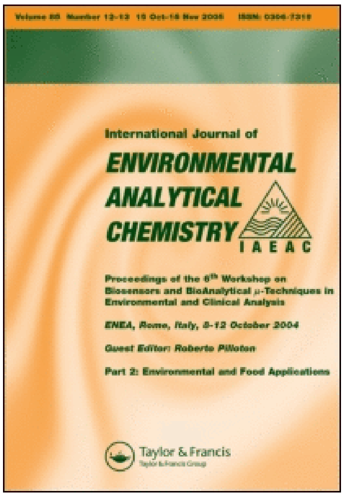

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Oil-in-water analysis using supercritical fluid extraction interfaced with fixed wavelength infrared detection

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To cite this Article Ramsey, Edward D. and Wei, Guo(2008) 'Oil-in-water analysis using supercritical fluid extraction interfaced with fixed wavelength infrared detection', International Journal of Environmental Analytical Chemistry, 88: 13, 957 — 968

To link to this Article: DOI: 10.1080/03067310802120847

URL: http://dx.doi.org/10.1080/03067310802120847

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 13, 15 November 2008, 957–968

Oil-in-water analysis using supercritical fluid extraction interfaced with fixed wavelength infrared detection

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(*Received 21 January 2008; final version received 10 April 2008*)

The combination of a direct aqueous supercritical fluid extraction system interfaced to a fixed wavelength infrared detector; measuring CH_2 ($\nu_{\text{asymmetric}}$) absorbance at $2930\,cm^{-1}$, has been successfully developed for the analysis of oil-in-water. Using an optional, in-line silica gel treatment procedure, method accuracy for determining Brent Delta crude oil in spiked 500 mL water samples was 92.0% to 94.5% with RSD 4.7% to 6.5%. The supercritical fluid extraction-infrared method enables a second analysis of the same water sample without silica gel treatment. For second sets of analyses without silica gel treatment, method accuracy for determining Brent Delta crude oil in spiked 500 mL water samples was 87% to 96.0% with RSD 7.5% to 9.5%. Results of this study indicate that the silica gel treatment procedure reduces the calculated level of Brent Delta crude oil-in-water by 6.6–12.4% relative to samples analysed without silica gel treatment. The results of a study involving Fourier transform infrared spectroscopy indicate a limit of detection for *n*-decane of approximately $0.5\,mg\,L^{-1}$ by measuring CH_2 ($\nu_{\text{asymmetric}}$) absorbance using the supercritical fluid extraction-infrared method. Sample preparation using direct aqueous supercritical fluid carbon dioxide extraction provides an indefinite means for the use of infrared techniques to measure oil-in-water.

Keywords: oil-in-water; supercritical fluid extraction; infrared; fixed wavelength

1. Introduction

The determination of oil in trade and process waters is a key environmental measurement that must be performed by many diverse industries on a global basis. Industry and environmental regulators have previously relied on infrared (IR) techniques to perform the measurement [1]. The continued long-term use of IR spectroscopy for the analysis has come into question due to the Montreal Protocol that also strictly controls the availability of organic solvents for laboratory use, in particular chlorofluorocarbons (CFCs) [2]. In 1994, the measurement of oil-in-water was the only environmental analytical method specifically identified for which an essential use exemption was granted by the Parties to the Montreal Protocol [3]. The exemption permitted the manufacture and supply of CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) to continue the use of IR methods for

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802120847
http://www.informaworld.com

oil-in-water analysis. The final phase out of CFC-113 for oil-in-water measurement as of first January 2002 [4] initially posed a threat to the continued use of IR methods that had heavily relied on the availability of this solvent. In order to extend the use of IR methods that involve direct analysis of a non-evaporated extract following liquid–liquid extraction, two organic solvents are currently in general use to measure oil-in-water. The United Kingdom Department of Trade and Industry (DTI) has approved [5] the use of tetrachloroethene, despite its toxicity. Whereas, the American Society for Testing Materials has introduced [6] Method ASTM D 7066-4 using the proprietary solvent S-316 (1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane). Using either of these currently approved solvents, IR methods for measuring oil-in-water can be accomplished using either Fourier transform infrared (FTIR) or fixed wavelength IR spectroscopy. Single wavelength IR analysis to determine oil-in-water involves the measurement of the CH_2 ($\nu_{\text{asymmetric}}$) absorbance value at $2930\,\text{cm}^{-1}$. The current withdrawal date for tetrachloroethene has been set at 2030 [7] and the DTI [8] will accept S-316 as a replacement solvent for tetrachloroethene. However, continued availability of S-316 to perform the measurement is not assured since it is a CFC [1]. Horiba, the manufacturer of S-316 are currently replacing S-316 with solvent H-997, also manufactured by Horiba, for their latest range of fixed wavelength IR instruments for measuring oil-in-water [9]. As with S-316 continued availability of H-997 is not assured since it is also an ozone depleting substance and its manufacture, export and use is strictly controlled by the Montreal Protocol. Solvent H-997 is a complex mixture whose principal constituents are HCFC-225ca (3,3-dichloro-1,1,1,2,2-pentafluoropropane) and HCFC-225cb (1,3-dichloro-1,1,2,2,3-pentafluoropropane) and its manufacturer reports that it is volatile [9]. Horiba report [9] different oil extraction efficiencies for S-316 and H-997 and this may serve to hinder the publication of new IR reference methods using H-997.

