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Determination of total petroleum hydrocarbons in soil by on-line supercritical fluid extraction–infrared spectroscopy using a fiber-optic transmission cell and a simple filter spectrometer

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Abstract

An on-line supercritical fluid extraction–infrared (SFE–IR) instrument is described for determining total petroleum hydrocarbons (TPHs) in soil samples. This instrument is constructed from a commercially-available SFE system and filter IR spectrometer, and an easily-constructed fiber optic IR cell. All SFEs are performed statically (i.e., no fluid flow once the SFE vessel is filled) for 30 min at 80°C and 340 atm. Detection limits for TPH were determined to be ca. 8 ppm for an IR cell with a 1-mm optical path, and are shown to degrade with increasing pathlength. The results from the application of this on-line SFE–IR instrument to the determination of TPHs in real-world samples show good agreement with those obtained from a standard Soxhlet extraction–IR method. Relative standard deviations of the on-line determinations are in the range of 7–10%. © 1997 Elsevier Science B.V.

Keywords: Infared spectroscopy; Detection, SFE; Petroleum; Fibre optic transmission cell; Optical pathlength; Hydrocarbons

1. Introduction

Supercritical fluid extraction (SFE) has a number of advantages over conventional solvent extraction such as speed of analysis, minimization of solvent waste and extraction efficiency. To date, the majority of SFEs have been performed in the off-line mode, i.e., the extract is collected through a flow restrictor into a small volume of solvent or onto a sorbent trap. On-line SFE methods, which involve directly coupling the SF extractor to a second analytical instrument, have been shown to possess a number of advantages chiefly because the restrictor can be eliminated. Specifically, if the restrictor is removed from the system then its concomitant problems are eliminated (e.g., plugging from matrix components and water). Additionally, on-line SFE methods generally eliminate the use of solvents used for either collecting the extract or desorbing the trap (many of which are environmentally hazardous). Finally, the loss of volatile analytes is greatly minimized in on-line methods because the analytical system is completely closed.

The use of optical spectroscopic detection for on-line SFE is advantageous over other types of detection (mass spectrometry, for example) because most optical detection systems are inexpensive, fast, easy-to-use and compact. Among the various optical spectroscopic methods available for direct interfacing to an SFE system, infrared (IR) spectroscopy is, perhaps, the most useful because it is unparalleled with respect to its specificity for molecular structure. Infrared spectroscopic detection in SFE, therefore, can be highly specific for a given molecule or class of molecules (e.g., carbonyls, nitrates, etc.).

Recent work in our laboratory has involved the

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development of a simple and low cost interface for SFE and IR spectroscopy [1,2]. The interface is constructed from two short lengths of chalcogenide fiber optic cables and a 1/8 in. (1 in.=2.54 cm) union cross. Graphitized polyimide ferrules are used to connect the fiber optics to the union cross. We have shown that this interface, which functions as a transmission cell, is rugged to pressures as high as 400 atm (1 atm=101 325 Pa). Additionally, the fiber optic cell has an easily adjustable optical pathlength and is simple to clean.

The purpose of this communication is two-fold. First, we examine the possibility of coupling the SFE system to a portable, scanning IR-filter spectrometer in an effort to design an inexpensive and simple on-line instrument for determining total petroleum hydrocarbons (TPHs) in soil samples. Recent on-line SF–IR methods have involved the use of Fourier transform infrared (FT-IR) spectrometers [1–3] which have the disadvantages in that they are complex to operate, fragile and expensive. In contrast, filter IR spectrometers are simple to operate, rugged and relatively inexpensive. Additionally, the use of a filter IR spectrometer is expected to produce a more lightweight and portable SFE–IR instrument (as opposed to one using an FT-IR spectrometer) that has the capability of being useful in field determinations.

The second goal of this work is to examine the effect of the optical pathlength on the light throughput and detection limits. As opposed to conventional transmission cells used in IR spectroscopy (i.e., windowed cells), the fiber optic transmission cell has a distinct difference in that the radiation exiting the fiber has a conical divergence and does not travel in a parallel fashion. Thus in contrast to conventional windowed cells, it may be anticipated that longer optical paths may actually lead to decreased light throughput and poorer detection limits.

