Sustainable oil-in-water analysis using a supercritical fluid carbon dioxide extraction system directly interfaced with infrared spectroscopy

Edward D. Ramsey,* Qiubai Sun, Zhiqiang Zhang, Wei Guo, Jing Y. Liu, Xiu H. Wu

School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China. E-mail: syphir2008@gmail.com

Abstract

A direct aqueous supercritical fluid extraction (SFE) system using carbon dioxide provides a sustainable means by which a vast range of industries may continue to depend on well established infrared (IR) techniques to determine oil-in-water. The SFE-IR method provides an environmentally friendly substitute for current national standard IR reference methods for measuring oil-in-water that rely on using increasingly restricted ozone depleting solvents whose manufacture is being phased out in accordance with international law. The SFE-IR analysis of a 500 mL water sample can be accomplished in 15 min. A rapid on-line SFE-IR calibration method has been implemented. With this calibration method, SFE-IR accuracy for determining diesel oil in 500 mL spiked water samples using single wave number measurement was 86.0%–98.8% with precision (RSD) ranging from 2.5%–7.0%. Using a general purpose calculation which involves measuring infrared absorbance values at three different wave numbers, SFE-IR method accuracy for determining diesel oil in 500 mL spiked water samples was 83.7%–92.2% with RSD 1.0%–9.3%. Data is presented that indicates current long established national standard IR reference methods involving three wave number calculations should be reviewed since, without careful consideration, the inclusion of calculated aromatic hydrocarbon species contributions to final oil-in-water concentration values may provide less accurate results.

Key words: oil-in-water; supercritical fluid extraction; infrared spectroscopy; sustainable; green technology

DOI:10.1016/S1001-0742(09)60276-X

Introduction

Due to grave concerns regarding damage to stratospheric ozone, the Montreal Protocol treaty was introduced in 1987 to limit and prevent further damage to this vital global protection layer for mankind. The Montreal Protocol has been hailed by the former Secretary General (Annan, 2007) to the United Nations as being the most successful international treaty thus far whose initial attention was focussed on eliminating chlorofluorocarbons (CFCs) as the major ozone depleting solvents (ODS). The relevant solvent legislation for developed countries affecting oil-in-water measurement has been reviewed to year 2008 (Ramsey, 2008). The Montreal Protocol considers that the world nations are divided into two categories, these being the so called developed and developing countries. In order to overcome political difficulties, the Montreal Protocol has set different agendas for developed and developing countries to phase out the manufacture and supply of ODS, thus providing the developing countries with a "catch-up" period as their industrial bases rapidly develop. Thus, both China and India were allowed supply of carbon tetrachloride for extracting oil from water for IR analysis until 1st January 2010 whereas the total phase out date

for supply of carbon tetrachloride to measure oil-in-water for developed countries was 1st January 1995. Phase out dates for various categories of solvents including CFCs and hydrochlorofluorocarbons (HCFCs) are available (Annan, 2007).

Oil-in-water analysis is an absolutely key environmental measurement which a vast number of diverse industries are mandated to perform, some examples include: onshore and offshore gas and oil industries, oil refineries, steel manufacturers, engineering industries that use oil emulsions to lubricate and cool cutting tools, mining industries, car manufacturers, food manufacturers, power plants and sewage plants. Ultimately, environmental agencies perform checks to ensure compliance with national oil-in-water discharge limits.

For many decades IR has been the main method for measuring oil-in-water. Typical national standard methods involve subjecting a water sample to a liquid-liquid extraction (LLE) sample preparation procedure using a suitable organic solvent. The separated organic solvent is then subjected to a drying stage using sodium sulphate. Finally, oil-in-water determination is performed by measuring IR absorbance of the CH_2 groups at 2930 cm^{-1} ($\nu_{asymmetric}$) or the use of an equation using absorbances measured at three wave numbers obtained for different hydrocarbon

functional groups.

For IR analysis of oil-in-water only three organic solvents are currently available, tetrachloroethene (TTCE) initially endorsed by the UK government Department of Trade and Industry (DTI, 2005) and the proprietary solvent 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane (S-316). Since TTCE is a suspected carcinogen, less toxic S-316 has been widely adopted by developed countries despite being relatively very expensive. In 2004 the American Society for Testing Materials (ASTM) approved and published ASTM Method D 7066-04 that uses S-316 as a means for the IR determination of oil-in-water (ASTM, 2004). However, the manufacturer of S-316 (Horiba, Japan) is already replacing S-316 with another Horiba proprietary solvent. This replacement solvent known as H-997 is a complex mixture whose principal components are 3,3-dichloro-1,1,1,2,2-pentafluoropentane (HCFC-225ca) and 1,3-dichloro-1,1,2,2,3-pentafluoropentane (HCFC-225cb). However, both S-316 and H-997 are HCFCs with ozone depleting potential. The current total phase out date for HCFCs for developed countries has been set for 1st January 2020 whereas the total phase out date for HCFCs for developing countries is 1st January 2040. The current phase out date for TTCE in developed countries is 2030 (Rintoul, 2006). Therefore, the use of TTCE, S-316 or H-997 represent stop-gap measures and do not provide sustainable means to measure oil-in-water using established IR methods involving solvent extraction of oil from water.