As of 1 January 2007, European nations party to the Oslo and Paris Convention (OSPAR) for 'The Protection of the Marine Environment of the North East Atlantic' accepted an OSPAR modified version [10] of gas chromatography (GC) Method ISO 9377-2 as the reference method for measuring oil-in-water. However, in recognition of the complexity of modified Method ISO 9377-2, OSPAR [11] and the DTI [8] will accept alternative simpler reference methods, such as those based on IR, if the alternative method is calibrated against the OSPAR GC method. OSPAR and the DTI must also be satisfied that the results of the alternative reference method are statistically equivalent to the OSPAR GC reference method. The DTI anticipates [8] that some offshore operators will calibrate the IR method using tetrachloroethene against OSPAR modified Method ISO 9377-2.

The supercritical fluid extraction-infrared (SFE-IR) method for measuring oil-in-water involves the use of environmentally benign, non-ozone depleting supercritical fluid carbon dioxide to perform oil extraction. Early studies involving a prototype SFE system interfaced to an FTIR spectrometer demonstrated the potential of the method to provide an environmentally clean alternative procedure for the determination of oil-in-water using IR methods [12,13]. The use of a production version of the SFE system interfaced to an FTIR spectrometer to measure oil-in-water that involved the development of a rapid on-line calibration procedure has been reported [14]. However, compact, field-portable fixed wavelength IR detectors are also very commonly used by industry, particularly offshore oil and gas operators, to measure oil-in-water due to the simplicity of their operation. The SFE-IR method using a pre-production SFE system has been the subject of an independent trial, involving the use of FTIR instrumentation, sponsored by the DTI, British Petroleum and Norway's Statoil and the trial report is now available in the public domain [15]. The trial report, prepared in 2003, concluded that the SFE-IR method provides comparable results to those using the then approved DTI tetrachloroethene extraction-based IR reference method. The report also finds that the SFE-IR method is well capable of determining the level of oil-in-water through the range likely to be present in offshore oil and gas platforms' produced water. The current OSPAR discharge limit [15] for oil in produced water from offshore oil and gas platforms is 30 mg L^{-1}. Although generally very positive about the SFE-IR method, the trial report raises the issue of the possible use of fixed wavelength IR detectors rather than more complex FTIR instruments.

The purpose of this report is to demonstrate that the patented [16,17] direct aqueous SFE system has now been successfully interfaced to a fixed wavelength IR detector for measuring oil-in-water. The report also demonstrates that the SFE-IR method has now been further developed to enable the optional use of a convenient, automated silica gel treatment procedure. This is an additional sample preparation stage, mandated by some environmental regulators [1,5,6]. This report also describes a rapid procedure that enables a second SFE-IR analysis of the same 500 mL water sample without silica gel treatment.