2. Experimental

2.1. Apparatus

A schematic diagram of the experimental system is shown in Fig. 1. An ISCO Model 260D Syringe Pump (Lincoln, NE, USA) was used to provide liquid CO_2 to a 6.94 ml Keystone Scientific extraction vessel (Bellefonte, PA, USA, P/N 68915). The SFE vessel was heated with a tube heater controlled by an Omega 6000 Model 6102 thermostatic temperature control (Stamford, CT, USA). All plumbing connections were accomplished with 1/16 in. stainless steel tubing.

The fiber-optic IR cell, which has been described previously, is constructed from two 5.5 cm lengths of chalcogenide-glass (AsSeTe) infrared fibers (Amorphous Materials, Garland, TX, USA), narrow-bore (1.5 mm I.D.) 1/8 in. stainless-steel tubing, graphitized polyamide ferrules and a 1/8 in. stainless steel union cross (Parker-Hannifin Corporation, Huntsvil-

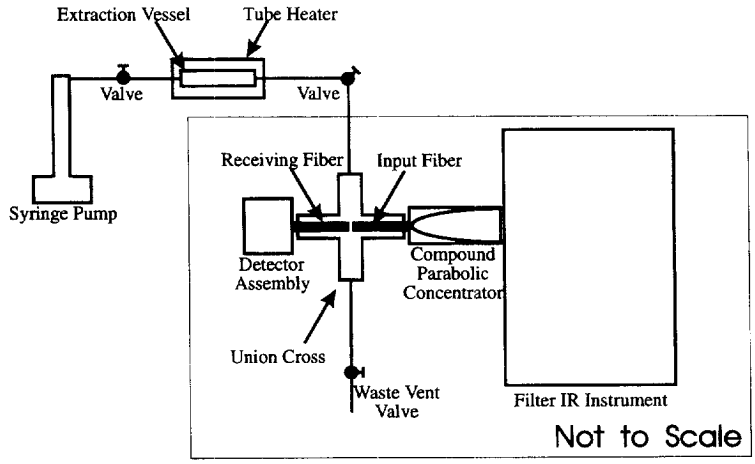

Fig. 1. Schematic diagram of the on-line SFE–IR system with filter instrument.

le, AL, USA, P/N 2KBZ-SS) [1]. The IR cell was operated at room temperature for these studies.

A Foxboro Model MIRAN 1A-CVF scanning filter IR (Bridgewater, MA, USA) was used as the spectrometer. The IR spectrometer was slightly modified for installation of the IR cell by removing the detector assembly from its factory mounted position and placing it outward from the sample area to a total distance of 6 in. from the exit slit of the IR (unless otherwise noted). This modification was accomplished by mounting the Foxboro instrument and the detector assembly on a 1×3 ft. (1 ft.= 30.4801 cm) optical plate (Edmund Scientific, Barrington, NJ, USA). The IR cell was then mounted in the normal sample compartment of the instrument. The exit slit of the instrument was fixed at 2-mm for all SFE–IR determinations and resulted in an approximate spectral resolution of 36 cm^{-1} at 3000 cm^{-1} (0.04 μm at 3.33 μm).

A Janos Technology (Townshend, VT, USA) compound parabolic concentrator (CPC, P/N-A0093-001) was evaluated as to its ability to couple light from the exit slit of the filter spectrometer to the input fiber optic of the cell (Fig. 1). The CPC possessed an entrance acceptance angle of 30°, and entrance and exit apertures of 9.74 mm and 2.52 mm, respectively.

For the TPH determinations using the Soxhlet extraction, the sample was determined in a Freon-113 solution on a commercially available Bio-Rad FTS-40 (Cambridge, MA, USA) FT-IR spectrometer. All spectra were collected at a speed of 2.5 kHz, an electronic filtering frequency of 1.12 kHz and a resolution of 4 cm^{-1} (0.005 μm at 3.45 μm). Sixty-four scans were coadded for each spectrum (both background and sample). Air was used as the IR background, and the spectrum of Freon-113 was subtracted from the spectrum of the TPH in the Freon-113 to determine the concentration of the TPH. A calibration curve was constructed from the reference oil (in Freon-113) over the anticipated concentration range.

