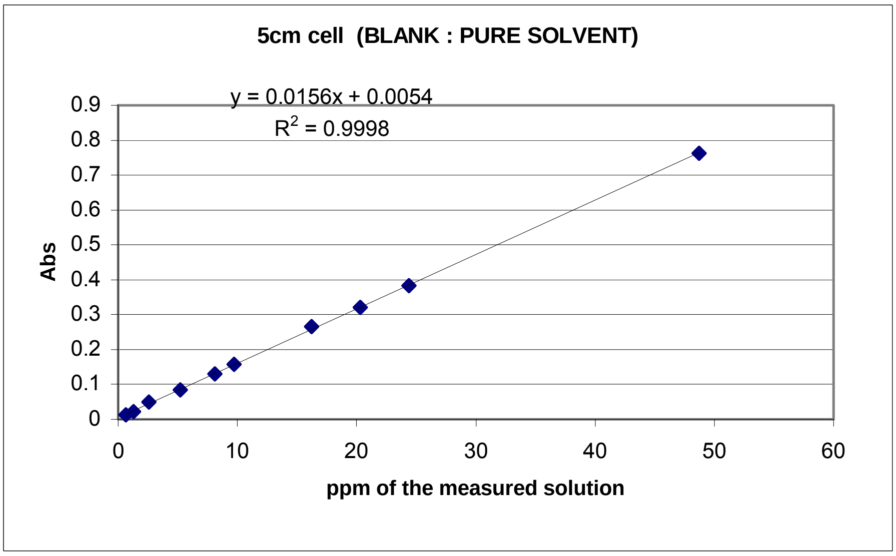

FIGURE 1: Calibration plot (untreated standard solutions)

Results showed good correlation coefficients, for the two types of calibrations. For instrument calibration in the range 0.6-50mg/l r^2 was 0.9998, while for method linearity in the range 1.6-50 mg/l r^2 was 0.9901.

Standard & Sample solutions stability study

Stability solutions studies for both standard and samples solutions have been carried out during the validation process. The final tetrachloroethylene solutions were stored at fridge temperature for a period of approximately 1 month without any problems be ascertained during intermediate controlling measurements.

Recovery

Recovery studies for two different sources of water (tap & lake) have been performed at seven level concentrations between 1.6 to 50 mg/L. These studies have been repeated in double trials except for two “critical“ levels where more replicates were carried out. Table 1 summarises the results for these two levels. As seen in Table 1, mean recoveries are in satisfactory levels, between 73 and 97%, with standard deviations exceeding 10% only at the lowest concentration level.

TABLE 1: % Mean Recoveries and related standard deviation values.

C (mg/l)	Tap water		Lake water	
	%R	SD (n)	%R	SD (n)
1.62	82.0	13.3 (8)	73.0	28.4 (8)
16.2	96.6	5.5 (9)	93.1	5.7 (8)

n= no of replicates

Precision

Precision was established in terms of: a. Assay repeatability and b. Intermediate repeatability. Two sets of six (6) sample preparations fortified at the above mentioned concentration levels of 16mg/L and 1.6mg/L were analyzed in single measurements against treated reagent water (method blank). Each set of determinations was carried out by a different analyst using the same lot of Reference Materials and the same Sample Water. Summarized results for method precision are shown in Table 2. Results show that overall SD is below 0.4 at both concentration levels and matrices. These values are quite satisfactory when compared to ASTM D 3921-96 where SDs of 0.6 and 3.0 are estimated for the low and high level concentrations respectively [7].

TABLE 2: Precision results at two different concentration levels

C in the final sol. (mg/l)	1st day -1st analyst SD (n=3)	2nd day – 2nd analyst SD (n=3)	InterAnalyst InterDay SD (RSD%) (n=6)
Tap water			
1.62	0.15	0.12	0.14 (12.3)
16.2	0.38	0.41	0.35 (2.4)
Lake water			
1.62	0.17	0.16	0.15 (7.29)
16.2	0.22	0.48	0.36 (2.2)

Detection and Quantitation limits

The recovery plot of each test for both water sources has been used in order to determine the Detection and Quantitation limit, based on the obtained regression (best-fit line) slope and the standard deviation of the response. The standard deviation of the response (S_{res}) for each recovery plot is calculated by the following equation [14]:

$$S_{res} = \sqrt{\frac{\Sigma(Y - Yest)^2}{n-2}}$$

where Y =actual Y axis values (absorbance of each level)

Y_{est} =estimated Y values based on the regression equation for the corresponding X

n = number of measurements

The values of the slope (m) and the standard deviation of the response (S_{res}) were used in order to statistically estimate the Detection (DL) and Quantitation (QL) limit based on the formulas :

$$DL = \frac{3.3 \ x \ Sres}{m} \quad \text{and} \quad QL = \frac{10 \ x \ Sres}{m}$$

The theoretical calculated results of DL and QL (respectively for tap water: 0.11 and 0.32mg/L & for lake water : 0.18 and 0.54mg/L) were verified by preparing and analyzing the corresponding solutions.

The predetermined specifications that have been established for the above experimental results have been successfully met:

for LD: the obtained signal (Absorbance) should be more (≥) 0.020 and for LQ: the above statistically estimated limit should be in the range in which the method was successfully validated (demonstrated that the analytical procedure is linear, accurate and precise).

Robustness

Robustness of the method was assessed by evaluating the effects of amounts of acid added in the sample (4-6 ml), sodium sulfate used in filtrations (8-12g) and extraction time (1-3min), with standard working conditions being in the middle of the above ranges. A three factor - three-level - fully randomized Box-Behnken experimental design [15] consisting of 15 runs of fortified (16 mg/L) tap water samples was used for the study. Analysis of the results showed that in the above ranges there are no significant linear, interaction or squared effects. Therefore, the method is assumed to be robust to small but significant deviations in the above experimental conditions.

4. CONCLUSIONS

Tetrachoroethylene is found to be a suitable replacement to Freon-113 for the determination of Oil and Grease in waters. Results obtained during the validation of the IR-based method that uses tetrachloroethylene as the extraction solvent show that the method is robust and demonstrates acceptable levels of precision and analyte recoveries, with detection limits close to 0.1 mg/L. For that reason the method is appropriate for monitoring incidents of oil spills in lakes and drinking water supply networks at levels >0.1ppm.

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