2. Experimental

An SFX 1020^{TM} (all enquiries to the author) automated oil-in-water supercritical fluid extractor was used for all SFE-IR studies. All SFE studies were performed using an extraction vessel temperature of 40°C with a flow rate of liquid carbon dioxide set to 25 mL min^{-1} until a SFE target pressure of 20.7 MPa was attained. The main body of the SFE vessel used in these studies is constructed from a solid bar of 316 grade stainless-steel in accordance with the American Society of Mechanical Engineers VIII standards for such equipment and therefore has been the subject of rigorous safety checks. The one litre capacity SFE vessel is designed such that 500 mL sample bottles are directly inserted into the vessel chamber. Solid phase extraction (SPE) cartridges packed with 500 mg silica gel, size 3 mL, were obtained from Varian Inc. (Palo Alto, CA, USA). In order to perform the silica gel treatment procedure, a modified Thar (Pittsburgh, Pennsylvania, USA) 25 mL SFE vessel acted as SPE cartridge holder. The fixed wavelength SFE-IR studies were performed using an InfraCal CVH fixed wavelength IR detector (Wilks Enterprise Inc., South Norwalk, CT, USA) factory set to provide digital absorbance values measured at 2930 cm^{-1}. All SFE-IR studies were performed using a 10 mL volume, high pressure IR inspection cell (all enquiries to the author) whose path length was 40 mm, constructed using quartz windows of 8 mm diameter. The fixed wavelength SFE-IR studies involved withdrawing the IR source and detector from the InfraCal chassis, fitting extension leads and then inserting these IR components into the end caps of the high pressure IR inspection cell that had been manufactured to accommodate this arrangement. This was necessary since the high pressure IR cell was too large to be inserted into the sample compartment of the fixed wavelength IR detector. The comparative SFE-FTIR and thin film FTIR study was performed with a Spectrum One FTIR spectrometer (PerkinElmer, Shelton, CT, USA). The thin film FTIR analysis was performed using Brent Delta crude oil applied between two sodium chloride discs. A limit of detection SFE-FTIR study was performed using a Nicolet Magna-IR 550 FTIR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). All FTIR spectra were obtained over the range 4000–400 cm^{-1}

using a resolution of 4 cm^{-1}, with 10 scans summed per analysis. A liquid draw-off cylinder using industrial grade liquid carbon dioxide was used to perform all SFE studies. All water samples were contained within unlined graduated Schott 500 mL borosilicate sample bottles (Merck, Lutterworth, Leicestershire, UK). Analar grade *n*-decane was obtained from Sigma-Aldrich (Poole, Dorset, UK). A sample of Brent Delta crude oil was obtained as a gift from SGS Redwood Services (Dyce, Aberdeen, UK) and was cold filtered prior to use for the rapid on-line SFE vessel bypass calibration procedure and IR stability check procedure whereas unfiltered Brent Delta crude oil was used to prepare spiked water samples.

3. Instrumentation and methodology

Operational aspects and the design of the SFE system used throughout these studies, without the silica gel treatment procedure, have been described in detail [14,18]. The SFE-IR method using silica gel treatment involves using the valve configuration shown in Figure 1. Once SFE target pressure of 20.7 MPa is reached, valve (F) opens to transmit an aliquot of supercritical fluid extract to the high pressure IR cell (L) for analysis. The appropriate setting for valve (I) is selected such that the aliquot of supercritical fluid extract flows through a disposable silica gel SPE cartridge, contained within the cartridge holder chamber (J), en-route to the high pressure infrared cell (L). Until valve (F) opens,

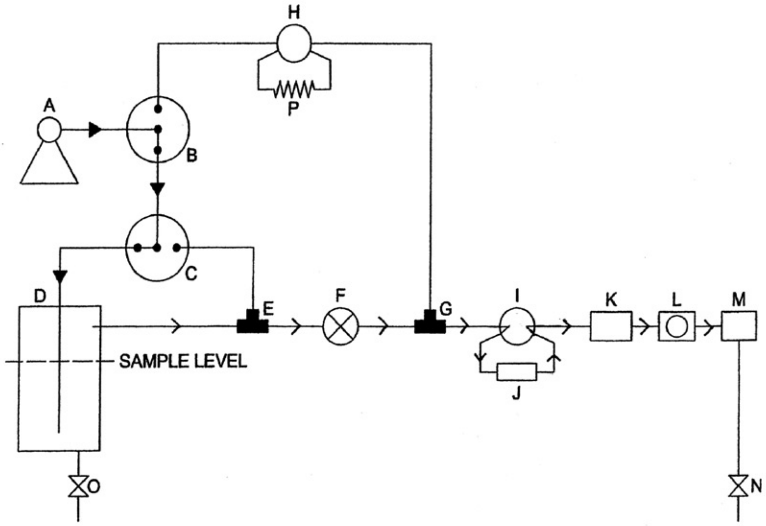

Figure 1. SFE system valve configuration to perform SFE-IR analyses of water samples using silica gel treatment.

Notes: Open arrows indicate flow of carbon dioxide once valve F opens. Where: A is liquid carbon dioxide pump, B is carbon dioxide supply selection valve, C is carbon dioxide flow supply valve, D is SFE vessel, E is T piece, F is automatic valve, G is T piece, H is HPLC injection valve, I is silica gel treatment selection valve, J is silica gel SPE cartridge holder, K is union, L is high pressure IR inspection cell, M is choke, N is exhaust valve, O is exhaust valve, and P is valve loop.