2.2. Reagents and samples

Carbon dioxide was used for the SFE determinations and was obtained from Air Products (SFE/SFC grade) and from Scott Specialty Gases (SFC grade). Reagent grade chemicals were obtained from Aldrich (Milwaukee, WI, USA) and were used as purchased. The standard IR reference oil, as indicated by the United States Environmental Protection Agency (US EPA), was used to calibrate for TPHs (a 2:3:3 volume mixture of chlorobenzene, hexadecane and isooctane) [4]. The liquid standards were introduced into the extraction vessel using an adjustable (10–100 μl) Eppendorf pipette.

Diesel contaminated and gasoline–diesel contaminated soil samples were obtained locally from farm and railroad sites. Freon-113 was used for the Soxhlet extractions, and was obtained from Aldrich. The detection limit extractions were performed on clean Ottawa sand from Fisher Scientific (Pittsburgh, PA, USA).

2.3. Procedures

SFEs were performed in the static extraction mode and were accomplished as follows. The valves separating the SFE vessel from the IR cell and the IR cell from the vent line were both closed (see Fig. 1). The weighed sample was then placed in the SFE vessel which was then sealed and pressurized to 185 atm at 30°C. The temperature of the SFE vessel was raised to 80°C which increased the pressure in the SFE vessel to ca. 340 atm (the maximum pressure attainable with the Keystone vessel). The sample was extracted for 30 min. Following the SFE of the sample, the valve separating the SFE vessel from the IR cell was opened which resulted in the high pressure transfer of the extract into the IR cell. After a short time period to allow mixing (i.e., 1–3 min), the valve separating the SFE vessel from the IR cell was closed, and the IR absorbance of the analyte(s) was acquired.

Calibration curves were constructed by plotting the optical absorbances of the analytes at 2932 cm^{-1} (3.41 μm) versus their concentration in parts-per-million by volume (ppmv, μl of analyte/μl of CO_2). As described in a prior publication from our laboratory [1], the concentration of TPH was first calculated in ppmv and converted to ppm (parts-per-million, wt of analyte/wt of matrix) using the volume information obtained from the SFE pump and:

$$\text{ppm} = \frac{\text{ppmv} \cdot d \cdot V_d \cdot 1000}{W} \quad (1)$$

where d is the density of the oil (0.83 g/ml), V_d is the system dead volume in l (i.e., the volume occupied by the CO_2 in the SFE vessel, the IR cell and the interconnecting plumbing) and W is the weight of the soil sample in g. The initial and final volumes of CO_2 in the pump were recorded so that the volume required to fill the extraction vessel could be calculated.

Soxhlet extractions were performed on the same samples in order to compare the SFE results with those of a standard method [4]. These extractions were performed, in triplicate, on 3 g soil samples in 150 ml of Freon-113 for 4 h. Following the extraction, the TPH was determined using IR absorbance. Concentration was determined using the peak height of the 2932 cm^{-1} (3.41 μm) band. For all the studies reported in this work, the detection limit is defined at that concentration which produces a signal equal to twice the peak-to-peak baseline noise.

3. Results and discussion

3.1. Instrumental parameters

The Foxboro MIRAN 1A-CVF instrument is a general purpose, multiple wedge, IR filter spectrometer. This instrument is designed for a variety of applications where simplicity of operation is important. As a means of meeting this goal, the optical system has been designed so that it is robust and flexible. In order to accommodate a variety of possible sample cells, the sample compartment utilizes a $LiTaO_3$ pyroelectric detector element with AgBr focusing lens that can be moved with respect to its location near the exit slit.

As received, the sample compartment of the Foxboro scanning IR instrument was not large enough for both the fiber optic IR cell and the compound parabolic concentrator (CPC, as discussed below) to be placed in it. Thus, the sample compartment was effectively lengthened by remounting the detector assembly and the main unit on an optical plate placed beneath the instrument. This slight modification is rather trivial, and does not require any physical changes to the Foxboro instrument or the fiber optic IR cell.

