



Short communication

Determination of total petroleum hydrocarbons in soil by dynamic on-line supercritical fluid extraction with infrared photometric detection

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Abstract

Total petroleum hydrocarbons (TPHs) in soil are determined by on-line dynamic supercritical fluid extraction (SFE) using infrared filter photometry detection. The filter photometer was constructed in the laboratory using a tungsten lamp, an optical notch filter that selects the C–H stretching vibration of the extracted organics, an optical chopper with demodulation electronics, and a PbSe detector. A modified high-pressure fiber optic flow cell was used to couple the SFE system to the photometer. Quantitation of TPHs was accomplished through the construction of calibration curves of integrated absorbance of C–H stretching (over time) versus concentration. Our studies show that the sensitivity of this system is affected by both the optical path length in the high-pressure cell and the SFE fluid flow-rate, and detection limits for TPHs are in the mid part-per-million range. The results of 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 standard Soxhlet extraction–IR methods.

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1. Introduction

Supercritical fluid extraction (SFE) is a useful alternative to conventional solvent extraction for the removal of organic pollutants from solid samples [1–3]. Analytical SFE can be divided into two categories based on whether or not fresh supercritical solvent is continuously supplied to the sample: static-mode extraction or dynamic-mode extraction. In static SFE, a fixed amount of solvent is applied to

the sample to accomplish the extraction. Fresh solvent is generally not applied to the sample to move the analytes until the extraction is finished. In dynamic SFE, fresh solvent is continuously applied to the sample for the duration of the extraction. Dynamic extractions are often preferred over static ones, for example, when analyte solubility in the supercritical fluid is important. However, it should be noted that some extractions employ a combination of static and dynamic steps.

Extractions with supercritical fluids, whether dynamic or static, can be carried out in the off-line mode or in the on-line mode [4,5]. In off-line SFE, the extracted analytes are removed from the fluid by

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first depressurizing it through a flow restrictor and then collecting the analytes in an appropriate solvent. The analytes are subsequently determined on a separate instrument (e.g. a gas chromatograph or an infrared spectrometer). On-line SFE methods avoid the use of the collection solvents by directly connecting the extraction system (either under pressure or depressurized) to the second instrument. On-line SFE methods have advantages in that they eliminate or minimize the use of secondary solvents, sample handling steps, and restrictor plugging. Additionally, volatile analytes are often better retained in on-line methods.

Successful on-line SFE methods using IR spectroscopy (SFE–IR) as a detector have been demonstrated [6–10]. On-line SFE–IR provides a convenient means of determining several classes of analytes directly in the supercritical fluid via their molecular spectra. Much of the previous work in on-line SFE–IR has focused on the use of Fourier transform (FT) instrumentation coupled with high-pressure flow cells. Although elegant, FT instrumentation is relatively expensive and complex, especially given the fact that many useful determinations require monitoring of only a single infrared band. For example, the measurement of total petroleum hydrocarbons (TPHs) can be accomplished through the absorbance of the C–H stretching vibration at ca. 2950 cm^{-1} [11]. Thus simpler, filter-based photometers that measure the absorbance at a single frequency would suffice for this determination.

In this work, we report on the development of an infrared filter photometer using a chalcogenide (As–SeTe) fiber optic interface for determining TPHs in soil samples by dynamic on-line SFE–IR. To our knowledge, this work represents the first application of on-line SFE–IR for the quantitative determination of TPHs in the dynamic extraction mode using a simple and inexpensive filter photometer. Previous work from our laboratory demonstrated the feasibility of using a filter instrument for detecting TPHs in on-line SFE experiments [6]. However, that work used a commercially-available instrument and, more importantly, carried out the extractions in the static mode. Preliminary results from this work indicate that dynamic on-line SFE–IR using the filter instrument has detection limits in the mid-part per million (w/w) range with excellent calibration linearity.