Source: This derivative figure, a modified version of that appearing in reference [14], has been produced with kind permission granted by Elsevier.

both the SPE cartridge holder and IR cell are isolated at atmospheric pressure. Valve (F) closes after the re-establishment of the SFE target pressure throughout the SFE-IR system and IR analysis is then performed. The silica gel treatment procedure removes co-extracted polar organics, providing a silica gel treated supercritical fluid carbon dioxide extract for IR analysis. With silica gel treatment, a 500 mL water sample can be analysed in a total of approximately 15.5 min using the SFE-IR method. The void volume of the SFE vessel when loaded with a 500 mL water sample is 150 mL. Hence, taking into account the void volumes of the loaded SPE cartridge holder and the IR cell, 5 mL and 10 mL, respectively, a total of 165 mL supercritical fluid carbon dioxide is used to extract a 500 mL water sample when silica gel treatment is directly applied. It is therefore possible to obtain a second SFE-IR analysis of the same water sample without using silica gel treatment since sufficient SFE extract is still available, isolated in the SFE vessel following the first SFE-IR analysis. The first stage of the procedure entails venting the SPE cartridge holder and IR cell using exhaust valve (N). The appropriate valve (I) position is then selected such that the SPE cartridge holder is isolated from the rest of the SFE-IR system. Following this carbon dioxide supply valve (B) is switched such that the flow of carbon dioxide will bypass the SFE vessel. With this valve configuration it is possible to clean the IR cell *in situ* using supercritical fluid carbon dioxide [14]. Sufficient numbers of clean cycles are performed until the fixed wavelength IR detector provides a zero digital absorbance value to confirm the IR cell has been cleaned. Once cleaned, carbon dioxide supply valve (B) is set to the position shown in Figure 1.

A second SFE-IR analysis for the same 500 mL water sample, without silica gel treatment, uses 175 mL supercritical fluid carbon dioxide for sample extraction. A second analysis is relatively rapid to perform since the sample loaded SFE vessel remains isolated at target pressure whilst the IR cell is being cleaned. The length of time to perform the second analysis is largely dependent on the number of IR cell clean cycles that need to be performed following the first analysis. In order to improve sensitivity, the void volume of the SFE vessel when loaded with a sample is minimised such that the concentration of the supercritical fluid extract is increased. This is largely facilitated by fitting the sample bottle with an aluminium cap. The measures taken to reduce void volume are illustrated in Figure 2.

4. Results and discussion

The fixed wavelength IR detector used in these studies provides digital absorbance values at a factory set wavelength of 2930 cm^{-1}. With a scanning FTIR instrument, maximum CH_2 ($\nu_{asymmetric}$) absorbance values are measured at 2933 cm^{-1} using the SFE-IR method since, as shown in Figure 3, SFE-IR spectra exhibit a shift to higher wavenumbers relative to conventional thin film infrared spectra. Examination of the Brent Delta crude oil SFE-FTIR spectrum, Figure 3, indicates only a small reduction in sensitivity, approximately 4%, is lost by measuring SFE-IR absorbance values at 2930 cm^{-1}. In order to conduct the fixed wavelength SFE-IR trial, the cleaned system was first used to analyse two blank 500 mL water samples. This was to set and then check that a stable zero digital fixed wavelength SFE-IR absorbance value was obtained for blank water samples. After this, the rapid on-line SFE vessel bypass calibration procedure [14] was used to calibrate the fixed wavelength SFE-IR system configured for silica gel treatment. This entailed analysing six sets ($n = 3$ per set) of Brent Delta

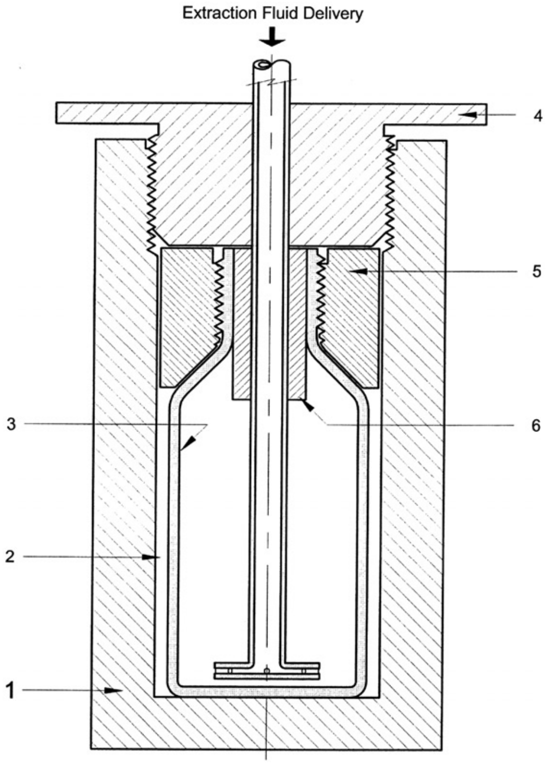

Figure 2. Diagram to illustrate arrangement for water sample bottle sealed in the SFE vessel chamber.
Notes: 1 is main body of SFE vessel, 2 is void, 3 is sample bottle, 4 is SFE vessel cap, 5 is aluminium cap connected to sample bottle and 6 is bored (not shown) void volume restrictor attached to carbon dioxide delivery tube.

