

A NEW ENVIRONMENTALLY CLEAN, RAPID, AUTOMATED METHOD FOR DETERMINING OIL/GREASE IN WATER USING SUPERCRITICAL EXTRACTION COUPLED ON-LINE WITH INFRARED TECHNOLOGY.

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As of January 2002 the supply of carbon tetrachloride and Freon 113 ceased to be available to those laboratories using long established infrared (IR) methods to determine oil and grease in water.

A new direct aqueous supercritical fluid extraction (SFE) system for IR spectroscopy has been specifically developed (US patent granted, other patents pending) to allow the determination of oil, grease and total petroleum hydrocarbons in: surface, sea-waters, industrial and domestic waste waters.

The new sample preparation system enables direct extraction of aqueous samples using supercritical fluid carbon dioxide as a replacement solvent and has the capability to provide a long-term solution for those environmental and industrial organisations who have expressed a strong preference for retaining an IR based method. Depending upon physical parameters, the solvating strength of supercritical fluid carbon dioxide can be adjusted to match those of a wide range of conventional organic solvents including Freons, carbon tetrachloride and hexane. It also transpires that supercritical fluid carbon dioxide is completely infrared transparent in the region used to measure oils and greases. Consequently, the quality of the SFE-IR data shows high fidelity with that obtained using traditional IR methods that have become industry standards.

The new automated technique involves direct coupling of a CST Ltd. SFE system to either a fixed wavelength or scanning infrared spectrometer. Once the whole aqueous sample bottle is loaded within the SFE instrument, analysis is performed by depressing a single start button. Analysis of a 500 ml water sample takes approximately 15 min. After the aqueous sample has been analysed, the sample bottle containing the extracted water is removed from the SFE system. The SFE system can then be rapidly cleaned *in situ*. On-line IR monitoring serves to ensure that the cleaning cycle is complete thereby ensuring no cross-contamination can occur. The technique is also tolerant to samples containing very high levels of particulates.

A comparative study with a traditional IR method (Her Majesty's Stationary Office) which requires an ozone depleting solvent, indicates that the SFE-IR method provides at least comparable quantification results. A series of interchangeable, different path-length IR cells are available to cover a range of oil in water analyses using the SFE-IR method.

The development of a rapid SFE-IR system calibration procedure and an optional in-line sorbent cleanup stage for the specific determination of petroleum hydrocarbons in the presence of supercritical fluid co-extracted vegetable oils serves to further improve sample throughput and capability.

The New SFE-IR Method for Determining Oil and Grease in Water Offers the Following Benefits:

- * Environmentally Clean – Capable of replacing IR methods which use ozone depleting solvents. Long term availability of carbon dioxide assured.
- * Provides Traditional Quality IR Data – Can be interpreted and manipulated using long-established procedures.
- * It is Safe – It does not require the use of any toxic, flammable solvents also CO₂ cylinder can be remotely located outside laboratory. No solvent disposal costs.
- * Absolute Minimal Sample Manipulation Stages – Promotes method reproducibility, insertion of the whole 500 ml sample bottle into the SFE system ensures any possible losses of hydrocarbons due to glass adherence are avoided.
- * Suitable for the Analysis of Volatile Hydrocarbons, e.g., hexane and BTEX species.
- * Suitable for Direct Analysis of Samples Containing very High Levels of Particulates, e.g., unaffected by presence of 10,000 ppm clay in a 500 ml water sample.
- * Optional In-Line Silica Gel Cleanup Stage Permits the Analysis of Petroleum Hydrocarbons in the Presence of Co-Extracted Vegetable Oils – Two analyses per single 500 ml water sample are possible within 20 min, i.e., total oil content and therefore vegetable oil content can be calculated *via* difference.
- * Optional Rapid Off-Line SFE-IR System Calibration Procedure for Quantification.
- * Rapid SFE System Clean Cycle – *In situ* IR monitoring ensures no cross-contamination.
- * Very High Level of Automation, User Friendly – Analysis initiated and controlled by depressing single start button enabling the user to “load and walk away.”
- * Simple Interfacing – Provides retrofit option of SFE system to previously acquired IR spectrometers.
- * Cheap to Run – Inexpensive cylinder containing 34 kg of liquid CO₂ sufficient to perform 150 analyses of 500 ml water samples (about 10 pence per sample).
- * Minimal Solvent Disposal Costs – Simple exhaust line to fume-hood /activated carbon trap or vent to atmosphere.
- * Reliable, Rugged and Flexible – SFE system trolley mounted, can be disconnected from IR and withdrawn or reconnected , either operation taking approximately 2 min.
- * Low SFE System Maintenance Service Schedule.

Development of an automated method for determining oil in water by direct aqueous supercritical fluid extraction coupled on-line with infrared spectroscopy

The
Analyst
FULL PAPER

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Received 2nd August 2000, Accepted 13th October 2000
First published as an Advance Article on the web 21st November 2000

A direct aqueous supercritical fluid extraction (SFE) system was developed which can be directly interfaced to an infrared spectrometer for the determination of oil in water. The technique is designed to provide an environmentally clean, automated alternative to established IR methods for oil in water analysis which require the use of restricted organic solvents. The SFE-FTIR method involves minimum sample handling stages, with on-line analysis of a 500 ml water sample being complete within 15 min. Method accuracy for determining water samples spiked with gasoline, white spirit, kerosene, diesel or engine oil was 81–100% with precision (RSD) ranging from 3 to 17%. An independent evaluation determined a 2 ppm limit of quantification for diesel in industrial effluents. The results of a comparative study involving an established IR method and the SFE-FTIR method indicate that oil levels calculated using an accepted equation which includes coefficients derived from reference hydrocarbon standards may result in significant errors. A new approach permitted the derivation of quantification coefficients for the SFE-FTIR analyses which provided improved results. In situations where the identity of the oil to be analysed is known, a rapid off-line SFE-FTIR system calibration procedure was developed and successfully applied to various oils. An optional in-line silica gel clean-up procedure incorporated within the SFE-FTIR system enables the same water sample to be analysed for total oil content including vegetable oils and selectively for petroleum oil content within a total of 20 min. At the end of an analysis the SFE system is cleaned using an *in situ* 3 min clean cycle.

Introduction

In response to growing international concern over the depletion of stratospheric ozone, the Vienna Convention for the Protection of the Ozone Layer led to an agreement opened for signature in March 1985. Although the potential severity of the problem was recognised, this document set out broad principles for ozone layer protection rather than imposing obligations upon nations to control and reduce the manufacture of ozone depleting substances. Building on this achievement, in September 1987, representatives from 27 countries signed the 'Montreal Protocol on Substances that Deplete the Ozone Layer'. This protocol committed every signatory nation, by 1999, to reduce its manufacture of certain chlorofluorocarbons (CFCs) by 50% of their level in use in 1986.^{1,2} Years of negotiation fostered by the United Nations Environment Programme (UNEP) has now resulted in 173 parties to the Montreal Protocol with its London (1990), Copenhagen (1992), Montreal (1997) and Beijing (1999) amendments.^{3,4}

Since its implementation, substances other than CFCs have also become subject to control measures under the Montreal Protocol, e.g., carbon tetrachloride, 1,1,1-trichloroethane, hydrofluorocarbons (HFCs), halons and methyl bromide.⁴ However, it was also recognised that certain essential uses for restricted solvents existed for which practical substitutes/technologies were not immediately available. As a consequence, in 1994, a list of global essential use exemptions was agreed at the 6th Meeting of the Parties to the Montreal Protocol.⁵ Amongst these exemptions were those identified for laboratory and analytical uses. These included the use of restricted solvents for equipment calibration, use as extraction

solvents, diluents or carrier solvents for chemical analysis and other critical analytical and laboratory purposes. In particular, the availability of restricted solvents for the determination of oil, grease and total petroleum hydrocarbons (TPHs) in surface and sea-waters and industrial and domestic aqueous waste fell within the essential use exemption category.