2. Experimental

2.1. Construction of IR cell

The fiber optic IR cell was constructed from a 1/8" stainless steel union cross in a similar manner as described previously [7] ($l=2.54\text{ cm}$). However, rather than using polyimide ferrules to effect the pressure seal on the fibers in the stainless steel alignment tubes as described in that work, they were glued into the tubing using epoxy cement. The epoxy was prepared by mixing Epo-Tek 353 ND part "A" with 353 ND part "B" (Epoxy Technology, Billerica, MA, USA) in the ratio of 10:1 (v/v). The mixture was introduced into the 1/8" stainless steel tubing arm, the optical fibers pushed into place, and the epoxy was cured in the arms by heating for 12 h at $60\text{ }^{\circ}\text{C}$. Following the curing process, the fiber optic ends were polished as described previously [7].

Two IR cells were constructed: one with an optical path length of 2.5 mm for calibration curves and sample determinations, and another with a path length of 1.0 mm to examine how the sensitivity was affected by path length. A simple cell stage was made in-house from 1/4" plate aluminum to allow for reproducible and stable replacement of the IR cell into the IR photometer (described below).

2.2. IR photometer

The photometer was constructed in this laboratory and a schematic diagram of it is shown in Fig. 1. The photometer consists of an inexpensive 50 W, 12 V tungsten lamp (General Electric) as a source of radiation, an $f/2$ concave mirror used to collect the source radiation and focus it onto the input fiber of the IR cell, an optical bandpass filter (Spectrogon, US Inc., Parsippany, NJ, USA; part BP-3330-145-D) notched at 2980 cm^{-1} to select the C–H stretching vibration, and a PbSe photodetector (Hamamatsu, Bridgewater, NJ, USA; part P394A). Additionally, an optical chopper, operating at 150 Hz, was used to modulate the IR radiation and was constructed from a synchronous motor and a chopper blade (Oriel, Stratford, CT, USA; part 75157). The chopper reference circuit, used to generate timing signals for

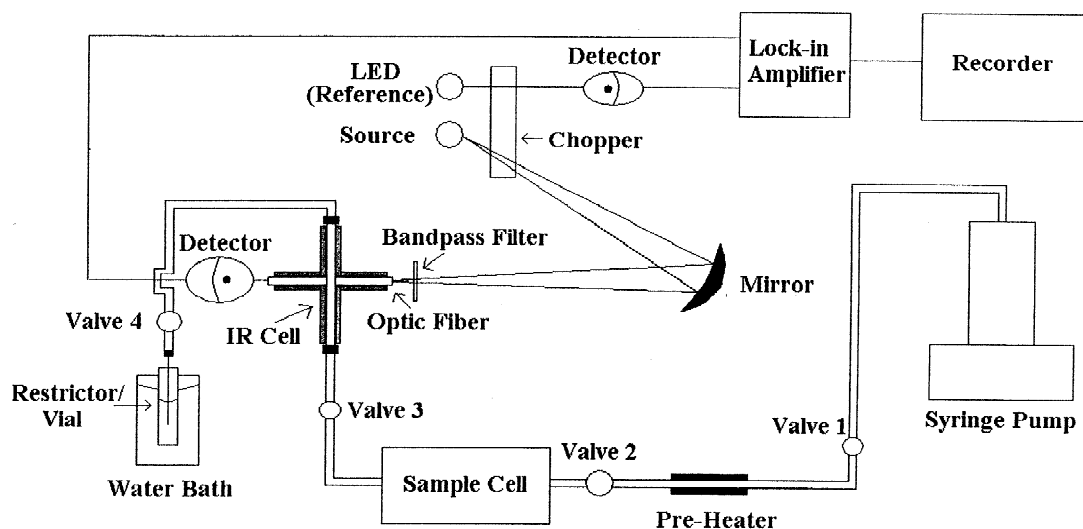


Fig. 1. Schematic diagram of dynamic on-line SFE-IR system.

the lock-in amplifier, was constructed in this laboratory using a near-IR (NIR) photodiode/phototransistor pair (Radio Shack, part 276-145). All of these parts were affixed to a 31 mm long \times 42 mm wide \times 6 mm thick aluminum plate using 6-mm-thick aluminum angle-irons. The angle-irons were attached to the plate using silicon adhesive.