crude oil which were manually injected, through the range 0.5–3.0 μL at 0.5 μL increments, using high performance liquid chromatography (HPLC) valve (H) to introduce calibration standards into the high pressure IR inspection cell. With the origin considered a data point, a seven point calibration graph was constructed expressing mean average digital absorbance values measured at 2930 cm^{-1} as a function of the number of μL Brent Delta crude oil analysed using the SFE vessel bypass calibration procedure. Using Microcal Origin$^{\text{TM}}$ software, a polynomial fit was selected to construct the calibration graph since the data points exhibited a curved relationship. This finding indicates that the use of a shorter path length, 10 mL volume IR cell to extend the dynamic range for the fixed wavelength IR detector used in these studies may become necessary for analysing heavily contaminated samples that provide more concentrated oil-in-water supercritical fluid extracts.

The next stage of the calibration procedure involves the rescaling of the first constructed calibration graph x-axis such that equivalent number of μL Brent Delta crude oil in spiked 500 mL water samples is expressed. The rescaling procedure, using Brent Delta crude oil, has been previously described using an SFE-FTIR system without the use of a silica gel treatment stage [14]. Briefly, the procedure involves correlating absorbance

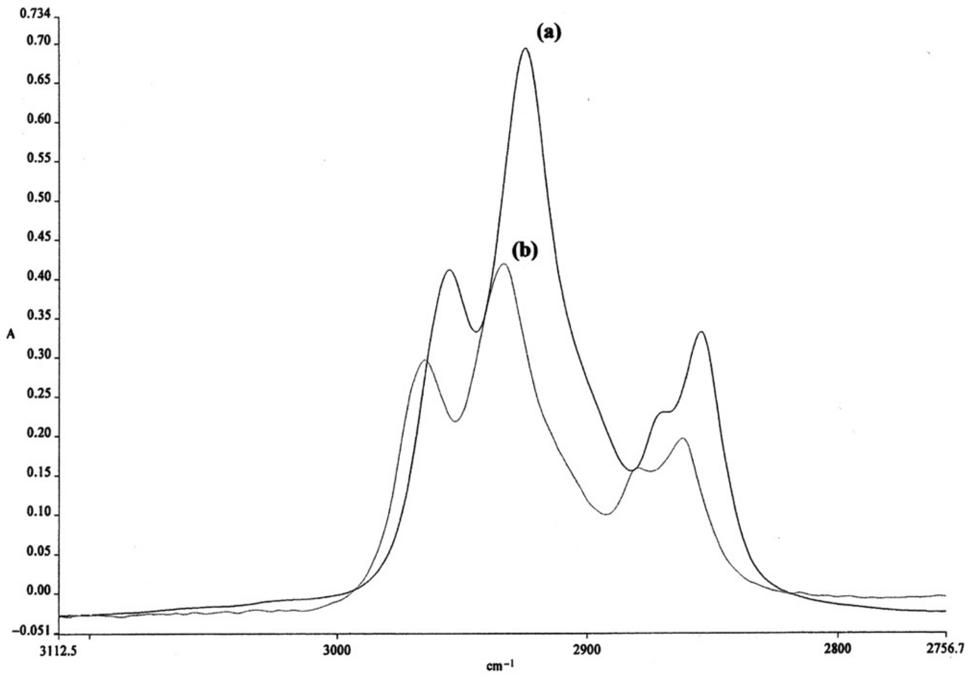

Figure 3. Brent Delta crude oil FTIR spectra obtained using (a) thin film sample preparation and (b) SFE-FTIR analysis of a spiked 500 mL water sample.

values obtained for 500 mL water samples spiked with Brent Delta crude oil with the absorbance values of the non-scaled calibration graph. With the use of silica gel treatment, the rescaling factor has to be adjusted to account for the void volume of the SPE cartridge holder. The rescaling factor is such that a 0.5 μL Brent Delta crude oil calibration standard provides the same fixed wavelength SFE-IR digital absorbance value that would be obtained for 7.76 μL Brent Delta crude oil spiked in 500 mL water samples. Figure 4 shows the fixed wavelength SFE-IR rescaled calibration graph obtained for Brent Delta crude oil.