Oil, grease and TPH analyses provide gross measurements of water contamination and are vital for the successful management of industrial discharges and waste-water treatment. A variety of analytical procedures have been developed for the determination of oil in water.⁶ This situation can be attributed to the wide range of physical and chemical properties of the constituent components within crude oils and associated products. The analytical procedures can be broadly divided into two classes,⁷ those based upon (i) integral procedures which involve gravimetry and infrared (IR), ultraviolet (UV) and fluorescence spectroscopic techniques and (ii) differential procedures which involve gas chromatography, gas chromatography combined with mass spectrometry and high performance liquid chromatography. From an industrial perspective, integral methods based upon IR and gravimetric procedures have become very firmly established as the general means by which oil in water determinations are performed.^{8,9} Differential methods, although more accurate, are relatively time consuming, expensive and require a higher level of technical skill.⁶

Gravimetric methods such as US Environmental Protection Agency (EPA) Method 413.1¹⁰ and Standard Method 5520B¹¹ involve liquid-liquid extraction (LLE) of water samples using 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). The extract is then dried using magnesium sulfate prior to the Freon 113 being evaporated, leaving the residual oil to be weighed. In general,

gravimetric procedures do not provide a means of characterising the composition of extracted oil and also fail to account for volatile hydrocarbon species which are lost during the evaporation of the extraction solvent. Methods involving IR confirmation represent the most widely accepted procedures for the determination of oil, grease and TPH in water.^{8,9} Although IR procedures such as Her Majesty's Stationery Office (HMSO)¹² and American Society for Testing and Materials (ASTM) Method 3921¹³ provide relatively low sensitivity for aromatic hydrocarbons compared with UV and fluorescence methods, IR spectroscopy is able to cover the whole range of hydrocarbons using relatively simple, inexpensive instrumentation suitable for routine use in industrial laboratories. As with gravimetric procedures, IR methods involve LLE and extract drying stages. The choice of extraction solvent is, however, extremely limited since IR methods involve measuring absorbance values of specific C-H vibrations of extracted hydrocarbon species through the 3030–2930 cm⁻¹ region. Hence IR methods have been developed using either Freon 113 or carbon tetrachloride as interference-free extraction solvents. A major drawback of traditional gravimetric and IR methods is that they are labour intensive, involving a number of 'wet chemistry' stages. This situation can be further compounded since these methods generally include an option whereby co-extracted polar species, such as vegetable oils, can be selectively removed from mineral oils in the LLE extract via an appropriate sorbent treatment procedure. The treated extract can then be assayed for petroleum hydrocarbon content.

In July 1998, the 17th Meeting of the Open-Ended Working Group of the Parties to the Montreal Protocol¹⁴ forwarded a series of draft proposals for consideration at the 10th Meeting of the Parties to the Montreal Protocol to be held later that year. Amongst these was the proposal that Freon 113 and carbon tetrachloride should be eliminated from the global exemption for laboratory and analytical essential uses in 2001 and subsequent years for determining oil, grease and TPH in water, i.e., both of these substances should enter the Negative List for this application. As a result of extended negotiations reflecting concern over the availability of alternative methods, a decision reached at the 11th Meeting of the Parties to the Montreal Protocol in 1999 eliminates the use of ozone depleting solvents for determining oil, grease and TPH in water from 2002.¹⁵ Hence IR and gravimetric methods for determining oil, grease and TPH in water using ozone depleting solvents are obsolescent. Consequently, many existing methods will need to be revised, re-evaluated or alternatives found.

A gravimetric procedure, EPA Method 1664, which uses hexane as an alternative extraction solvent, has been specifically developed for the determination of oil, grease and TPH in aqueous samples.¹⁶ Method 1664 is performance-based, thereby permitting alternative extraction and concentration techniques provided all performance specifications and quality control stages incorporated within the procedure are met. Hence Method 1664 permits the use of solid phase extraction (SPE) as an alternative to LLE. The results of a comparative gravimetric study involving SPE cartridges specifically developed for determining oil in water and LLE procedures have been published.¹⁷ The SPE procedure allowed more rapid analyses despite additional steps being necessary to avoid SPE cartridge blockage when aqueous samples contained high levels of particulates. In part, Method 1664 was developed to provide a low cost alternative to instrument based techniques for determining oil, grease and TPH in water.¹⁸ However, Method 1664 is not just a simple replacement gravimetric method for those based on Freon 113 LLE; its successful implementation depends upon satisfying extensive quality control parameters which can be difficult to achieve consistently owing to a range of problems.¹⁹

Methods based on UV and fluorescence spectroscopy for determining oil, grease and TPH in water involve determining

the amount of aromatic hydrocarbons present in the sample, with the total petroleum hydrocarbon content being calculated on a proportional basis.^{7,20} Hence, successful quantitative studies require prior knowledge of the levels and compositions of constituent hydrocarbons in the oils and greases being analysed. Additional problems may arise owing to the presence of interfering species, e.g., UV methods can be affected by nitrates²⁰ and plant pigments can interfere with fluorescence methods.⁷ Although potentially very sensitive in appropriate situations, these techniques are best suited for effluents containing an aromatic content and cannot be used for alkane-based oils and greases or vegetable oils.

Tetrachloroethene has been suggested as a substitute LLE solvent for established oil in water IR methods.¹⁸ However the toxicity and ozone depleting properties of tetrachloroethene represent significant problems which serve to limit its long term suitability as an alternative solvent for IR spectroscopy. A field portable IR analyser has been developed whose operational wavelength can be factory-adjusted for specific applications.^{21,22} The system can be supplied to permit the determination of oil in water using a hexane LLE procedure. After LLE, an aliquot of the hexane extract can be placed in a sample well or applied to a disposable IR card. Once the hexane has evaporated, the infrared filterometer provides a means of determining the amount of oil extracted by measuring the absorbance at 2930 cm⁻¹. Although being more specific than gravimetric procedures, this non-scanning IR technique does not allow the characterisation of extracted oils.