In order to couple the radiation emanating from the monochromator into the input fiber of the IR cell, a CPC was used on the input fiber optic. The CPC, shown schematically in Fig. 1, is a non-imaging optical "funnel" that serves to concentrate light to an approximate point. A CPC was selected instead of a lens because the space between the exit slit of the monochromator and the input fiber would have required a lens with a shorter focal length than was available. A CPC was not used on the exit fiber because the detector focusing lens has an adequate collection angle, and a second CPC did not significantly improve the light throughput.

Ideally, the exit aperture of the CPC should be the same as the core diameter of the fiber. The chalcogenide fiber optics used in the IR cell have core diameters of ca. 0.75 mm. However, the smallest obtainable exit aperture of a commercially available CPC has a diameter of 2.52 mm. Thus, the CPC used in this experiment was not optimal because the exit aperture of the CPC was larger than the fiber optic core diameter. However, the use of the CPC resulted in an average throughput improvement of a factor of five over butting the fiber directly to the exit slit.

3.2. Spectral presentation

Fig. 2 shows a typical single-beam spectrum

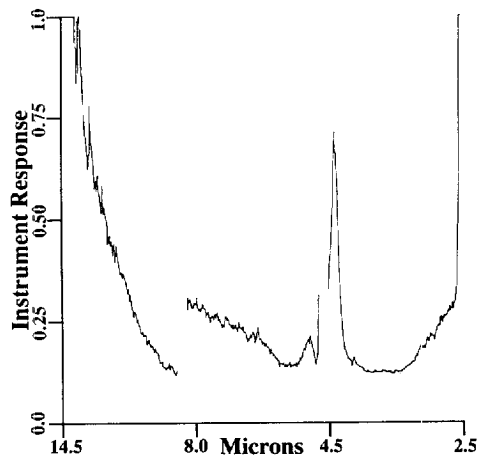

Fig. 2. Single-beam infrared spectrum of the fiber optic IR cell under atmospheric conditions.

obtained through the empty IR cell (under atmospheric conditions) at an optical path of 1 mm. Although this instrument possesses the feature of scanning, it should be noted that it is not a true double-beam instrument. Rather, it is a single-beam instrument with a manual electronic offset for zeroing at each wavelength. Hence, the baselines in these spectra are functions of the wavelength since electronic zeroing is not performed while scanning. The large instrument responses at ca. 2.5 μm and 14.5 μm are due to both instrumental and fiber optic cut-offs (i.e., the IR spectrometer and IR cell do not work outside these limits). Additionally, discontinuities occur in the single-beam spectra at 8.0 μm and 4.5 μm arising from filter changes in the instrument.

It has been shown that the C–H stretching band at 2932 cm^{-1} (3.41 μm) is effective for quantitating TPHs in soil by on-line SFE–IR [1]. Fig. 3 shows a spectrum of the reference oil in CO_2 at 340 atm obtained with this system. As shown by comparing the spectra in Figs. 2 and 3, the C–H stretching vibration is clearly visible at 2932 cm^{-1} (3.41 μm). The CO_2 bands are seen in the ranges of 3800–3500 cm^{-1} (2.63–2.86 μm) and 2500–2150 cm^{-1} (4.00–4.65 μm), along with Fermi resonance bands (from the CO_2) at ca. 1400 cm^{-1} (7.13 μm). Neither the CO_2 nor the fiber optic absorbances interfere with the absorbance due to the C–H stretch at 2932 cm^{-1} (3.41 μm) which is used for quantitation of TPHs in soil (as discussed in Section 3.3). However, it should be noted that the fiber optic cable has a small spectral feature at 2245 cm^{-1} (4.45 μm).