As shown in Fig. 1, the emission light source was focused onto one end of the input fiber by the focusing mirror and through the bandpass filter. The detector was placed as close as possible to the output end of the other fiber. Stray radiation striking the detector was eliminated by winding black electrical tape around the stainless steel tubing holding the output fiber-optic end.

The output of the photodetector was amplified using a standard operational amplifier circuit configured as a voltage follower with gain. This amplified signal was demodulated using a Princeton Applied Research (Princeton, NJ, USA) model JB-8 lock-in amplifier. The output of the lock-in amplifier was fed into an OmniScribe chart recorder (Houston Instruments, Austin, TX, USA). Transmittance extractograms were digitized into absorption (AU) curves through the use of Un-Plot-It automated Digitizing System (Silk Scientific, Orem, UT, USA). Absorption area was calculated with the use of Quattro Pro software.

2.3. SFE apparatus

Carbon dioxide was introduced into the system with the use of an ISCO model 260D syringe pump (Lincoln, NE, USA) at a pressure of 200 atm and flow-rates in the range of either 0.85–1.00 ml/min or 1.90–2.05 ml/min (1 atm=101.325 Pa). The flow-rate of the fluid was controlled by a 13-cm linear silica capillary restrictor (I.D., 29 μ m). A Keystone scientific 6.94 ml stainless steel extraction vessel (Bellefonte, PA, USA; part 68915) was used for the SFE cell. The extraction cell was heated to 77–80 $^{\circ}$ C with a tube heater controlled by an Omega model 6102 thermostatic temperature control (Stamford, CT, USA).

A 1-m-long preheating coil, made from 1/8" stainless-steel tubing and covered with heat tape, was used to heat the CO₂ prior to admittance into the extraction cell. All interconnecting tubing was heated to 80 $^{\circ}$ C with heat tape. The fiber optic IR cell was heated to 40 $^{\circ}$ C with the use of water circulating through an aluminum jacket (laboratory-built) surrounding the cell. The restrictor was kept warm by inserting it into a hot water bath.

2.4. Reagents and samples

SFC/SFE-grade carbon dioxide (Air Products,

Allentown, PA, USA) was used for these experiments. The standard IR reference oil as indicated by the United States Environmental Protection Agency (EPA) was used to calibrate for TPHs [11]. The reference oil consists of a mixture of reagent-grade chlorobenzene–*n*-hexadecane–isooctane (2:3:3, v/v). The liquid standards were introduced into the extraction vessel using an adjustable Eppendorf pipette. Real world sample “A” was obtained by sampling soil adjacent to a fuel tank on a local farm site as previously described [9], and sample “B” was obtained by sampling soil near railroad tracks. Freon-113 was used for the Soxhlet extractions and was obtained from Aldrich.

2.5. SFE procedure

All SFEs were carried out in the dynamic mode and were accomplished as follows: valves 2 and 3 (Fig. 1) were first closed, and valves 1 and 4 were opened. Then, the weighed sample (about 2 g) was placed in the SFE vessel which was sealed and pressurized to 200 atm by opening valve 2. The SFE temperature was set to 80 °C. Valve 4 was then opened to start the extraction. Fluid flow-rates for the real-world determinations were adjusted to ca. 1 ml/min.

The extraction system was cleaned on-line by simply flushing it with carbon dioxide dynamically or statically (the IR cell or extraction cell did not require disassembly for cleaning). For static cleaning, the extraction system was pressured to 170 atm, and valves 2 and 4 were closed. After 3 min, valve 4 was opened to depressurize the system. This venting and pressuring cycle was repeated several times until a stable baseline was obtained. For dynamic cleaning, all valves were opened and CO₂ was allowed to flow through the system until a stable baseline was obtained.

2.6. Calibration

A calibration curve was prepared from successive injections of 15-, 40-, 65-, 90- and 115- μ l aliquots of the EPA reference oil into the extraction cell. The aliquots were treated to the same extraction conditions as the soil samples. For each aliquot, triplicate determinations were carried out. Calibration

curves were prepared by plotting the area of the absorption versus amount of reference oil.