In principle, an ideal LLE solvent for measuring oil, grease and TPH in water via IR spectroscopy should be non-absorbing throughout the 3030–2930 cm⁻¹ region and be capable of efficiently extracting hydrocarbons from aqueous samples whilst being environmentally friendly. Additionally, the solvent should be non-toxic, non-flammable and freely and cheaply available at high purity with no disposal costs. Supercritical fluid carbon dioxide matches all of these criteria. A method based on supercritical fluid extraction (SFE) using carbon dioxide has been developed (EPA Method 3560) for the determination of TPH in soil.²³ The technique involves off-line IR analysis (EPA Method 8840) of extracted hydrocarbons, after collection of the SFE restrictor output in a small volume of tetrachloroethene. The underlying theory and principles of SFE coupled on-line with IR spectroscopy (SFE-IR) have been reviewed,^{24,25} with several reports describing this technique being applied for TPH determination in soil.^{26,27} Recently we reported the development of direct liquid SFE-FTIR instrumentation, specifically developed for the determination of oil in industrial effluents and discharge waters.²⁸ The system is based on a stop-flow IR measurement of the SFE extract. This eliminates the use of a restrictor device and associated blockage problems which may arise due to extracted water freezing and/or analyte deposition at the point of decompression during dynamic SFE of aqueous matrices.²⁹ The automated system has been developed to allow rapid unattended analyses of 500 ml water samples with minimum sample handling. Since the whole sample bottle is placed within the SFE vessel, losses of hydrocarbons which can result from glass adherence during sample transfer stages are eliminated. The method is also suitable for the determination of volatile hydrocarbons and is not affected by the presence of very high levels of particulates in water samples.²⁸

The objective of this study was to evaluate further the applicability of the direct aqueous SFE-FTIR method for determining a range of oils and comparing its level of performance against that achievable using an established LLE IR method. The development of a rapid system calibration procedure and an optional in-line sorbent clean-up stage for the specific determination of petroleum hydrocarbons in the presence of co-extracted vegetable oils serves to improve sample throughput further.

Experimental

A custom-built stainless-steel vessel with an internal volume of 1 l, equipped with integral heaters and thermocouple assembly, was used for all SFE-FTIR studies. The SFE vessel was constructed in accordance with the American Society of Mechanical Engineers ASME VIII (NCS) standards. Once fabricated, the SFE vessel was pressure tested to 42 MPa before being fitted with a 28 MPa rupture disc assembly prior to use. A Gilson Model 307 pump (Anachem, Luton, Bedfordshire, UK) equipped with a Gilson supercritical fluid chromatography refrigeration unit was used to supply liquid carbon dioxide (Messer UK, Reigate, Surrey, UK) to the extraction vessel. The SFE vessel was interfaced to the FTIR spectrometer via a high pressure FTIR cell of 8 mm pathlength, constructed with 2 mm diameter quartz windows. In practice, provided that a suitable sample mount is available, the direct aqueous SFE system can be linked to most manufacturers' IR spectrometers in under 2 min. The SFE system control modules house all valves, pressure transducers and heater controls necessary for operation. An *in situ* clean-up column was incorporated into the SFE system between the SFE vessel and the high pressure FTIR cell. The clean-up column consisted of a finger-tight 3 ml capacity high pressure SFE vessel (Thar Designs, Pittsburgh, PA, USA) loosely packed with 100–80 mesh silica gel (Jones Chromatography, Hengoed, Glamorgan, UK) and was plumbed into the system using a high pressure selection/isolation valve.

Fig. 1 shows the direct aqueous SFE system (patents pending). The exhaust from the SFE vessel and FTIR cell were vented into a fume cupboard via an appropriate length of rubber hose. Aqueous extractions were performed using a vessel temperature of 40 °C with a flow rate of liquid carbon dioxide of 25 ml min⁻¹ until an SFE pressure of 17.22 MPa was attained. In the event that a liquid carbon dioxide cylinder becomes empty during an analysis, a time-out alarm on the SFE system is activated and the cylinder can be changed without affecting the results. A Nicolet Magna-IR 550 spectrometer (Nicolet Instruments, Warwick, UK) equipped with OMNIC software was used for acquisition and processing of SFE-FTIR data. Spectra were obtained over the range 4000–400 cm⁻¹, using a resolution of 4 cm⁻¹, with 200 scans summed per analysis.

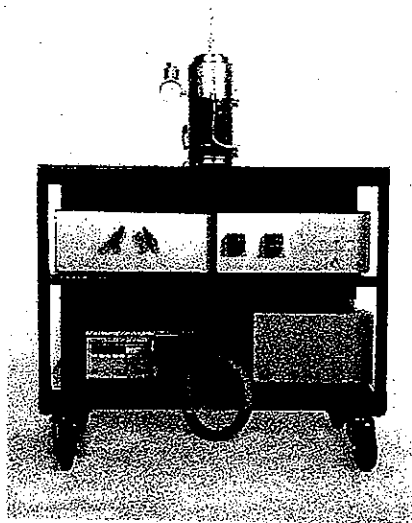


Fig. 1 The direct aqueous SFE system designed for oil in water determination using on-line IR spectroscopy. Base tier: liquid carbon dioxide pump (left), pump-head refrigeration unit (right). Middle tier: valve control module (left), electronic control module (right). Top tier: 1 l capacity SFE vessel.

Automobile gasoline, diesel and 20W/50 engine oil were obtained from a local garage. Samples of kerosene and white spirit were supplied by Hyder (Runcom, Cheshire, UK). IR spectroscopic grade carbon tetrachloride and tetrachloroethene were obtained from Sigma-Aldrich (Poole, Dorset, UK). Analytical-reagent grade benzene, hexadecane, pristane and ethylbenzene standards were obtained from Sigma-Aldrich. Analyses were performed using 500 ml water samples contained within 500 ml graduated Schott bottles (Merck, Lutterworth, Leicestershire, UK). Spiked samples were prepared by injecting oil samples into the bulk of the water sample. Owing to its viscosity, engine oil was diluted with benzene (5 g in 10 ml benzene solution) to facilitate the use of a syringe in preparing spiked water samples. All samples were prepared and stored at room temperature prior to analysis. The samples were analysed by placing the open sample bottle in the SFE vessel, which was then sealed. Unattended analysis is initiated via a single start switch on the SFE electronic control module. As previously described, spiked water samples are thoroughly agitated and acidified *in situ* during the initial stages of SFE.²⁸ Baseline SFE-FTIR data were acquired using a 500 ml de-ionized water sample. At the end of each analysis the sample bottle was replaced with an aluminium plug which almost completely filled the sealed SFE vessel void volume. With this arrangement it is possible to clean the SFE vessel, high pressure IR analysis cell and all ancillary plumbing *in situ* using supercritical fluid carbon dioxide within 3 min. Alternatively, the SFE system valve settings can isolate the SFE vessel such that only the high pressure IR cell and associated transfer lines can be cleaned *in situ*. Off-line analyses of carbon tetrachloride or tetrachloroethene solutions of hexadecane, pristane, ethylbenzene and oil standards were performed using a quartz cuvette of 1 cm pathlength with the same acquisition parameters as used for SFE-FTIR analyses.