In order to assess the accuracy of the fixed wavelength SFE-IR method, four sets ($n=6$ per set) of 500 mL water samples spiked with known quantities of Brent Delta crude oil were analysed. Using the rescaled calibration graph, the quantities of Brent Delta crude oil in the spiked water samples were then calculated by interpolation of digital absorbance values measured at 2930 cm^{-1}. The results shown in Table 1 demonstrate that the fixed wavelength SFE-IR method using silica gel treatment is capable of accurately determining the quantity of oil-in-water. Table 1 also includes the fixed wavelength SFE-IR results obtained for sets ($n=3$ per set) of spiked 500 mL water samples analysed a second time without silica gel treatment. The fixed wavelength SFE-IR values obtained without silica gel treatment, initially calculated using the rescaled calibration graph, are corrected to take into account the different volume of supercritical fluid carbon dioxide used to perform a second extraction. Results in Table 1 indicate that the silica gel treatment procedure reduces the calculated amount of Brent Delta crude oil-in-water by 6.6% to 12.4% relative to samples analysed without silica gel treatment. The results of this study demonstrate that

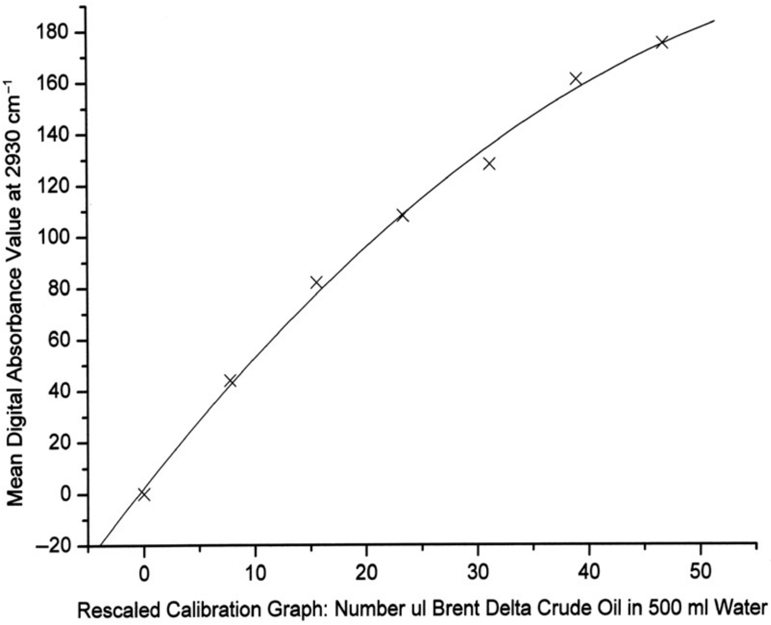

Figure 4. SFE vessel bypass calibration graph, with rescaled *x*-axis, obtained for Brent Delta crude oil using a fixed wavelength SFE-IR system.
Note: The equation calculated using Microcal Origin^{TM} software to perform the polynomial fit is $y = 2.33 + 5.43x - 0.037x^2$.

Table 1. Summary of fixed wavelength SFE-IR quantification results with and without silica gel treatment for 500 mL water samples spiked with Brent Delta crude oil.

Actual amount of oil in 500 mL spiked water samples μL^{-1}	Mean calculated[a] amount of oil in 500 mL spiked water samples with and without silica gel treatment μL^{-1}	Standard deviation,[b] expressed as amount of oil in 500 mL water samples with and without silica gel treatment μL^{-1}	Accuracy (%)[c] with and without silica gel treatment
5 (8.4)[d]	4.6 [5.2][e]	0.3 [0.4][e]	92.0 [96.0][e]
10 (16.8)	9.2 [10.5]	0.6 [1.0]	92.0 [95.0]
20 (33.6)	21.1 [22.6]	1.0 [1.7]	94.5 [87.0]
40 (67.2)	37.6 [41.8]	2.2 [3.6]	94.0 [95.5]

Notes: [a]For each spike level $n = 6$ with silica gel treatment and $n = 3$ without silica gel treatment; [b]Calculated using $n-1$ degrees of freedom; [c]Accuracy (%) = 100 −| 100− [(mean calculated value/actual value) × 100] |; [d]Values in parentheses are equivalent mg L^{-1}; [e]Values in square brackets obtained for Brent Delta crude oil without silica gel treatment

the SFE-IR method using a fixed wavelength IR detector, modified to fit a 40 mm path length IR cell, provides accurate oil-in-water analyses through the range up to and beyond the OSPAR permitted maximum discharge limit [15] for offshore oil and gas platforms' produced water.

