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Recovery of diesel fuel from soil by supercritical fluid extraction– gas chromatography

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Abstract

An analytical method based on CO₂ supercritical fluid extraction (SFE) followed by gas chromatography (GC) was evaluated, compared to Soxhlet extraction, and found to determine accurately and precisely diesel fuel contamination of standard soil samples at a total petroleum hydrocarbon level of 100 µg/g in soil. While both extraction methods have the same 3% relative repeatability standard deviation for determination of total hydrocarbon contamination at this level, SFE requires much less time, uses less organic solvent and provides better recovery of the more volatile *n*-C₁₀ to *n*-C₁₂ hydrocarbons. Published by Elsevier Science B.V.

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1. Introduction

Diesel fuel contamination of soil remains a significant environmental problem and measurement challenge [1,2]. While a non-extractive thermal desorption mass spectrometric method has been recently described [3], analytical systems based on quantitative extraction prior to chemical analysis are the only methods currently accepted by regulatory agencies. These extraction systems include ultrasonic agitation, simple liquid extraction, continuous liquid extraction (the classical Soxhlet), pressurized fluid extraction (PFE, originally termed accelerated solvent extraction or ASE) and supercritical fluid extraction (SFE)

[4–8]. Soxhlet, PFE and SFE are components of standard/regulatory methods [6,7,9,10].

Soxhlet extractions require considerable time (typically 16–20 h), are extremely labor intensive, are not amenable to automation and require the use of large volumes (~200 ml) of often toxic organic solvents. Subsequent evaporative concentration of the extracted analytes releases these solvents to the atmosphere; these vapors are themselves environmental pollutants. Methods using PFE are automated but still require moderate solvent volumes (~40 ml) and evaporative concentration of the analytes [8]. SFE methods typically are rapid (~5 min), easily automated, require very little organic solvent (~2 ml) and thus are more environmentally benign [11,12].

The nature of the analyte, the matrix and analyte–matrix interactions influence extraction efficiencies [14]. The extreme temperature, solvent polarity and duration of traditional Soxhlet extractions are in-

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tended to minimize matrix effects at the cost of very non-selective extraction. In contrast, SFE conditions are typically chosen to provide somewhat selective extraction; this often requires fine tuning of SFE conditions (temperature, pressure, density, organic modifiers, etc.) to each new analyte–matrix combination. Nonetheless, SFE has been successfully used for a variety of analytes in soils, including: total petroleum hydrocarbons [13,14], volatile aromatics [15], polynuclear aromatic hydrocarbons [16,17] and organochlorine and organophosphate pesticides [18]. We have previously shown that SFE is a rapid and efficient method for extracting diesel fuel from pure clay matrices [11].

There is no single nationwide level for declaring a soil hydrocarbon contaminated. Many State regulatory bodies have established threshold values for hydrocarbons in soil at or near 100 $\mu\text{g/g}$ [19]. As part of our ongoing efforts in environmental metrology and standards development, we have successfully applied the SFE method developed for clay matrices to a well-characterized distillate fuel oil in a representative soil. We report here the results of our validation studies of this SFE method versus classical Soxhlet at the 100 $\mu\text{g/g}$ contamination level.

2. Experimental²

2.1. Collection and preparation of soil

Wet top soil was collected at the Gaithersburg, MD, USA, campus of the National Institute of Standards and Technology (NIST). The soil was oven-dried for 18 h at 110°C, pulverized using a mechanical coal grinder and sieved. Soil particles of 250–600 μm diameter (30–60 mesh size) were collected and used for all experiments. Samples of this soil fraction were extracted using SFE and analyzed for the presence of hydrocarbons using

capillary gas chromatography (cGC). There was no evidence of hydrocarbon fuel contamination.