Results and discussion

Evaluation of the applicability of the direct aqueous SFE-FTIR procedure for determining a range of different oils

Recently, we described the potential of direct aqueous SFE-FTIR for the determination of automobile diesel in 500 ml water samples.²⁸ In order to evaluate further the performance of the SFE-FTIR procedure as a general means for determining oils in discharge effluents, a range of water samples spiked with various species of oil were analysed. The oils selected were gasoline, white spirit, kerosene and engine oil. These oils were amongst those originally used to develop^{30,31} the HMSO method.¹² Each oil was analysed at four different spike levels ($n = 5$ for each level). Fig. 2(a) shows the results obtained for white spirit. The quality of the on-line SFE-FTIR data obtained for white spirit, kerosene and engine oil was evaluated using the five absorbance values obtained at 2932 cm⁻¹ ($\nu_{\text{asymmetric}} \text{CH}_2$) for each set of spiked water samples. For gasoline, whose major constituent components are branched alkanes, the five most intense absorbance values obtained at 2960 cm⁻¹ ($\nu_{\text{asymmetric}} \text{CH}_3$) were used for each set of spiked water samples. Using these sets of data with standard OMNIC FTIR quantitative software, graphs were constructed such that calculated levels of oil present were plotted against actual levels present in the spiked 500 ml water samples. All these graphs were constructed using a partial least squares curve fit with the origin considered as a data point. Fig. 2(b) shows the graph obtained for white spirit.

The results for the oils are summarised in Table 1. With the exception of engine oil, all other oils studied exhibited linear dynamic ranges in excess of 130 ppm. The upper linear dynamic

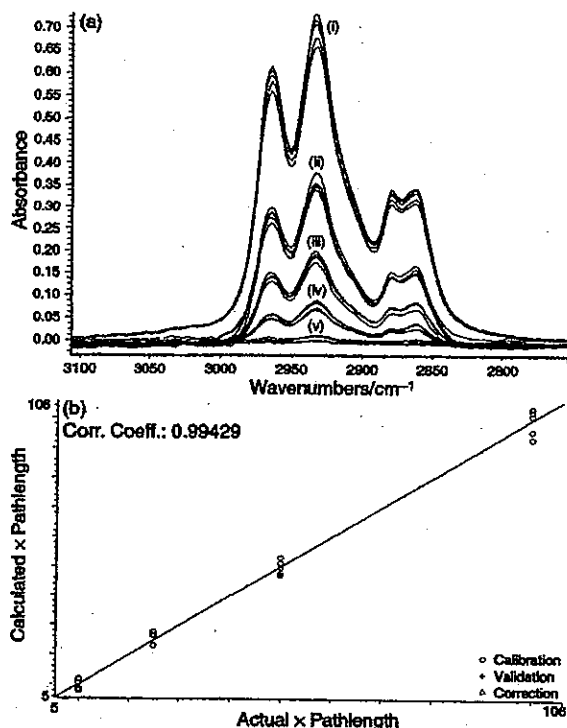


Fig. 2 (a) On-line SFE-FTIR spectra obtained for four sets ($n = 5$ per set) of 500 ml water samples spiked with the following levels of white spirit: (i) 156; (ii) 78; (iii) 39 ppm; and (iv) 15.6 ppm. The results for four blank water samples are shown in (v). (b) Graph obtained for the calculated number of microlitres of white spirit against actual number of microlitres in the 500 ml spiked water samples. The FTIR high pressure cell pathlength was 8 mm. Calculated vs actual plot, white spirit; $r = 0.9943$.

range for engine oil using the SFE-FTIR system lies in the region of 70–100 ppm. The lower linear dynamic range associated with engine oil is attributed to its complex formulation which contains components specifically designed to adhere strongly to metallic surfaces. In practice, we believe the SFE efficiency to be almost complete within the linear dynamic range for each of the oils. This view is supported by the fact that repeated SFE-FTIR analyses of 500 ml water samples initially spiked with 25 μ l of oil failed to provide IR spectra for the oils.²⁸ Additionally, we found that no increase in spectral intensity for any of the five oils could be gained by increasing the extraction pressure from 17.22 to 25.83 MPa at 40 °C. Consequently, these experiments serve to confirm that the oils are almost completely extracted at 17.22 MPa since more dense, higher solvating strength supercritical fluid carbon dioxide³² did not improve extraction efficiencies.

As reported previously,²⁸ carryover can sometimes occur owing to oil deposition within the SFE vessel when the supercritical extract is decompressed during the vent cycle. This problem tends to arise when oil levels in aqueous samples exceed 40 ppm and/or the oil has a high affinity for metal surface adherence. In practice, cross-contamination can be rapidly eliminated by placing an aluminium plug in the SFE vessel following each analysis. The aluminium plug almost completely fills the chamber within the sealed vessel, enabling an SFE clean cycle to be completed within 3 min. *In situ* IR monitoring can be used to confirm the efficiency of the clean cycle. In the case of gasoline and white spirit, no carryover problems occurred after analysing water samples spiked with 134 and 156 ppm, respectively.

In order to evaluate the performance of the SFE-FTIR oil in water analyser for real samples, two diesel contaminated discharge water samples were supplied and independently analysed using the system by an industrial company (Hyder). The results for the two samples are shown in Fig. 3 along with the analysis obtained for a freshly prepared diesel spiked water sample. These results serve to confirm the capability of the SFE-FTIR procedure for quantifying oil levels in industrial effluents.

Table 1 Summary of quantitative results obtained for the on-line SFE-FTIR analyses of oil spiked water samples.^a The results for diesel have been published previously²⁸

Oil	Actual amount of oil in 500 ml spiked water samples/ μ l	Mean calculated amount of oil in 500 ml spiked water samples/ μ l	Correlation coefficient ^b	Standard deviation, ^c expressed as amount of oil in 500 ml water samples/ μ l	Accuracy (%) ^d
Gasoline	100 (134)	100.9 (135.2)	0.9829	6.7 (8.9)	99.1
	50 (67)	45.3 (60.7)		2.5 (3.4)	90.6
	25 (33.5)	26.9 (36.1)		3.0 (4.1)	92.4
	10 (13.4)	11.9 (15.9)		1.3 (1.8)	81
White spirit	100 (156)	99.7 (155.5)	0.9943	4.4 (6.9)	99.7
	50 (78)	49.6 (77.4)		2.5 (3.8)	99.2
	25 (39)	26.2 (40.8)		1.7 (2.7)	95.2
	10 (15.6)	9.6 (14.9)		1.6 (2.6)	96
Kerosene	100 (162)	99.6 (161.4)	0.9912	3.5 (5.6)	99.6
	50 (81)	50 (81)		5.1 (8.0)	100
	25 (40.5)	24.9 (40.3)		3.3 (5.3)	99.6
	10 (16.2)	10.6 (17.2)		1.1 (1.8)	94
Diesel	80 (137.6)	80.9 (139.2)	0.9909	2.4 (4.1)	98.9
	50 (86)	47.9 (82.4)		4.1 (7.1)	95.8
	25 (43)	23.9 (41.1)		1.0 (1.7)	95.6
	10 (17.2)	11.3 (19.4)		0.9 (1.6)	87
Engine oil, 20W/50	70 (70)	71.6 (71.6)	0.9546	6.3 (6.3)	97.7
	45 (45)	38.6 (38.6)		3.0 (3.0)	85.8
	20 (20)	23.1 (23.1)		1.7 (1.7)	84.5
	10 (10)	11.7 (11.7)		1.6 (1.6)	83

^a Concentration values expressed in ppm are shown in parentheses. ^b The correlation coefficients are derived from four point calibration graphs, where for each oil the calculated number of microlitres are plotted against actual number of microlitres in spiked 500 ml water samples. For oils other than diesel, $n = 5$ for each individual spike level. For diesel, $n = 4$ for each individual spike level. ^c Calculated using $n - 1$ degrees of freedom, here and thereafter. ^d Accuracy (%) = $100 - |100 - [(mean\ calculated\ value/actual\ value) \times 100]|$, here and thereafter.