In response, the United States Environmental Protection Agency (EPA) has introduced gravimetric Method EPA 1664A (US EPA, 2000) that uses n-hexane for LLE of water samples. This method is designed to determine n-hexane extractable material which is not adsorbed by silica gel treatment (SGT), the assumption being that the dried n-hexane extracted residue is oil, free from any interfering co-extracted material. As a total alternative to IR and gravimetric methods, a gas chromatography (GC) method involving n-pentane LLE has been introduced by the International Organisation for Standardisation (ISO). GC Method ISO 9377-2 uses flame ionisation detection (FID) with the total integration of hydrocarbon peak areas being used to determine the level of oil-in-water (DTI, 2005; ERDU-OED, 2005). Method ISO 9377-2 as modified by the European nations party to the Oslo and Paris Convention (OSPAR) for "The Protection of the Marine Environment of the North East Atlantic" is now performed on many OSPAR offshore oil and gas platforms despite requiring the use of hydrogen for FID operation and generally being more complex to operate and maintain than IR methods. Additionally, the GC method provides results that do not correlate with IR methods meaning that historical IR data bases cannot be used to determine relative discharge performance.

In its supercritical fluid phase environmentally benign carbon dioxide is remarkably versatile since by controlling its density it can selectively imitate the solvating characteristics of a wide range of conventional organic solvents (Luque de Castro et al., 1994). Of particular relevance, the density of carbon dioxide can be controlled to imitate the solvating properties of carbon tetrachloride, n-hexane and n-pentane. Hence, supercritical fluid carbon dioxide appears to be the ideal candidate to measure oil-in-water using IR since its availability will not be affected by increasingly stringent solvent legislation.

The automated SFE-IR method uses patented (Ramsey, 2001, 2004) technology that ensures laboratory errors are reduced since an absolute minimum of sample manipulation stages are involved. Due to its industrial significance, at a very early stage the prototype SFE-IR instrument attracted the attention of the United Nations Environment Programme (United Nations, 2001). An independent trial of the SFE-IR method sponsored by the UK DTI, British Petroleum and Norway's Statoil (State Oil), has been performed, co-ordinated by the UK National Engineering Laboratory. The trial largely focussed on measuring various types of crude oils and gas condensates typically associated with the discharge of process water from offshore oil and gas platforms. The trial report (Yang, 2003) although generally very positive does make some suggestions regarding further improvements.

This manuscript seeks to demonstrate that the further developed and improved SFE-IR method for the analysis of oil-in-water provides a sustainable, inexpensive green solution for the continued use of IR methods for this vital environmental measurement. Additionally, results are presented that demonstrate long established three wave number IR calculations used to measure oil-in-water should be critically reviewed since reliance on automatic inclusion of an aromatic IR absorbance value can be a source of error without careful consideration.

1 Experimental

An SFX^{TM} 1010 automated oil-in-water supercritical fluid extractor (all enquiries to the first named author) 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 until a SFE target pressure of 20.7 MPa was attained. The main body of the SFE vessel used in these studies was constructed from a solid bar of 316 grade stainless-steel in accordance with strict regulations of the American Society of Mechanical Engineers VIII standards for such equipment. The SFE-IR studies were performed using a PerkinElmer (Shelton, CT, USA) Spectrum One Fourier transform infrared (FT-IR) spectrometer with the IR spectra obtained over the range 4000–400 cm^{-1} using a resolution of 4 cm^{-1}, with 10 scans summed per spectrum. All SFE-IR studies were performed using a high pressure IR inspection cell (all enquiries to the first named author) whose pathlength was 40 mm. 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). Analytical grade samples of n-hexadecane, toluene, and 2,6,10,14-tetramethylpentadecane (pristane) were obtained from Sigma-Aldrich (Poole, Dorset, UK).

A sample of automobile diesel oil was obtained from a garage.

2 Results and discussion

2.1 Rapid on-line SFE-IR system calibration procedure

Previous reports have described the calibration of early version SFE-IR systems using 500 mL spiked water samples as calibration standards (Minty et al., 1998, 2000). Although this method provides a satisfactory procedure to construct SFE-IR calibration graphs it is relatively time consuming. Primarily, this is because the analysis of each spiked 500 mL water calibration standard using the full SFE-IR procedure takes approximately 15 min and generally three calibration standards are analysed at each calibration level. Also, between analysing each calibration standard the whole SFE system including the 1 L capacity SFE vessel has to be carefully cleaned *in situ* using carbon dioxide. The cleaning procedure has been fully described (Minty et al., 2000) and although being time consuming is self-diagnostic to ensure SFE-IR system cleanliness thereby eliminating the possibility of cross-contamination.