Throughout these studies a 1 μL aliquot of Brent Delta crude oil was periodically analysed, without the silica gel treatment procedure, using the SFE vessel bypass valve configuration. This was performed to establish the stability of the fixed wavelength IR detector and to decide whether the fixed wavelength SFE-IR system needed recalibration. The procedure is such that if a 5% variation in digital absorbance values is obtained for the 1 μL Brent Delta crude oil stability standards then the fixed wavelength SFE-IR system is recalibrated. The criteria for this set of values is as follows: a 1 μL Brent Delta crude oil aliquot injected using the SFE vessel bypass valve configuration procedure without silica gel treatment is equivalent to analysing 16 μL Brent Delta crude oil in 500 mL of water [14]. Taking into account the density of Brent Delta crude oil this equates to 26.9 mg L^{-1} oil-in-water, close to the OSPAR maximum discharge limit of 30 mg L^{-1} [15]. Hence, allowing for a 5% drift in digital absorbance values, the tolerances ensure sufficient fixed wavelength IR detector stability in the current critical range of performance for the OSPAR offshore oil and gas operators. Comparative studies [19] have indicated that FTIR spectrometers are generally more stable and for a longer period of time than certain fixed wavelength IR detectors using the SFE-IR method. The Brent Delta crude oil used to perform the rapid on-line SFE vessel and stability check procedure was cold filtered prior to use. This was because the sample of Brent Delta crude oil contained suspended particulate matter including fine particles of sand that could serve to score the HPLC rotor face that is composed of relatively soft material. The Brent Delta crude oil used to spike water samples was not filtered since particulate matter is not extracted from water samples using the SFE-IR method. The SFE-IR method is extremely tolerant to water samples that contain very high levels of solids [12]. For real process water samples, that must be directly collected into the sample bottle from an approved turbulent sample point [8], the final oil-in-water measurement is calculated by applying a correction factor to accommodate for the fact that volumes other than exactly 500 mL water will be extracted. The actual volume of water extracted is determined by obtaining the mass of the sample being aware of the density of the process water at the temperature used to perform the SFE-IR method. This procedure enables the volumes of supercritical fluid carbon dioxide to extract real water samples to be determined and hence derivation of correction factors. It seems probable that silica gel treatment will reduce the amount of oil in real process waters contaminated with Brent Delta crude oil by an increased amount since such waters also typically contain polar fatty acids [1,15].

A silica gel treatment procedure using a prototype direct aqueous SFE system interfaced to an FTIR spectrometer to analyse finished oil products in water has been reported previously [13]. The method involved the manual preparation of high pressure silica gel treatment columns. The use of commercially available inexpensive pre-packed silica gel SPE cartridges, contained within a high pressure holder, for silica gel treatment now conveniently replaces that procedure. If the level of oil-in-water is below 30 mg L^{-1} it is possible to use a single SPE cartridge at least twice to perform silica gel treatment for water samples [19]. However, this minor saving of analysis cost is out weighed by the longer period of time required to clean the SFE-IR system since cleaning the SPE cartridge holder containing a previously used SPE cartridge presents many more surfaces. As with the SFE vessel, cleaning of the emptied SPE cartridge holder inner wall and other surfaces is more rapidly accomplished if the emptied SPE cartridge holder assembly is first cleaned with a swab moistened with ethyl ethanoate and then warm air dried. The re-use of SPE cartridges was not studied in great detail since current approved methods involving liquid–liquid extraction do not involve the re-use of silica