The high pressure IR analysis cell used throughout these studies was a modified preparative supercritical fluid chromatography UV cell which provided 2 mm diameter quartz windows and 8 mm pathlength. It is expected that improved detection limits should be achievable using an IR analysis cell of greater dimensions. An increase in IR cell window diameter should provide an improved signal-to-noise ratio whereas a longer pathlength would increase the sensitivity. Such high pressure IR cells suitable for the analyses of supercritical fluids have been developed.³³

Comparison of the Infrared HMSO method with the SFE-FTIR procedure for determining oil in water

In 1951, Simard *et al.*³⁴ first described an IR method in which a three component synthetic oil mixture of isooctane, hexadecane and benzene (37.5 + 37.5 + 25 by volume) could be used for the determination of oils in waste water. The procedure involved summing the absorbances which were attributed to the vibrations of CH₂, CH₃ and aromatic CH groups, respectively, and relating these values to those obtained for oil which had been extracted from water using carbon tetrachloride. It became apparent that the accuracy of this IR method could be greatly improved by using calibration standards prepared from a sample of oil identical with that which was to be measured.³⁵ Often, however, this is not possible, *e.g.*, the sample may have been obtained from a site in which numerous oil species have become mixed following discharge from several sources. Under these circumstances, a three component synthetic oil is still widely used as the calibration standard for the IR procedure despite associated errors of ±20% being quoted.³⁰ A recent report³⁶ indicated that errors substantially larger than this figure can occur using summed IR absorbance values. Whittle *et al.*^{30,31} developed an IR method in which the molar absorptivities of the CH₃ (2960 cm⁻¹), CH₂ (2930 cm⁻¹) and the aromatic CH (3030 cm⁻¹) groups are taken into account to correct for the errors associated with simple addition of unbiased absorbance

values. The procedure, which formed the basis for the HMSO IR method,¹² involves constructing three equations for three reference compounds, each rich in either CH₃, CH₂ or CH aromatic protons. A typical set of reference compounds include hexadecane, pristane and ethylbenzene. The equation is as follows and is applied to each set of IR absorbance values for standard solutions of the reference compounds:

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

where: *c* = concentration in mg l⁻¹, constant for each reference compound, *x*, *y* and *z* = coefficients related to the molar absorptivities of the CH₂, CH₃ and aromatic CH groups, respectively, *A* = absorbance value at the specified wavelength and *F* = a correction factor and can be calculated^{30,31} from hexadecane absorbances by basing the correction on the absorbance at 2930 cm⁻¹ and letting $F = A_{2930}/A_{3030}$.

Once the values of the *x*, *y* and *z* coefficients have been determined, the HMSO equation is applied to the absorbance values of the oil to be measured and its concentration is calculated. In order to evaluate the accuracy of a similar approach for the SFE-FTIR procedure, a comparative study was undertaken. An initial series of analyses were performed to solve the values of *x*, *y* and *z* using standard carbon tetrachloride solutions of hexadecane, pristane and ethylbenzene according to the HMSO method. These values are subsequently referred to as the HMSO coefficients. Following these experiments, the values of SFE-FTIR *x*, *y* and *z* coefficients were determined using mean SFE-FTIR absorbance values for 500 ml water samples spiked with 80 ppm of each of the three reference compounds (*n* = 5, for each compound). The two sets of coefficients were then appropriately used to calculate the levels of oil in carbon tetrachloride standard solutions and the 500 ml spiked water samples (compositions are given in Table 1) used in the previous section. The quantitative results are summarised in Table 2.

It is considered that the results obtained for each oil's carbon tetrachloride standard solution, calculated using the HMSO coefficients, represent those obtainable in an ideal situation, *i.e.*, these results cannot be adversely affected by any manipulation errors and/or incomplete carbon tetrachloride extraction efficiencies, had the HMSO method been applied to spiked water samples. A recent report³⁶ described surprisingly low extraction efficiencies for various oils including the components of a synthetic oil mixture using a carbon tetrachloride LLE procedure. The results in the second column of Table 2 are subsequently referred to as minimum HMSO errors hereafter.

As shown in Table 2, application of the HMSO coefficients to the SFE-FTIR analyses obtained for kerosene, diesel and engine oil provide quantification results whose errors closely match the corresponding minimum HMSO errors for these oils. However, the errors associated with the SFE-FTIR quantification results obtained for gasoline and white spirit derived using the HMSO coefficients do not correlate with the minimum HMSO errors. When the SFE-FTIR derived coefficients were applied to the SFE-FTIR analyses for the oils, column four in Table 2, the results for kerosene and engine oil provided a good match with the minimum HMSO errors. With the exception of diesel, the results obtained for the SFE-FTIR analyses of the other oils are approximately equivalent using either the HMSO coefficients or the SFE-FTIR coefficients.

The results in Table 2 indicate that for all oils, a greater error occurs when the SFE-FTIR derived coefficients are applied to the results of SFE-FTIR analyses of oils in water relative to the corresponding minimum HMSO errors. These three sets of results serve to demonstrate that application of coefficients derived from reference compounds can introduce significant errors for various species of oils and their mixtures. According to one report,³⁷ a reference oil recommended in EPA Method 8440 for samples of unknown petroleum hydrocarbons resulted in analyses having significantly larger errors than any recorded

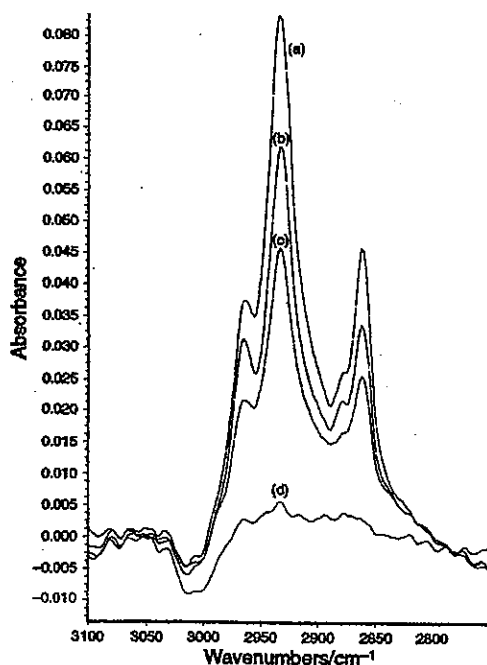


Fig. 3 SFE-FTIR analyses obtained for: (a) 500 ml of industrial effluent containing 4 ppm diesel, (b) 500 ml of water spiked with 3 ppm diesel, (c) 500 ml of industrial effluent containing 2 ppm diesel and (d) 500 ml of blank water.

in Table 2 using either the HMSO coefficients or the SFE-FTIR coefficients.