In order to greatly reduce the amount of time required to calibrate the SFE-IR system a rapid on-line calibration procedure has been developed and previously described in detail (Ramsey, 2008) that does not require the use of 500 mL spiked water calibration standards. Figure 1 shows the plumbing and valve configuration of the direct aqueous SFE-IR system used in these studies which unlike a previous SFE-IR configuration (Ramsey and Guo, 2008) did not incorporate an optional SGT clean-up stage. Briefly, the new calibration method involves selecting the valve configuration shown in Fig. 1b. With this configuration it is possible to make manual injections of the calibration oil via high performance liquid chromatography (HPLC) valve (H) so that aliquots of oil are rapidly transferred into the high pressure IR cell (L). The electronically actuated valve (F) remains closed during the calibration process which effectively bypasses the SFE vessel. Since the volume of the IR cell and associated transfer lines is small in comparison to the void volume of the SFE vessel containing a 500 mL water sample, SFE target pressure is rapidly reached typically in 1 min facilitating rapid analyses of calibration standards. After an SFE vessel bypass calibration standard has been analysed, the IR cell is vented and once valve (N) is closed again the high pressure IR cell is cleaned *in situ* using supercritical fluid carbon dioxide. A sufficient number of IR cell clean cycles are performed to obtain a zero IR absorbance value to ensure the IR cell is cleaned. The small volume of the IR cell means that the SFE vessel bypass calibration procedure provides the additional advantage of more rapid cleaning between running calibration standards.

Following consultation with the originator (Whittle, 1998) of Her Majesty Stationary Office (HMSO) three wave number infrared method (HMSO, 1983) for measuring oil-in-water, diesel (aliphatic chain lengths C_{10}–C_{22})
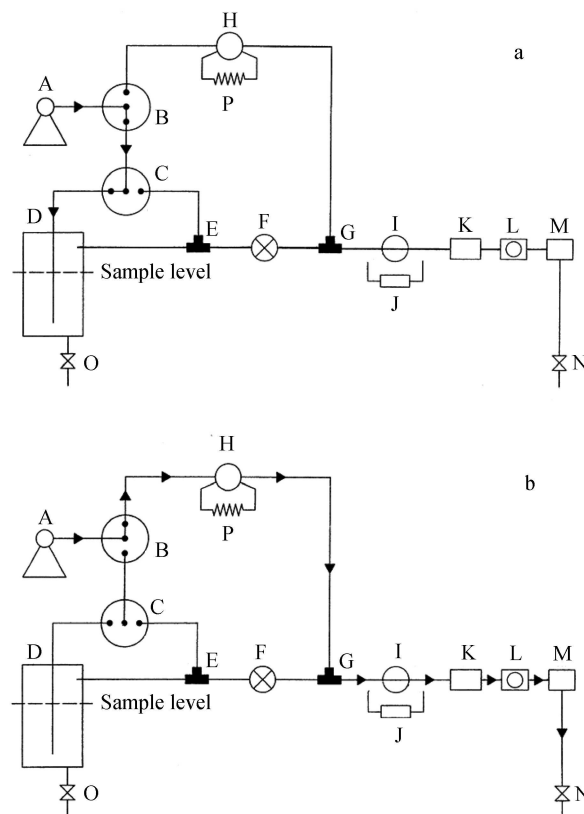

Fig. 1 SFX^{TM} 1010 SFE valve configurations to perform SFE of water samples (a) and bypass calibration procedure (b). A: liquid carbon dioxide pump; B: supply valve; C: distribution valve; D: SFE vessel; E: T piece; F: automatic valve; G: T piece; H: HPLC injection valve; I: port for optional silica gel cleanup selection valve; J: optional silica gel cartridge holder; K: union; L: high pressure IR inspection cell; M: choke; N: exhaust valve, O: exhaust; P: HPLC valve loop.

was selected as representative oil whose composition is typical of that found in engineering and trade process discharge waters. Figure 2 shows examples of IR bypass calibration spectra obtained for diesel through the range 0.5–3.0 μL incremented by 0.5 μL using a 5 μL HPLC
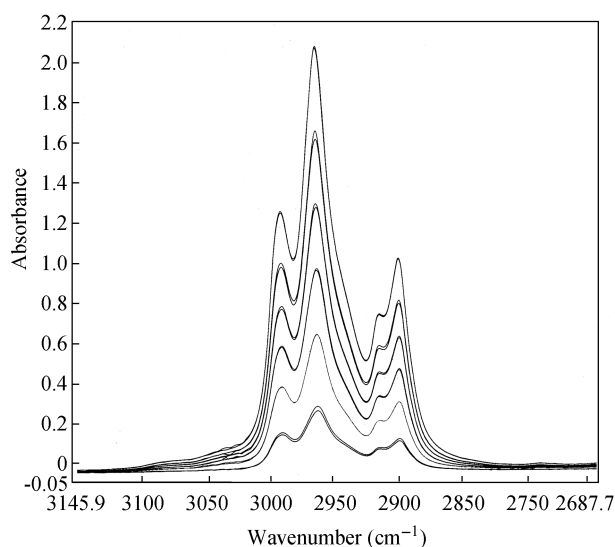