2.7. Soxhlet extraction/standard method

Soxhlet extractions were carried out in triplicate on each of the real world samples for 4 h using Freon-113 as a solvent. Following the extraction, the cooled samples were then evaporated to approximately 5 ml each in volume through gentle heating. The samples were then diluted to 10 ml (total volume) with Freon-113.

For the TPH determinations using the Soxhlet extraction, the samples were detected in a Freon-113 solution on a commercially available Bio-Rad FTS-40 FT-IR spectrometer (Cambridge, MA, USA) using a 2-mm ZnSe cell. 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. 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.

Concentrations of 3000, 9000 and 13 000 ppm (v/v) (ppmv) of the EPA reference oil were made in Freon-113 and used to construct a calibration curve. The concentrations of the TPH in the samples were obtained on the basis of this curve.

3. Results and discussion

3.1. The epoxy fiber-optic IR cell

The fiber optic IR cell is inexpensive to build, easy to clean if contaminated, and easy to replace and construct. However for this work, we modified the previously designed cell by gluing the fibers into the stainless steel tubing rather than using the polyimide ferrules to effect the pressure seals. We found that repeatedly opening the valves (Fig. 1) to pressurize and depressurize the system resulted in the eventual failure of the polyimide seals and a subsequent lengthening of the optical path length over time. Of course, this change in optical path length made it impossible to obtain quantitative measure-

ments. Therefore, epoxy was used to hold the fibers rigidly inside the tubing in order to keep the optical path length stable during the experiments. The epoxy fiber-optic IR cell worked well as an SFE–IR interface for the 1 year duration of these experiments.

3.2. Photometer

Previous work in our laboratory has shown that the chalcogenide (AsTeSe) fiber-optic has a very good transmittance window between 2500 and 3500 cm^{-1} [6–8]. Vibrational stretching bands from C–H bonds occur in the 2900–3050 cm^{-1} spectral region. Since, supercritical CO_2 is relatively free of vibrations in this spectral region, we employed a bandpass filter notched in the 3050–2920 cm^{-1} spectral region to quantify all organic molecules which possess C–H moieties.

The filter photometer constructed in this laboratory is a single-beam device. However, an electronic double-beam measurement is obtained directly on the read-out by setting the transmittance to unity without the presence of reference oil in the system. As stated in the Experimental section, transmittance is then converted to absorbance via computer software.

3.3. Quantitative principle

This infrared filter photometer measures the optical absorption of C–H bonds in the high-pressure CO_2 stream following their removal from the matrix. Fig. 2 shows example “extractograms” (i.e. plots of the optical absorbance vs. time) obtained from a 40- μl aliquot of reference oil (dashed line) and a real-world sample (sample “A”) contaminated with petroleum hydrocarbons (solid line). Note that these extractograms occur in real time.

In general, Beer’s law ($A = ebc$, where A is the absorption, e is the absorptivity, b is the path length and c is the concentration) relates the absorption of a spectral band to its concentration. Similarly as employed by ultraviolet absorption detectors used in high-performance liquid chromatography, the area under the extractogram’s absorption curve (the total absorption, A_T) can be related to the total concentration by integrating Beer’s law:

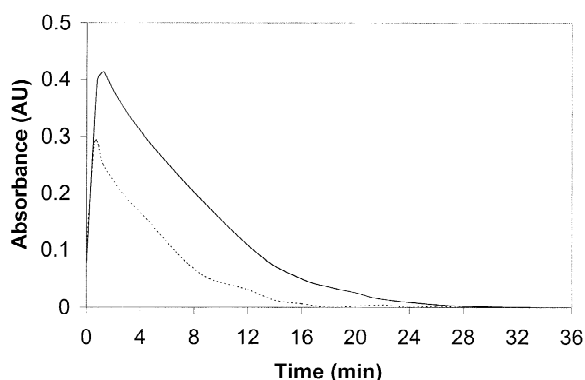


Fig. 2. Example extractograms obtained from the on-line SFE–IR system. The solid line is an extractogram of a 40- μl aliquot of the reference oil and the dashed line is an extractogram from a sample of soil contaminated with petroleum hydrocarbons (sample “A”).

$$A_T = \int A dt = eb \int c dt \quad (1)$$

Thus based on Eq. (1), a standard calibration curve is constructed by plotting the total areas of C–H absorption for reference oil aliquots of different sizes versus their concentrations. The total absorption areas from the unknown samples are then measured and compared to this standard curve in order to determine their concentrations of petroleum hydrocarbons.