In order to determine optimum x and y coefficients to apply to the on-line SFE-FTIR data, the SFE-FTIR absorbance values of the oils themselves were used in conjunction with Microcal Origin™ software. The z coefficient was not evaluated for the five oils since their IR spectra indicated a low aromatic content. With this approach, a response surface was constructed in which the summed error associated with the SFE-FTIR results of oil in water analyses for each of the five oils was expressed as a function of varying x and y values. The summed error was based on modulus values for each oil in order to prevent errors of different sign being self-cancelling. From the response surface shown in Fig. 4, the values obtained for x and y which resulted in the minimum summed error for the five oils were reapplied to the results obtained for the SFE-FTIR analyses. As shown in column five of Table 2, with the exception of kerosene this approach provided lower mean errors than the minimum HMSO errors.

Development of a rapid off-line calibration procedure for the SFE-FTIR system

Despite the widespread use of three component synthetic oils to derive coefficients for calculating the levels of oil in aqueous samples, it is well known that more accurate IR analyses can be performed using calibration standards prepared from the actual oil which is to be measured.^{12,13,30,35,36} Although preparing calibration graphs using SFE-FTIR results obtained from water samples spiked with the oil to be quantified poses no significant problems, the fact that a single analysis takes approximately 15 min means that time could be saved by developing a rapid off-line calibration procedure. Accordingly, a series of experiments were performed using 500 ml water samples spiked with white spirit and standard tetrachloroethene solutions of white spirit. The SFE-FTIR analyses of 500 ml water samples spiked with 50 μ l white spirit provided IR spectra whose CH_2 ($\nu_{\text{asymmetric}}$) absorbance values approximate to that obtained for a standard solution of 5 μ l white spirit in 100 ml of tetrachloroethene. The results of these analyses allowed the derivation of a dilution factor. Following this experiment, an off-line, five point calibration graph was prepared ($r = 0.9995$) using standard tetrachloroethene solutions of white spirit. The off-line calibration graph was constructed such that it would permit the SFE-FTIR determination of white spirit in 500 ml water samples through the range 12.5–156 ppm range via interpolation of CH_2 ($\nu_{\text{asymmetric}}$) absorbance values. It was noted that the maximum values obtained for C–H absorbances in the SFE-FTIR spectra of the oils showed a small shift to higher wavenumbers relative to the corresponding wavenumbers for their tetrachloroethene standard solutions. In practice, this did not pose a problem since the OMNIC™ quantitative software facilitates specifying a

maximum absorbance value within a range of wavenumbers. Table 3 summarises the results for the determination of white spirit in water obtained using the off-line calibration graph. In order to test the general applicability of this approach, sets of 500 ml water samples each spiked with one of the five oils were analysed via SFE-FTIR and quantification was performed using the off-line system calibration procedure. The quantitative results are summarised in Table 4. High levels of accuracy were obtained for quantifying the other four oils using off-line tetrachloroethene calibration standards whose concentrations were based on the dilution factor previously determined for white spirit. These results further confirm almost identical SFE efficiencies for all of the five oils studied.

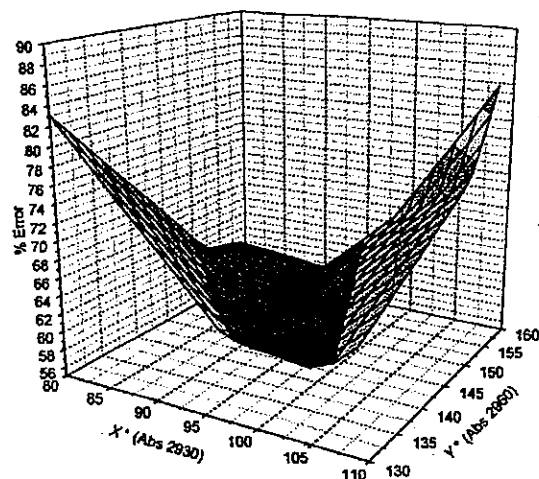


Fig. 4 Response surface obtained using Microcal Origin software, in which sets of summed modulus errors associated with five oils are expressed as a function of x and y coefficient values applied to their CH_2 ($\nu_{\text{asymmetric}}$) and CH_3 ($\nu_{\text{asymmetric}}$) IR absorbance values, respectively, using the HMSO calculation.³⁰

Table 3 Determination of white spirit spiked into 500 ml water samples using the off-line calibration procedure. Results derived using absorbance values at 2932 cm^{-1} . For each individual spike level, $n = 3^a$

Actual amount of white spirit in 500 ml water sample/ μ l	Mean calculated amount of white spirit in 500 ml water sample/ μ l	Standard deviation, expressed as amount of white spirit in 500 ml water sample/ μ l	Accuracy (%)
100 (156)	100 (156)	2.3 (3.6)	100
50 (78)	51.5 (80.3)	0.7 (1.1)	97.1
20 (31.2)	18.8 (29.3)	2.8 (4.3)	94.2

^a Concentration values expressed in ppm are shown in parentheses.

Table 2 Comparison of the application of x , y and z coefficients for determining oil levels in standard solutions of carbon tetrachloride and on-line SFE-FTIR analyses

Oil	HMSO coefficients applied to carbon tetrachloride standards ^a (% mean error)	HMSO coefficients applied to on-line SFE-FTIR analyses ^b (% mean error)	SFE-FTIR coefficients applied to on-line SFE-FTIR analyses ^b (% mean error)	Graphically optimised coefficients applied to on-line SFE-FTIR analyses ^b (% mean error)
Gasoline	-9.5	-27.8	-24.4	-7.6
White Spirit	-6.5	-18.2	-18.8	-1.7
Kerosene	-0.9	4.8	2.8	21.1
Diesel	-18.4	-19	-34.8	0
Engine oil, 20W/50	-26.1	-26.1	-28.9	-14.6

^a Errors derived from duplicate analyses of carbon tetrachloride oil standards. Oil concentrations: 130–160 ppm. ^b Errors derived from 20 spiked 500 ml water samples for each oil, except for diesel where the error associated with 16 samples is quoted. The compositions of the spiked water samples are given in Table 1.

The dilution factor was based on determining the concentrations of white spirit in tetrachloroethene solution whose CH_2 ($v_{\text{asymmetric}}$) absorbance values matched those obtained for SFE-FTIR analyses of white spirit spiked water samples. Under these circumstances, a lower quality match was obtained for the white spirit CH_3 ($v_{\text{asymmetric}}$) absorbance values. The CH_3 ($v_{\text{asymmetric}}$) absorbance values obtained for the tetrachloroethene white spirit solutions were of lower intensity than those obtained for the on-line SFE-FTIR analyses when the CH_2 ($v_{\text{asymmetric}}$) absorbances were matched. However, as shown in Table 4, a good correlation exists between the quantitative results obtained for each oil using absorbance values obtained at 2960 and 2932 cm^{-1} , applying the same dilution factor initially derived from matching white spirit CH_2 ($v_{\text{asymmetric}}$) absorbances. These results indicate that the CH_3 ($v_{\text{asymmetric}}$) to CH_2 ($v_{\text{asymmetric}}$) absorbance ratios for each of the five oils obtained at 17.22 MPa are approximately equivalent to the corresponding ratios obtained for their tetrachloroethene standard solutions. Hence the oils' high pressure IR spectra are not significantly influenced by pressure to the extent that separate CH_2 ($v_{\text{asymmetric}}$) and CH_3 ($v_{\text{asymmetric}}$) dilution factors must be determined for the off-line calibration method.