Fig. 2 Series of duplicate spectra obtained for 0.5–3.0 μL diesel, incremented by 0.5 μL through the range, using the SFE bypass calibration method.

syringe. In some instances the spectra obtained for the individual sets of diesel calibration standards superimpose. The SFE conditions used by the SFE-IR method are selected such that the solvating strength of supercritical fluid carbon dioxide is controlled to imitate (Luque de Castro et al., 1994) the extraction capability of n-hexane which is widely used for approved GC and gravimetric oil-in-water reference methods which involve a LLE stage.

As has been previously reported (Ramsey, 2008; Ramsey and Guo, 2008), the SFE-IR spectra obtained for oils exhibit shift to higher wave numbers. A linear calibration graph was constructed expressing the average CH_2 ($\nu_{asymmetric}$) absorbance values measured at 2933 cm^{-1} for each set ($n = 3$ per set) of calibration standards as a function of the number of μL diesel manually injected via the HPLC valve (H). The high pressure IR cell cleaned *in situ* provided zero absorbance values at 2933 cm^{-1}. With the origin being considered a data point, the seven point SFE-IR calibration graph constructed using a linear fit through the origin provided a correlation coefficient of 0.99843. After this the SFE-IR vessel bypass calibration procedure involves the re-scaling of the X-axis values such that the equivalent number of μL diesel spiked into 500 mL water samples is expressed. In practice this is achieved by comparing the SFE-IR results obtained for 500 mL diesel spiked water samples with the first constructed calibration graph such that a conversion factor may be obtained. From these studies it was determined that 500 mL water samples spiked with 20 μL diesel provided average absorbance values at 2933 cm^{-1} equivalent to 1.25 μL diesel manually injected using the valve configuration shown in Fig. 1b. Hence, the conversion factor is such that a manual injection of 0.5 μL diesel using the bypass calibration procedure equates to 8 μL diesel spiked into a 500 mL water sample. The high pressure IR cell and associated transfer lines have a volume of 10 mL. Hence, in order to account for the dilution factor used to re-scale the X-axis of the SFE vessel bypass calibration graph, it is determined that the SFE vessel has a void volume of 150 mL when loaded with a sample bottle containing 500 mL water sample. This means that a water sample of exact 500 mL volume is extracted using a total of 160 mL supercritical fluid carbon dioxide. The re-scaled X-axis SFE-IR calibration graph obtained for diesel is shown in Fig. 3.

In order to evaluate the SFE-IR bypass calibration procedure three sets ($n = 3$ per set) of 500 mL water samples spiked with known levels of diesel were analysed using the SFE-IR valve configuration shown in Fig. 1a. The analysis of a water sample entails inserting the sample bottle directly into the SFE vessel chamber which is then rapidly sealed and then initiating the water sample extraction programme. Electronically actuated valve (F) remains closed until the SFE target pressure of 20.7 MPa is attained at which point pump (A) automatically stops dispensing liquid carbon dioxide. After a short period of time valve (F) opens such that a plug of supercritical fluid extract flows into the high pressure IR cell which is isolated at atmospheric pressure whilst the water sample is subjected to the SFE cycle. The transfer of a 10 mL aliquot of supercritical extract
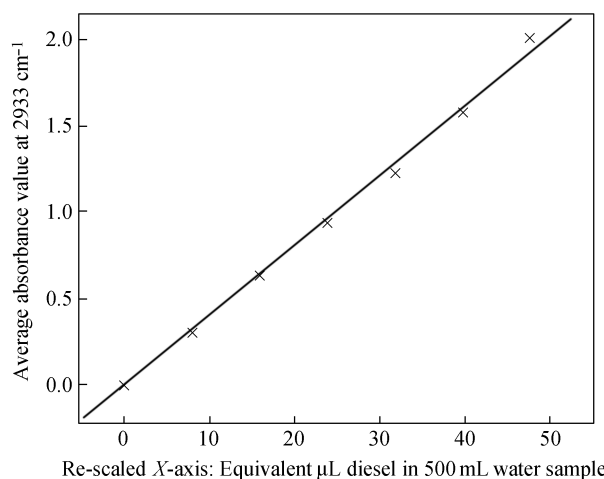

Fig. 3 SFE vessel bypass calibration graph with re-scaled X-axis, correlation coefficient 0.99843.

from the SFE vessel to the high-pressure IR analysis cell results in a temporary lowering of the SFE target pressure which is restored throughout the SFE system by pump (A) delivering more carbon dioxide until the SFE target pressure of 20.7 MPa is restored. After target pressure is re-established and after a short period of time to ensure re-stabilization of the SFE target pressure, valve (F) closes and infrared analysis is commenced. Figure 4 shows the SFE-IR spectra obtained for three sets ($n = 3$ per set) of 500 mL water samples spiked with diesel. The quantity of diesel in each 500 mL water sample is then calculated by interpolation of absorbance values measured at 2933 cm^{-1} using the calibration graph shown in Fig. 3.