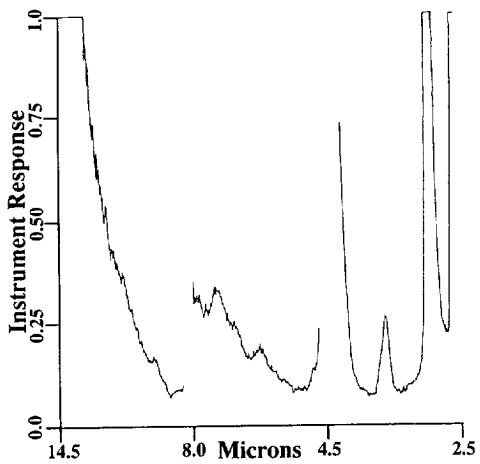

Fig. 3. Single-beam infrared spectrum of the reference oil in CO_2 at 340 atm.

3.3. Calibration

In order to establish the linear working range, calibration curves of the reference oil (in CO_2) were prepared at several pathlengths using the C–H stretching absorption at 2932 cm^{-1} (3.41 μm). These calibration curves are shown in Fig. 4. Also shown in Fig. 4 is a calibration curve of the reference oil in Freon-113 obtained in a standard ZnSe cuvette (path of 0.2 mm) on the Foxboro instrument. This figure clearly shows that the LDR of calibration for all paths, including the off-line calibration, is small (ca. two orders of magnitude) and exhibits downward curvature at concentrations exceeding ca. 5000 ppmv. This curvature is believed to arise from the large optical bandpass that this instrument possesses (36 cm^{-1} at 3000 cm^{-1}). Specifically, it is well-known that Beer's law deviates significantly from linearity for polychromatic radiation [5]. In contrast to this work, good calibration linearity (at least three orders of magnitude) was obtained in prior work when an FT-IR instrument was used at 4 cm^{-1} resolution.

Table 1 shows experimentally determined detection limits of TPHs at three optical pathlengths. As can be seen from inspecting this table, the detection limits increase as the optical path increases for this IR cell with the optimum pathlength occurring at ca. 0.33 mm. It should be noted that Table 1 does not include data for optical paths shorter than about 0.33 mm because shorter paths were difficult to measure, and fiber misalignment becomes severe (as discussed below).

The detection limits are poorer for the longer paths because the fiber optic transmission cell is different from conventional windowed cells. Specifically, the radiation exiting the input fiber (internal to the IR cell as shown in Fig. 5) diverges significantly. This divergence is expected to adversely affect the light throughput of the cell as the optical pathlength is increased. In turn, as the light throughput decreases, the signal-to-noise ratio becomes poorer. The effect of the optical path on the amount of light transmitted through the fiber optic cell can be detailed as

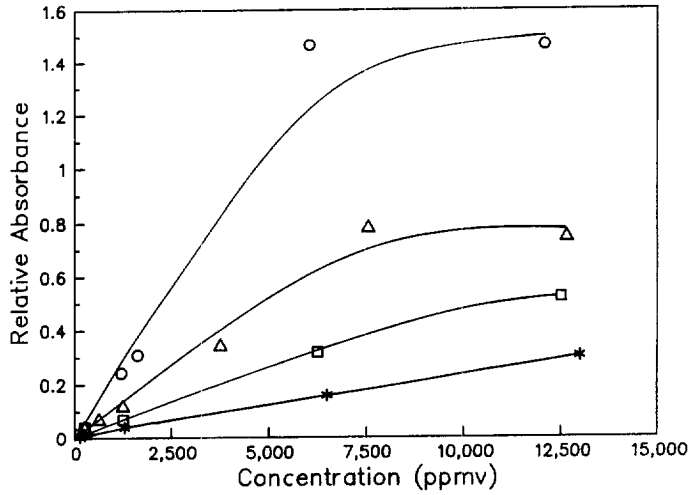

Fig. 4. Calibration curves of the reference oil as functions of optical pathlength. On-line SFE–IR curves are denoted by the circles (2.0 mm path), triangles (1.0 mm path), and squares (0.33 mm path). The calibration curve obtained in the 0.2 mm ZnSe cuvette is denoted with the stars. All curves were obtained using the C–H absorption band at 2932 cm^{-1} (3.41 μm).