Analysis of mineral oils in the presence of vegetable oils

Gravimetric and IR methods for the determination of oil, grease and TPH in water generally include an optional sorbent clean-up procedure to remove selectively co-extracted polar species, such as vegetable oils, from the LLE extract prior to final analyses.^{8-13,16,31} In order to provide similar capability, an optional high pressure silica gel clean-up stage was incorporated into the SFE-FTIR system. In practice, the SFE-FTIR clean-up column can be selected by a single valve switch. Once this option is selected, the supercritical fluid extract flows through the silica gel column en route to the high pressure IR analysis cell. In order to evaluate the effectiveness of the in-line sorbent clean-up procedure, a series of SFE-FTIR analyses of water samples spiked with diesel, benzene and sunflower oil were performed. As shown in Fig. 5, the high pressure silica gel clean-up procedure is highly effective in selectively removing supercritical fluid carbon dioxide dissolved vegetable oil. The aromatic C-H absorbances for benzene are observed at 3150–3000 cm^{-1} . The results obtained for benzene serve to confirm previous findings²⁸ that the SFE-FTIR method is suitable for the determination of volatile hydrocarbons, which represents a limitation of gravimetric procedures. Following these initial experiments, 500 ml water samples spiked with different levels of diesel and sunflower oil were analysed using the SFE-FTIR in-line clean-up procedure. The outcome of these analyses is summarised in Table 5, in which the off-line calibration procedure was applied to the results obtained for diesel. Inspection of Table 5 clearly demonstrates that diesel can be accurately quantified using the in-line sorbent clean-up procedure when water samples are also contaminated with vegetable oil.

Table 4 Quantitative determination of various oils using the off-line calibration procedure. Dilution factor: as determined for white spirit. Calculations performed using SFE-FTIR absorbance values obtained at (i) 2960 and (ii) 2932 cm^{-1} . For each individual spike level, $n = 5$, except for diesel, where $n = 4$

Oil	Concentration of oil in 500 ml spiked water samples (ppm)	Mean calculated concentration of oil in 500 ml spiked watersample (ppm)	Standard deviation (ppm)	Accuracy (%)
Gasoline	67	(i) 66.9; (ii) 63.8	(i) 4; (ii) 4	(i) 99.9; (ii) 95.2
White spirit	78	(i) 75.1; (ii) 75	(i) 4.4; (ii) 3.5	(i) 96.3; (ii) 96.2
Kerosene	81	(i) 87.3; (ii) 83.3	(i) 7.7; (ii) 6.6	(i) 92.2; (ii) 97.2
Diesel	86	(i) 90.5; (ii) 86	(i) 7.4; (ii) 7.7	(i) 94.8; (ii) 100
Engine oil, 20W/50	70	(i) 68.3; (ii) 67.2	(i) 5.6; (ii) 5.4	(i) 97.6; (ii) 96

Since the void volume of the clean-up vessel and ancillary plumbing is low, it is possible to perform two analyses for a single water sample very rapidly, i.e., total oil content and petroleum oil content. With this procedure, the small volume of SFE extract first analysed is vented from the system and the IR analysis cell and associated plumbing are then cleaned using the appropriate stages of the SFE-FTIR system clean cycle. A second analysis of the sample's SFE extract can then be performed with or without the silica gel clean-up being selected. The second analysis is very rapid since the SFE vessel remains pressurised during the partial clean cycle. As a result, the total time required to perform both assays for a single sample is less than 20 min. Once the analysis is complete, the high pressure clean-up column can be rapidly removed, cleaned and reloaded with fresh silica. In practice, this can be performed within the 3 min required to complete the full SFE-FTIR system's clean cycle.

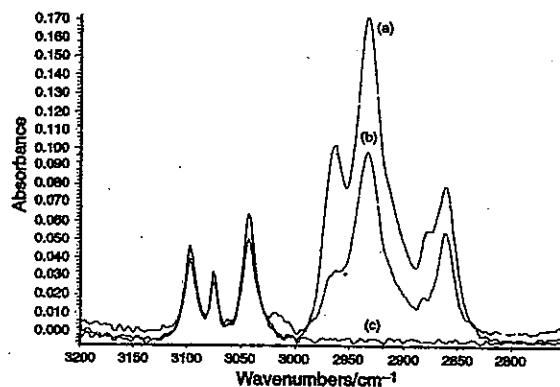


Fig. 5 SFE-FTIR spectra obtained for 500 ml water samples spiked with (a) diesel + benzene + sunflower oil (20 + 30 + 15 μl) with in-line silica gel clean-up, (b) benzene + sunflower oil (30 + 15 μl) without in-line silica gel clean-up and (c) benzene + sunflower oil (30 + 15 μl) with in-line silica gel clean-up.

Table 5 Summary of quantitative SFE-FTIR analyses for diesel, obtained for 500 ml water samples spiked with diesel, sunflower oil and benzene using the on-line silica clean-up column. Results derived using off-line calibration procedure applied to the absorbance values obtained at 2932 cm^{-1}

Amount of diesel + sunflower oil + benzene used to spike 500 ml water samples/ μl	Actual level of diesel in spike (ppm)	Calculated level of diesel in 500 ml water sample ^a (ppm)	Accuracy (%) ^a
5 + 15 + 30	8.6	(i) 7.5; (ii) 7.9	(i) 87.2; (ii) 91.9
10 + 15 + 30	17.2	(i) 16.5; (ii) 16.3	(i) 95.9; (ii) 94.8
20 + 15 + 30	34.4	(i) 34.6; (ii) 35.2	(i) 99.4; (ii) 97.7

^a Results for duplicate analyses shown.

Conclusions

The SFE-FTIR procedure affords a very rapid, simple and environmentally clean method for determining oil in discharge waters and effluents. Unlike established gravimetric and IR methods which rely upon LLE, the SFE-FTIR method involves an absolute minimum of sample handling stages. Once the sample bottle is sealed within the chamber of the SFE vessel, analysis is performed by depressing a single button on the instrument control panel. At the end of an analysis, the SFE-FTIR system can be cleaned within 3 min, during which *in situ* IR monitoring provides a means to ensure that no cross-contamination between water samples can occur.

As with other IR methods, more accurate analyses can be performed using calibration standards prepared from the actual oil to be analysed. When this is not possible, coefficients may be derived from reference compounds following the HMSO method. These coefficients can then be applied to the SFE-FTIR results. In practice, more accurate SFE-FTIR analyses can be obtained using coefficients calculated from the SFE-FTIR analyses of the various oil types likely to be encountered. With the exception of this improvement, the data generated using the SFE-FTIR system can be interpreted using established/preferred procedures. When the identity of the oil to be analysed is known, a rapid off-line system calibration procedure can be used to improve sample throughput further. With this exception, the SFE-FTIR procedure does not expose the analyst to any toxic and/or flammable organic solvents. It is envisaged that the use of permanently sealed cuvettes containing off-line calibration solutions would effectively minimise the normal hazards associated with using organic solvents.