The results of these single wave number quantification studies are shown in Table 1. The results obtained demonstrate the capability of the SFE-IR method to accurately determine oil-in-water using the rapid SFE-IR bypass calibration method. Importantly, the results shown in Table 1 clearly demonstrate that the SFE-IR method is well suited to determine discharge limits of oil-in-water in produced water discharged from offshore oil and gas platforms. Current limits set by various nations typically specify 30–40 mg/L (30–40 ppm) as the upper oil-in-water discharge limit range (Veil, 2006) for offshore operators. Additionally, the report of an independent SFE-IR trial (Yang, 2003) performed using 500 mL spiked water calibration standards concluded that the single wave number SFE-IR method provides comparable results in terms of accuracy to the DTI approved IR method using TTCE with manual LLE for sample preparation. The full development of the rapid SFE-IR bypass calibration procedure now affords higher precision for obtaining sets of calibration spectra compared with the use of 500 mL spiked water calibration standards.

SFE-IR limits of detection (LOD) are influenced by the performance of individual manufactures' IR systems. Hence, it is not possible to specify a single LOD value since the SFE system can be interfaced to a wide range of new or previously purchased IR instruments. However, using a modern FT-IR system n-decane in water at the 0.5 mg/L level should provide a CH_2 ($\nu_{asymmetric}$) signal:noise

Table 1 Summary of single wave number quantitative results obtained for SFE-IR analyses of diesel oil in 500 mL spiked water samples using the SFE vessel bypass calibration method.

Spike level (μL)	Mean calculated level [a] (μL)	Standard deviation[b] (μL)	Accuracy[c] (%)
10 (17.2)	11.4 (19.6)	0.7 (0.4)	86.0
20 (34.4)	20.4 (35.1)	0.9 (0.5)	98.0
40 (68.8)	40.5 (69.7)	0.7 (0.4)	98.8

Concentration values expressed in mg/L are shown in parentheses.
[a] For each spike level $n = 3$; [b] calculated using $n-1$ degrees of freedom; [c] accuracy (%) = 100 – |100 – [(mean calculated value/actual value) × 100]|.
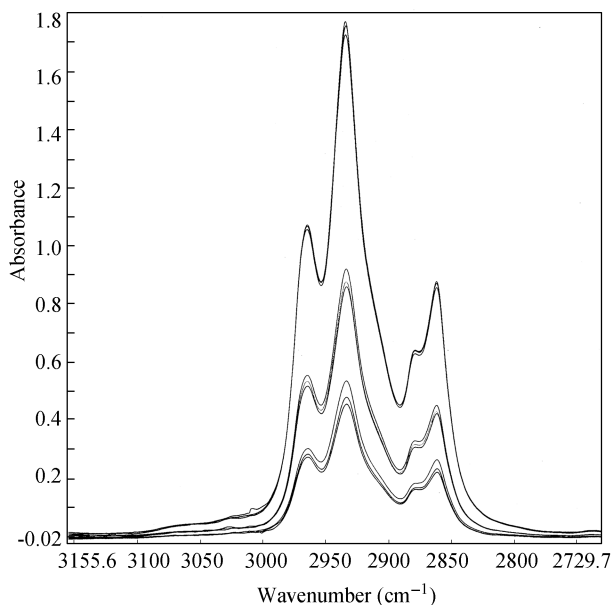

Fig. 4 SFE-IR spectra obtained for three sets ($n = 3$ per set) of 500 mL water samples spiked with 40, 20 and 10 μL diesel.

ratio measured at 2933 cm^{-1} approximating to 5:1 using a 40 mm pathlength cell of 10 mL volume (Ramsey and Guo, 2008).

Routine manual injection of a fixed aliquot of reference oil using the valve configuration shown in Fig. 1b has also been found to be an extremely useful, rapid and convenient way to check IR system stability especially for fixed wavelength IR detectors that tend to be less stable than FT-IR instruments.