Table 1
Detection limits for TPHs as a function of optical pathlength

Pathlength (mm)	Detection limit (ppmv)[a]	Detection limit (ppm)[b]
0.33	12	8
1.0	32	21
2.0	50	33

[a] As μl reference oil/l of CO_2.
[b] As μg reference oil/g of sand.

follows. The single-beam response of the instrument with the fiber optic cell in the sample compartment can be shown to be given as [6]:

$$S = R_o I \quad (2)$$

Where S is the single-beam signal measured at the readout device, R_o is the fraction of light transmitted across the fiber optic gap, and I is the wavelength-dependent instrument response function. This function converts the fraction of light reaching the detector to the value that is read on the readout meter and accounts for filter efficiency, source brightness, mirror and fiber light losses, etc. For relative measurements of S (i.e., normalized to the largest single-beam response), the exact magnitude of I need not be known since it is constant for a given experimental set-up. Normalized measurements of S are satisfactory in this study because we are interested in determining which pathlength has the largest throughput.

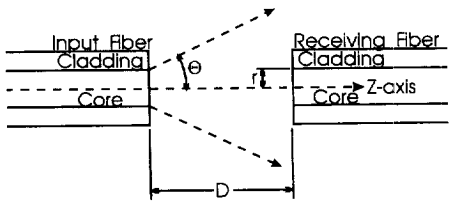

Fig. 5. Pictorial diagram showing the light divergence in the fiber optic cell as a function of the optical pathlength. D is the optical path, r is the fiber core radius and Θ is the divergence angle.

The fraction of radiation transmitted across the fiber optic path, R_o, is simply equal to the overlap of the area of the receiving fiber end and the area of the radiation impinging upon it (i.e., transmitted by the input fiber). This concept is shown schematically in Fig. 5. Using simple geometrical arguments, R_o is

related to the pathlength and the diameter of the fibers as

$$R_o = \frac{r^2}{(r + D\tan\Theta)^2} \quad (3)$$

where r is the core radius of the fiber optic cable, D is the distance between the two fibers and Θ is the angle the radiation disperses from the normal after it exits the fiber optic cable. The dispersion angle is calculated using the average numerical aperture (NA) reported from the manufacture (0.55) and the refractive index of air (1.00) using the equation:

$$\Theta = \sin^{-1}(NA/\eta) \quad (4)$$

For this system, Θ is calculated to be ca. 30°.

It should be noted that an approximation has been made in the calculation of Θ. Specifically, under typical use the fibers are extended into liquid or supercritical CO_2 and not air. Thus, the refractive index of CO_2, under the actual conditions, should be used. However, we performed the measurements in an empty IR cell under atmospheric conditions because it was experimentally more convenient (as discussed below). The refractive index of supercritical CO_2 is ca. 1.19 at 220 atm and 50°C [7]. Thus, η does not vary by more than 20% from atmospheric to supercritical conditions for CO_2. This variation causes Θ to change by not more than 3° (i.e., a change of ca. 10% to 27.5°).

In order to examine the trends in Eq. (2), an investigation on the effect of the optical pathlength of the fiber cell on throughput was conducted. Experimentally, this was accomplished by mounting the fiber optic cell in the filter spectrometer with the receiving fiber positioned in the system, but not seated. The pathlength was varied by 0.5 mm increments which was determined by measuring the length of the receiving fiber extending out from the cell arm. It should be noted that the focusing optics were realigned after each movement. The single-beam response was then monitored at 3.41 μm as a function of optical pathlength.

The results of this study are shown graphically in Fig. 6. The points in the graph on Fig. 6 show the observed percent relative single-beam response (i.e., normalized to the maximum response) at 0.5 mm path increments and the line in the graph shows Eq.

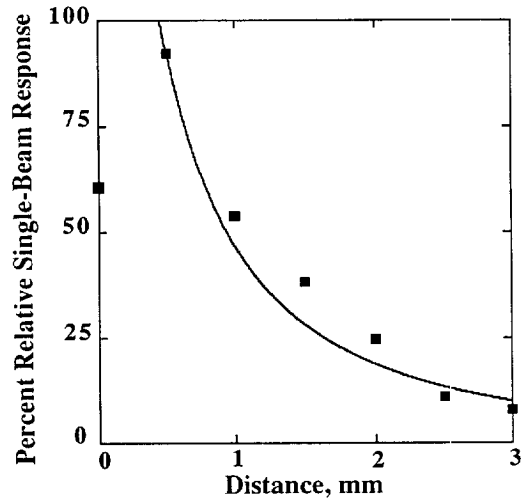

Fig. 6. Experimentally determined (solid squares) and theoretically determined (the solid line) light throughput of the fiber optic IR cell. All measurements have been normalized.