3.4. Calibration and sensitivity

Calibration curves were obtained from the reference oil over the range of 15–115 μl (1479–11 336 ppmv, $\mu\text{l/l}$) using several optical path lengths and CO_2 flow-rates. The calibration curve data are summarized in Table 1. The data shown in this table can be used to draw two major conclusions, both of

Table 1
The effect of path length and CO_2 flow-rate on TPH calibration

Path length (mm)	Flow-rate ^a (ml/min)	Calibration data		
		Slope (AU/ppmv)	Intercept (AU)	r^2
1.0	2.0	1.6×10^{-5}	1.2×10^{-4}	0.996
1.0	1.2	2.4×10^{-5}	2.5×10^{-4}	0.991
1.0	0.9	3.4×10^{-5}	1.2×10^{-4}	0.997
2.5	0.9	8.2×10^{-5}	4.1×10^{-4}	0.996

^a Average.

which are easily explainable using Beer's law. First, as the flow-rate of CO₂ increases, the sensitivity (calibration slope) decreases. This linear decrease arises because the sample is diluted with CO₂ and, thus, its concentration decreases. Secondly, as the path length increases, the sensitivity approximately increases linearly as well.

The detection limit of TPHs for this system, defined as the concentration of the reference oil where the absorbance is equal to twice the peak-to-peak baseline noise, was determined by extracting aliquots of 4 µl of reference oil in a fiber-optic cell that used a 1-mm path length. Triplicate extractions yielded average detection limits of 83 ppm (w/w). Of course, it should be realized that the detection limits may be altered by adjusting the optical path length in the fiber optic cell.

3.5. Preliminary application to real world samples

The TPH in two "real-world" soil samples were determined to show that this system works with naturally occurring matrices. In these experiments, about 2 g of each sample was extracted in triplicate for each determination. For these samples, calibration was based on a standard working range of 15–115 µl (1479–11 336 ppmv) of reference oil.

Results for the determination of TPH by this method, as well as those obtained from other analytical methods, are shown in Table 2. As can be seen in this table, the TPH determined by dynamic on-line SFE–IR agrees remarkably well with both the standard Soxhlet procedure and static on-line SFE–IR methods, as expected. Additionally for these two samples, there was no plugging of the outlet restrictor and the flow-rate of fluid was stable during the experiment.

As an aside, it is interesting to compare the extractograms obtained for the real-world samples and the reference oil. As shown in Fig. 2, it can be observed that the onset of the extraction occurs at a slightly longer time for the natural sample than for the reference oil spike. Additionally, the naturally-occurring sample requires a longer extraction time to remove the hydrocarbons and results in an extractogram with a larger degree of tailing.

4. Conclusions

The determination of TPHs in soil samples by dynamic on-line SFE–IR using an infrared filter photometer is simple, fast and nonpolluting. The epoxied IR cell used in this work was found to be reliable and durable, and it was relatively cheap and easy to build and replace. As predicted by Beer's law, measurement sensitivity was found to be altered by both flow-rate and optical path length. Specifically, it was found that the sensitivity linearly increases as the flow-rate of supercritical fluid decreases and linearly increases with increasing path length of the IR cell. The application of this on-line method to the determination of TPHs in real-world samples shows results in excellent agreement with those obtained from standard Soxhlet extractions.

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Table 2

Comparison of results from on-line dynamic SFE determination of TPHs in soil samples with Soxhlet extraction and on-line static SFE determinations

Sample	Soxhlet (ppm)	On-line static SFE–IR ^a (ppm)	On-line dynamic SFE–IR (ppm)
A	38 500 (11) ^b	38 040 (24)	39 200 (12)
B	17 170 (7)	18 400 (7)	19 748 (5)

^a Results adapted from Ref. [7].

^b All results shown with %RSD from triplicate measurements (in parentheses).

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