2.2 Application of the three wavenumber HMSO calculation with the SFE-IR method for determining diesel in water

In situations where water samples are gathered from a sample point which provides mixed discharges from different manufacturing processes the precise composition of the combined oils vary. For these situations, IR procedures involving the use of equations that involve measuring the absorbance values of extracted oils at three wave numbers have become firmly established. Three wave number equations, including that originally published by Her Majesty Stationary Office (HMSO, 1983), typically take into account (Whittle et al., 1980; McCrum and Whittle, 1982) the different molar absorptivities of the CH$_3$ (2960 cm^{-1}), CH$_2$ (2930 cm^{-1}) and the aromatic CH (3030

cm^{-1}) functional groups to enable final oil-in-water calculation. The procedure initially involves the construction of three equations for three reference compounds, each rich in either CH$_3$, CH$_2$ or CH aromatic protons. The HMSO equation is as follows and is applied to each set of IR absorbance values for standard solutions of the reference compounds (Eq. (1)):

$$c = xA_{2930} + yA_{2960} + z(A_{3030} - A_{2930}/F) \qquad (1)$$

where, c is concentration (mg/L), coefficients x, y and z relate to the molar absorptivities of the CH$_2$, CH$_3$ and aromatic CH groups respectively, A is absorbance value at the specified wavenumber and F is a correction factor calculated (Whittle et al., 1980) from n-hexadecane absorbances by basing the correction on the absorbance at 2930 cm^{-1} and letting $F = A_{2930}/A_{3030}$. The three reference compounds used to derive the x, y, z and F coefficients of the SFE-IR method were n-hexadecane, pristane and toluene. The derivation of the coefficient values takes into account the 10 mL volume of the 40 mm pathlength high pressure IR inspection cell used throughout these studies. The rapid SFE vessel bypass calibration system procedure was used to rapidly introduce weighed 1–3 μL HPLC syringe aliquots of sets ($n = 3$ per set) of the three individual reference compounds into the high pressure IR inspection cell. Due to the SFE-IR spectra showing a shift to higher wavenumbers, the absorbance values for the CH$_2$, CH$_3$ and aromatic CH groups were measured at 2933, 2965 and 3035 cm^{-1}, respectively. The values of the coefficients were calculated as: $x = 63.4$, $y = 84.4$, $z = 671$ and $F = 91.65$. These coefficients can then be applied into new Eq. (2), constructed to correct for the SFE-IR wave number shift and 40 mm pathlength infrared cell. The equation which takes into account other physical parameters is (Eq. (2)):

$$c = [xA_{2933} + yA_{2965} + z\{A_{3035} - (A_{2933}/F)\}]40VD/ML \qquad (2)$$

Terms having been previously specified with additional terms being: V is volume of supercritical fluid carbon dioxide used to extract the sample ($V = 160$ mL for a single SFE-IR analysis of a 500 mL water sample), D is the dilution factor (value of 1 for a 10 mL volume IR cell), M is mass of sample and L is IR cell pathlength in mm. For real world samples the value of V has to be adjusted using the SFE-IR method. This is because the recommended (DTI, 2005) sample collection protocol for process water samples entails gathering the sample directly into the sample bottle from a turbulent discharge stream. Consequently, it is highly improbable that a water sample of exactly 500 mL will be collected. Hence, individual values of V need to be calculated when volumes other than 160 mL supercritical fluid carbon dioxide are used to extract water samples. This is achieved in practice by obtaining the mass of the process water sample, term M in Eq. (2), and then determining the volume of the process water sample being aware of its density at the temperature used to perform SFE-IR analysis. Following

this the correct value of V is considered which enables the correct oil-in-water concentration to be determined. It is possible to use alternate interchangeable different pathlength high pressure IR cells other than 40 mm pathlength to accommodate for the concentration of the supercritical fluid extract. All standard high pressure IR cells are constructed to provide a 10 mL volume. This means that if the 40 mm pathlength cell used to calculate the values of x, y and z coefficients and F value is changed with a different pathlength standard IR cell to measure the oil content of a water sample then Eq. (2) corrects for change in pathlength according to Beer-Lambert law.

The same SFE-IR spectra obtained for the three sets (n = 3 per set) of 500 mL water samples spiked with diesel, Fig. 4, that had been used to evaluate the rapid SFE vessel bypass calibration procedure were also used to apply the SFE-IR method using the three wave number Eq. (2) derived from the HMSO method. Using the absorbance values measured at CH_2, CH_3 and aromatic CH groups at the previously specified wave numbers the quantity of diesel in the spiked water samples was calculated. The results of these calculations, summarized in Table 2, serve to demonstrate that the modified three wave number HM-SO calculation (Eq. (2)) using the SFE-IR method are in good general agreement with those shown in Table 1 using the single wave number SFE vessel bypass calibration procedure and analysis method.