The incorporation of an optional in-line silica gel clean-up stage permits the specific determination of petroleum hydrocarbons when aqueous samples also contain vegetable oils. Using the silica gel option it is possible to perform two assays for a single 500 ml water sample within 20 min for (i) total mineral and vegetable oils and (ii) mineral oil content.

An inexpensive cylinder containing 34 kg of liquid carbon dioxide allows the analyses of more than 150 500 ml water samples using the SFE-FTIR procedure. In practice, the liquid carbon dioxide cylinder can be remotely located outside the laboratory. The SFE-FTIR system operation costs are highly competitive compared with established IR and gravimetric methods, which require the use of relatively expensive organic solvents for LLE with associated disposal costs.

In summary, the development of a direct aqueous SFE system which can be directly interfaced to an IR spectrometer provides an alternative, environmentally clean, cost-effective method for determining oil in water. The instrumentation is easy to use, rugged and has been developed in close collaboration with several industrial laboratories which routinely perform oil in water analyses.

Acknowledgements

We thank Nicolet Instruments for the extended loan of a Magna-IR 550 spectrometer and financial support. We also thank Dr P. J. Whittle (Hyder) and Dr N. Winstone-Cooper (British Steel, Port Talbot, UK) for their expert advice.

References

- 1 I. H. Rowlands, *Environment*, 1993, 35, 25.
- 2 P. M. Morrisette, *Nat. Resour. J.*, 1989, 29, 793.
- 3 UNEP News Release, *Vienna Convention Lauded-Fifteen Years after Signature*, 2000, <http://www.unep.ch/ozone/press-rel/press-rel-21032000.htm>.
- 4 The Ozone Secretariat UNEP, *Handbook for the International Treaties for the Protection of the Ozone Layer*, UNEP, Nairobi, 5th edn., 2000.
- 5 The Ozone Secretariat UNEP, *Report of the Sixth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer*, October 6-7, 1994, Nairobi, http://www.unep.org/ozone/gmop_nbo.htm.
- 6 M. K. Stenstrom, F. Sami and G. S. Silverman, *Environ. Technol. Lett.*, 1986, 7, 625.
- 7 I. A. Nemirovskaya, V. V. Anikiev, N. Theobald and A. Rave, *J. Anal. Chem.*, 1997, 52, 349.
- 8 S. Rotteri, H. Boertzler, J. P. Dubreuil, J. Evers, J. Ilsbroux, H. G. Remstedt, H. J. Somerville and H. Van Strien, *Determination of Hydrocarbons in Aqueous Effluents from the Oil Industry by Infrared Analysis*, Concawe Report 1/84, The Hague, 1984.
- 9 *Standard Methods for Analysis and Testing of Petroleum and Petroleum Related Products*, Proposed Method BW/95, Institute of Petroleum, Wiley, New York, 1995.
- 10 *Code of Federal Regulations, Part 136-Guidelines Establishing Test Procedures for the Analysis of Pollutants*, 40 CFR, Part 136, Method 413.1, US Government Printing Office, Washington, DC, 1994.
- 11 American Public Health Association, American Water Works Association and Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 18th edn., 1992, pp. 5-24-5-29.
- 12 *The Determination of Hydrocarbon Oil in Waters by Solvent Extraction and either Infra Red Absorption or Gravimetry 1983*. Her Majesty's Stationery Office, London, 1983.
- 13 American Society for Testing and Materials, *Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water, Method D3921*, ASTM, Philadelphia, 1985.
- 14 The Ozone Secretariat UNEP, *Report of the 17th Meeting of the Open-Ended Working Group of the Parties to the Montreal Protocol*, 7-8 July 1998, Geneva, <http://www.unep.org/ozone/17oewgpr.html>.
- 15 *Summary of the Eleventh Meeting of the Parties to the Montreal Protocol and the Fifth Conference of the Parties to the Vienna Convention, Earth Negotiations Bull.*, 19 (6), International Institute for Sustainable Development, 1999, <http://www.iisd.ca/linkages/vol19/enb1906e.html>.
- 16 USEPA Office of Water, *n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons), Method 1664*, Water Resource Centre, Washington, DC, 1995.
- 17 M. J. M. Wells, D. M. Ferguson and J. C. Green, *Analyst*, 1995, 120, 1715.
- 18 D. Noble, *Anal. Chem.*, 1993, 65, 693.
- 19 R. S. Johnson, *Environ. Test. Anal.*, 1998, 7, 32.
- 20 T. Bastow, W. H. Durnie, A. Jefferson and J. Pang, *Appl. Spectrosc.*, 1997, 51, 318.
- 21 P. A. Wilks, *Am. Lab.*, 1996, 28, 52.
- 22 P. A. Wilks, *Proc. Annu. ISA Anal. Div. Symp.*, 1998, 31, 211.
- 23 V. Lopez-Avila, R. Young, R. Kim and W. F. Beckert, *J. Assoc. Off. Anal. Chem.*, 1993, 3, 555.
- 24 L. T. Taylor and S. L. Jordan, *J. Chromatogr. A*, 1995, 703, 537.
- 25 B. Minty, E. D. Ramsey, A. T. Rees, D. I. James, P. M. O'Brien and M. I. Littlewood, in *Analytical Fluid Extraction Techniques*, ed. E. D. Ramsey, Kluwer, Dordrecht, 1998, pp. 353-364.
- 26 D. L. Heglund, D. C. Tilotta and S. B. Hawthorne, *Anal. Chem.*, 1994, 66, 3543.
- 27 R. W. Current and D. C. Tilotta, *J. Chromatogr. A*, 1997, 785, 269.
- 28 B. Minty, E. D. Ramsey, I. Davies, D. I. James, P. M. O'Brien and M. I. Littlewood, *Anal. Commun.*, 1998, 35, 277.
- 29 E. D. Ramsey, B. Minty and R. Babecki, in *Analytical Supercritical Fluid Extraction Techniques*, ed. E. D. Ramsey, Kluwer, Dordrecht, 1998, pp. 123-129.
- 30 P. J. Whittle, W. A. McCrum and M. W. Horne, *Analyst*, 1980, 105, 679.
- 31 W. A. McCrum and P. J. Whittle, *Analyst*, 1982, 107, 1081.
- 32 *Analytical Supercritical Fluid Extraction*, ed. M. D. Luque de Castro, M. Valcarcel and M. T. Tena, Springer, Berlin, 1994, pp. 88-119.
- 33 M. Poliakoff, S. M. Howdle and . Kazarian, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 1275.
- 34 R. G. Simard, I. Hasegawa, W. Bandaruk and C. E. Headington, *Anal. Chem.*, 1951, 23, 1384.
- 35 G. P. Coles, R. M. Dille and D. L. Shull, *Am. Chem. Soc., Div. Pet. Chem., Prepr.*, 1975, 20, 641.
- 36 Y. Daghbouche, S. Garrigues, A. Morales-Rubio and M. de la Guardia, *Anal. Chim. Acta*, 1997, 345, 161.
- 37 V. Lopez-Avila, J. Benedicto, D. S. Dodhiwala and R. Young, *J. Chromatogr. Sci.*, 1992, 30, 335.