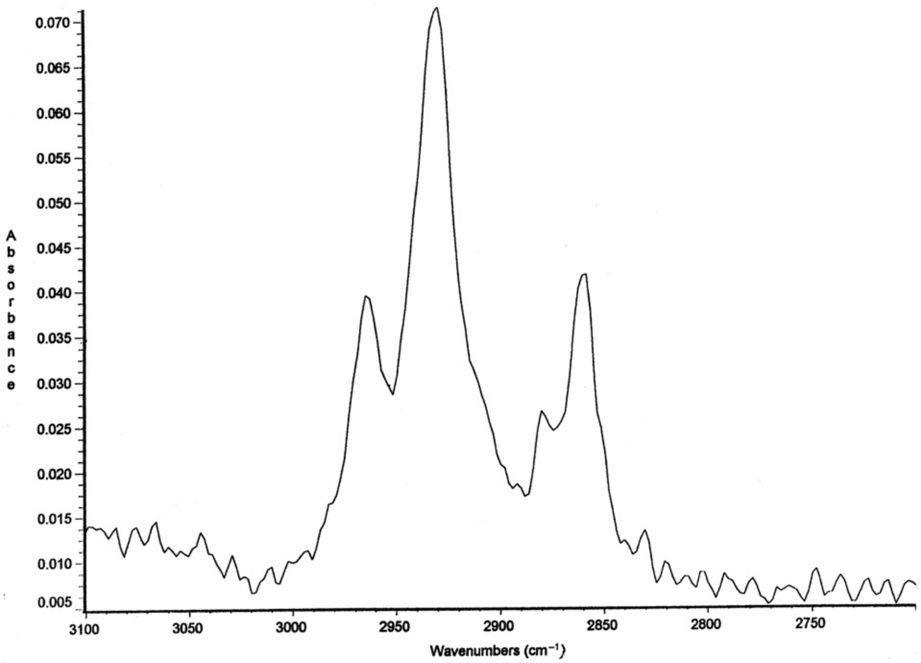

Figure 5. SFE-IR analysis using a FTIR spectrometer equipped with a 40 mm path length IR cell for a 500 mL water sample spiked with *n*-decane at the 0.5 mg L^{-1} level.

gel [5,6]. Since the silica gel remains tightly packed within used SPE cartridges this facilitates their convenient disposal. In comparison, gravimetric, GC and IR methods [1,5,6] using manual silica gel treatment following liquid–liquid extraction generate loose silica gel waste that must be dried prior to disposal and depending on the method, emptied columns must be subsequently cleaned. To help eliminate the possibility of cross-contamination, the SFE-IR method is largely self-diagnostic to ensure complete system cleaning between analyses [14]. Hence, apart from the sample bottle, no further dependence on meticulously cleaned auxiliary sample preparation equipment is required. Exhaust from the SFE vessel is vented through a hose that can be either inserted into a fume-hood or connected to a pipe that vents to atmosphere. Consequently, carbon dioxide disposal cost is minimal. In comparison IR methods involving liquid–liquid extraction require safe storage of used solvents that cannot be recycled until their eventual disposal. The SFE-IR method also solves another issue that is sometimes neglected, namely that solvents used in liquid–liquid extraction sample preparation methods are to some extent water soluble, for example the solubility of H-997 in water is 0.033 g 100 mL^{-1} [9]. Hence, disposal of water samples that have been extracted with conventional organic solvents is a potential source of inadvertently releasing these solvents into the environment.

A complete SFE-IR system can be assembled using different manufacturers' FTIR or fixed wavelength IR instruments which may be either brand new or previously purchased. Therefore, the exact specification of a single SFE-IR method detection limit value is not straight forward since it will be influenced by infrared system performance. In practice it is difficult to assess random digital noise values for fixed wavelength IR detectors. According to the manufacturer [20] of the fixed wavelength IR detector used in these studies, the fixed wavelength IR detector should provide a limit of detection approximating to that obtainable using an FTIR system equipped with the same IR cell. As shown in Figure 5, the direct aqueous SFE system interfaced to a FTIR instrument can provide an SFE-FTIR signal-to-noise ratio better than 5 : 1 for CH_2 ($\nu_{\mathrm{asymmetric}}$) absorbance measured at $2933\,\mathrm{cm}^{-1}$ for a 500 mL water sample spiked with *n*-decane at the $0.5\,\mathrm{mg\,L}^{-1}$ level.

5. Conclusions

The SFE sample preparation procedure has been developed to provide a means for the indefinite use of IR methods to measure oil-in-water using either fixed wavelength IR or FTIR instrumentation. Future international solvent legislation will not affect the laboratory scale use of carbon dioxide. The SFE-IR method can be directly performed with or without silica gel treatment for a single water sample. It is also possible to analyse a single water sample with and without silica gel treatment. The integrated SFE-IR method is designed to use an absolute minimum of sample manipulation stages, to reduce the risk of human error, since the sample bottle is sealed in the SFE vessel extraction chamber prior to analysis. In continuation of this design goal, the SFE-IR method has been modified to enable an optional rapid silica gel cleanup procedure using disposable SPE cartridges rather than manual preparation of silica gel columns. Although not described in this report, the SFE sample preparation system has been successfully interfaced [19] to other manufacturers' fixed wavelength IR detectors whose instruments use different sample presentation stages. Consequently, a range of flexible interfacing techniques have been developed to enable oil-in-water analyses using fixed wavelength SFE-IR systems. Due to the spectral transparency of supercritical fluid carbon dioxide, there is the potential to consider alternative detection means such as fluorescence with the direct aqueous SFE sample preparation system [16]. The fact that the United States Environmental Protection Agency has approved and published three SFE analytical procedures [14] is a source of reassurance concerning official acceptance of analytical SFE technology.

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