When the precise identity of the oil-in-water to be analysed is effectively invariant, e.g., a crude oil from a specific oil field, it is recommended that the more accurate SFE-IR bypass calibration procedure with single wave number analysis should be used. This SFE-IR method also allows the use of simple, compact, field-portable fixed wavelength infrared detectors (Ramsey and Guo, 2008) often used by field personnel. Since GC-FID Method ISO-9377 as modified by OSPAR does not consider the contributions of the aromatic species: benzene, toluene, ethylbenzene and the isomers of xylene to the final oil-in-water calculation (DTI, 2005; ERDU-OED, 2005), Table 2 also indicates the quantities of diesel calculated to be present in the spiked water samples if the aromatic contribution is removed from Eq. (2). The partial application of Eq. (2) to the SFE-IR results obtained for diesel provides more accurate values. This is attributed to the observation, Fig. 4, that the aromatic contribution calculated for the diesel SFE-IR spectra use absorbance values measured at 3035 cm^{-1} arise

from absorbance tailing phenomena rather than clearly defined aromatic absorbance signals. Hence, on this occasion the value calculated for the correction factor F does not totally eliminate the peak tailing contribution made to the aromatic absorbance value when Eq. (2) is fully applied. This was the preliminary finding regarding diesel in a detailed SFE-IR study largely concerning the determination of crude oil-in-water (Ramsey, 2008). As shown in Fig. 4, depending upon diesel concentration different degrees of signal tailing at 3035 cm^{-1} are observed in the aromatic region. Hence, stemming from these additional studies involving diesel there is now confirmation that a fundamental problem may arise with full application of three wave number equations derived from Eq. (1). The problem is that the value of F, a calculated constant can only compensate for situations where irrespective of oil-in-water concentration peak tailing in the aromatic region is also constant. In view of this apparent limitation, full application of three wave number equations using a baseline correction factor designed to compensate for signal tailing in the aromatic region should in the authors' opinion be critically reviewed. Such three wavenumber equations have formed the basis of several national standard IR methods for many decades and are routinely used without question. However, full implementation of three wavenumber calculations seems only applicable to those situations where a clear aromatic signal is observed. This would avoid calculating an oil-in-water contribution from a baseline signal whose value apparently varies with concentration of aliphatic hydrocarbons. Figure 5 illustrates the point since the three aromatic IR absorbance values observed for benzene can be accurately estimated despite being detected on a tailing baseline signal.

When real process water samples are analysed environmentally benign gaseous carbon dioxide exhaust from the SFE-IR system is vented to atmosphere either directly through a simple laboratory exhaust pipe or via a fumehood. This is because industrial water samples typically contain noxious compounds such as hydrogen sulphide (Nordic Council of Ministers, 2003) which are also extracted using the SFE-IR method. In comparison IR and

Table 2 Summary of quantitative SFE-IR results for diesel oil in 500 mL spiked water samples derived using a general purpose three wave number calculation method

Spike level (mg/L)	Mean calculated level[a] (mg/L)	Standard deviation[b] (mg/L)	Accuracy[c] (%)
17.2	20.0 (17.6)	1.6 (1.7)	83.7 (97.7)
34.4	37.1 (32.0)	1.2 (1.2)	92.2 (93.0)
68.8	75.2 (64.8)	0.7 (0.8)	90.0 (94.2)

Values in parentheses are those calculated by removing the aromatic contribution.
[a] For each spike level $n = 3$; [b] calculated using $n - 1$ degrees of freedom; [c] accuracy (%) = 100 − | 100 − ((mean calculated value/actual value) × 100)|
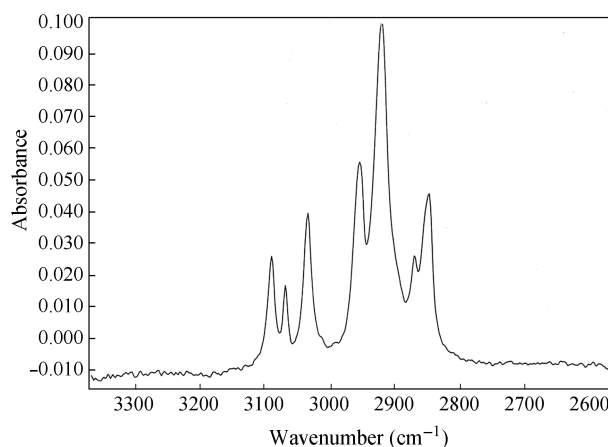

Fig. 5 SFE-IR spectrum obtained for a 500 mL water sample spiked with 22 mg benzene and 7.3 mg n-decane, equivalent to 44 and 14.6 mg/L, respectively.

GC methods using LLE sample preparation require the safe storage of used extraction solvents prior to their safe disposal.