(2) (normalized to the maximum value) down to a pathlength of 0.45 mm. As demonstrated in this figure, the experimental work shows good agreement with the theory. As expected, when the pathlength was decreased, it was found that the transmittance of light through the cell increased, up to the point at which the misalignment of fibers caused a decrease in the transmittance (in the range of 0.3–0.5 mm). Perfect co-linear alignment of the two fiber ends within the cell with a zero pathlength (fibers touching) was not possible due to their positions in the tubing. Specifically, the outside diameter of the fiber is 1.00 mm and the stainless-steel tubing used to align the fibers has an inside diameter of 1.50 mm. Therefore, the fibers may "sit" to opposite sides of the tubing after the ferrules have been seated. This is especially exaggerated for these fibers because they are coiled as obtained. If the pathlength is close to zero, and one of the fibers is shifted off the z-axis (as identified in Fig. 5), the light throughput would decrease because the overlap area would be poor.

It should be noted that this fiber "misalignment" does not result in errors in the quantitation of analytes because the absorbance measurements are relative (to the empty cell). The fiber optic transmission cells are constructed using visual alignment, and, although we try to minimize the alignment errors, slight variations in alignment typically result

Table 2
Comparison of on-line SFE/IR determinations of TPHs in soil with Soxhlet extraction/IR determinations

Analyte/Matrix	Sample size (g)	On-line SFE–IR, ppm (%R.S.D.)[a]	Soxhlet extraction–IR, ppm (%R.S.D.)[a]
Diesel/soil	1	18 400 (7)	17 200 (7)
Diesel/soil	8	260 (10)	242 (18)
Gas–Diesel/soil	1	3530 (7)	3200 (7)

[a] R.S.D.s from triplicate extractions.

in variations in maximum throughput on the order of up to 30% for short pathlengths. However for a given IR cell, once the fibers are seated, no change in throughput is noted.

3.4. Application to real samples

The on-line SFE–IR system was used to quantitate TPH in various local "real world" soil samples and the results are shown in Table 2. Table 2 also presents the TPH determinations obtained from the standard Soxhlet method using IR detection. It should be noted that the on-line SFE–IR determinations used an optical path of 1 mm in the IR cell.

As demonstrated in Table 2, the results obtained from the on-line SFE–IR determinations agree remarkably well with those obtained from the standard method. Additionally, the relative standard deviations (R.S.D.s) of the two methods are comparable. As expected, the on-line SFE–IR results are slightly higher (but still within the R.S.D.s of the measurements) than those of the Soxhlet–IR determinations because of volatility losses in the Soxhlet method.

4. Conclusions

This work shows that a sensitive and reliable on-line SFE–IR instrument can be constructed from a commercially available IR filter spectrometer, a fiber optic IR cell, and a commercially available SFE system. We have shown that the optical throughput is maximized for the fiber optic IR cell when the optical pathlength is short. However, it was found experimentally that fiber misalignment at very short pathlengths minimizes the radiation overlap and results in a much lower light throughput than predicted. In a similar fashion, the detection limit of real analytes was found to increase as the optical path was lengthened (excluding the short pathlengths where fiber misalignment occurs).

Application of this on-line SFE–IR system to the determination of TPH in real samples shows results in agreement with the standard method. For a fiber cell with a 1 mm optical pathlength, detection limits for TPHs (using the 2932 cm^{-1} C–H stretching band) on the order of 8 ppm can be obtained with LDRs of calibration ca. two orders in magnitude. The R.S.D.s obtained using on-line SFE–IR are in the 7–10% range and compare favorably with those from the Soxhlet method.

Acknowledgements

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