3 Conclusions

The results of this current oil-in-water study further demonstrate that the SFE-IR method provides a sustainable green procedure for using relatively simple IR procedures for this vital environmental protection measurement. Furthermore, as demonstrated by the results of this study, automatic full implementation of oil-in-water IR calculations involving three different wavenumbers may not be applicable in circumstances where no clear aromatic IR signals are detected. Due to the vast number of oil-in-water analyses that must be performed, estimated at many millions annually on a global basis (Nordic Council of Ministers, 2003), the arrival of the further developed SFE-IR method is of industrial significance. The use of TTCE, S-316 and H-997 currently provide a non-sustainable means to continue the use of IR methods using traditional LLE sample preparation techniques. However, the long term availability of the cheap, ubiquitous and inexhaustible supply of carbon dioxide is absolutely assured by virtue of biological activity. The SFE-IR method involves an absolute minimum of sample handling stages and apart from the sample bottle no other glass-ware is required. This greatly reduces the risk of errors associated with manual sample manipulation stages and the dependency on the use of meticulously clean auxiliary laboratory glass-ware. The SFE-IR method uses instrumentation that has been designed to be: safe, environmentally friendly, cost effective, compact and easy to use and the achievement of these goals are amongst the findings of the independent trial report (Yang, 2003). Use of the SFE-IR method also means that historical IR data bases compiled over many years can be consulted to determine current relative discharge performance. The further developed SFE-IR method now offers the opportunity for the indefinite use of IR measurements to determine oil-in-water free from concerns about future solvent legislation.

References

Annan K, 2007. The ozone hole. 1–3. http://www.theozone hole.com/montreal.htm

ASTM, 2004. Standard Test Method for Dimer/Trimer of Chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination, American Society for Testing Materials, Method Designation D 7066-04, ASTM, West Conshohocken, PA 19428-2959, United States. 1–9. www.astm.org

DTI, 2005. Guidance Notes for The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges Part 1: Notes The Offshore Petroleum Activities (Oil Pollution Prevention and Control Regulations). Department of Trade and Industry, United Kingdom. 1–51. http:// www.og.dti.gov.uk/environment/Samplinganalysis_part1_140906.doc

ERDU-OED, 2005. Guidance Notes on The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharge, Part 2: DTI Approved Oil in Water Analysis Reference Methods. The Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulations. Energy Resources and Development Unit. Offshore Environment and Decommissioning (ERDU-OED), United Kingdom. 1–36. http://www.producedwaterclub.com/ne/upload/gnote-Part2.pdf

HMSO, 1983. The Determination of Hydrocarbon Oil in Waters by Solvent Extraction and either Infra Red Absorption or Gravimetry. Her Majesty's Stationary Office, London.

Luque de Castro M D, Valcarcel M, Tena M T, 1994. Analytical Supercritical Fluid Extraction, Springer, Berlin. 88–119.

McCrum W A, Whittle P J, 1982. Infrared determination of petroleum oil – Part II Extraction from water and removal of interferences. *Analyst*, 107(1278): 1081–1085.

Minty B, Ramsey E D, Davies I, James D L, O'Brien P M, Littlewood M L, 1998. Analysis of oil in water at the low-ppm level using direct supercritical fluid extraction coupled online with infrared spectroscopy. *Analytical Communication*, 35: 277–280.

Minty B, Ramsey E D, Davies I, 2000. Development of an automated method for determining oil in water by direct aqueous supercritical fluid extraction coupled on-line with infrared spectroscopy. *Analyst*, 125: 2356–2363.

Nordic Council of Ministers, 2003. Use of Ozone Depleting Substances in Laboratories. TemaNord 2003:516, Copenhagen. 1–170. http://www.norden.org/is/utgafa/utgefid-efni/2003-516?set_language=is

Ramsey E D, 2001. United States Patent No. US 6,168,955 B1.

Ramsey E D, 2004. European Patent No. EP 0873507 B1.

Ramsey E D, 2008. Determination of oil-in-water using automated direct aqueous supercritical fluid extraction interfaced to infrared spectroscopy. *The Journal of Supercritical Fluids*, 44(2): 201–210.

Ramsey E D, Guo W, 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.

Rintoul S, 2006. New infrared methods for analyzing produced water. *World Oil Magazine*, 227 (12): 1–4.

United Nations, 2001. Infra-red analysis of oil in water. United Nations Asian and Pacific Centre for Transfer of Technology, New Delhi. *Ozone Layer Protection*, 4(48): 9–10.

United States EPA, 2000. Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136). United States Environmental Protection Agency, Office of Water. http://www.epa.gov/ water-science/methods/1664guide.pdf

Veil J A, 2006. Why are Produced Water Discharge Standards Different Throughout the World? Environmental Science Division Argonne National Laboratory. 13th IPEC, San Antonio, Texas, October 19th. ipec.utulsa.edu/Conf2006/Papers/Veil_prodwater.pdf

Whittle P J, 1998. Personal communication.

Whittle P J, McCrum W A, Horne M W, 1980. Infrared determination of petroleum oil: New approaches to the calculation. *Analyst*, 105(1252): 679–684.

Yang M, 2003. Testing and Evaluation of the Supercritical Fluid Extraction and Infrared (SFE-IR) Oil-in-Water Analysis Method. Project No. SFE001, Report Number2003/223, National Engineering Laboratory, United Kingdom 1–71. http://www.og.dti.gov.uk/ environment/SFEInfraredOIW(TUVNEL).pdf