2.2. Preparation of diesel contaminated soil samples

NIST Standard Reference Material (SRM) 1624b Sulfur in Distillate (Diesel) Fuel Oil, a well-defined material comparable to a commercial diesel fuel oil [20], was used to prepare fuel-contaminated samples. Soil material containing 102.0 μg diesel fuel per g soil was prepared by weighing: (1) 705.51 g of the sieved soil into a 3000 ml round-bottom flask containing approximately 1500 ml of hexane and (2) 71.97 mg of SRM 1624b into a 100 ml flask containing 50 ml of hexane. The diluted SRM 1624b solution and two subsequent solvent rinses were transferred from the 100 ml flask to the 3000 ml flask containing the soil. This flask was attached to a rotary evaporator and immersed in a 40°C water bath. The hexane solvent was slowly removed over 30 min under slight vacuum. The resulting coated soil was a free-flowing, visually homogeneous powder. It was stored at room temperature in a 1000 ml glass bottle fitted with a PTFE-lined cap. This soil was analyzed periodically over 9 months; there were no changes in the peak area ratios of the $n\text{-C}_{10}$ to $n\text{-C}_{22}$ hydrocarbons during this period.

2.3. SFE procedure

Samples were extracted with SFE-grade CO_2 using an automated SFE instrument under the conditions shown in Table 1. All the samples were extracted in a 7.5 cm \times 1.1 cm I.D. stainless-steel

Table 1
SFE conditions

Parameter	Value
Supercritical fluid extractor	HP 7680A
Extractant	CO_2
Organic modifiers	None
Extractant density	0.8 g/ml
Extractant pressure	37.0 MPa (365 atm)
Extractant flow-rate	2 ml/min
Extraction temperature	80°C
Static extraction time	0 min
Dynamic extraction time	20 min

²Certain commercial equipment, instruments or materials are identified in this paper to specify adequately the experimental procedures used. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

extraction vessel having an internal volume of 7 ml. Approximately 6 g of soil were accurately weighed, sandwiched between disks of pre-cleaned filter paper and loaded into the head of the extraction thimble. Excess vessel volume was minimized by placing a loosely fitting glass rod below the sample bed (see Figure 1, Ref. [11]). The extraction vessel endcaps were hand-tightened, the vessel was placed in the extractor and the sample was immediately extracted.

After depressurization, the extracts were collected on a stainless-steel trap (6 cm×0.45 cm I.D.) packed with octadecylsilyl-modified silica. The trap temperature was maintained at 10°C during analyte collection and 40°C during analyte elution. The trap was eluted with 1.6 ml of a 5%-volume fraction methylene chloride in hexane after each extraction. A weighed amount of a toluene solution containing 20 µg/g biphenyl and 20 µg/g anthracene internal standards was added to the eluate. The volume of the eluate was reduced to 0.5 ml under a stream of argon. The resulting extracts were capped and stored at room temperature (for a maximum of 4 h) for subsequent GC analysis.

2.4. Soxhlet extraction procedure

New cellulose extraction thimbles were pre-ex-

tracted for 4 h with methylene chloride, oven-dried and stored in foil until use. Approximately 6 g of soil were accurately weighed directly into a cleaned thimble. Soil samples were extracted for 8 h with 250 ml methylene chloride. After cooling, a weighed portion of the toluene solution containing biphenyl and anthracene internal standards was added to the 250 ml boiling flask. The flask was then agitated to ensure mixing of the internal standards, and the extract was filtered through glass wool (to remove soil fines) into a clean 250 ml round-bottom flask. The extract was concentrated on a rotary evaporator in a waterbath held at 25°C to about 35 ml, transferred to a 50 ml centrifuge tube, and reduced to 1 ml under a stream of argon. Five ml of hexane were added to this concentrate to ensure adequate exchange into the solvent needed for GC analysis, the vessel was agitated and the volume reduced under a stream of argon to ~0.5 ml. This final volume was transferred to a 1.8 ml autosampler vial, capped and stored at room temperature (also a maximum of 4 h) for subsequent analysis.

2.5. Gas chromatographic analysis

The extracted diesel samples were analyzed by cGC under the conditions listed in Table 2. On-

Table 2
Gas chromatographic conditions

Parameter	Value
Gas chromatograph	HP 5890 Series II
Autoinjector	HP 7673
Injection mode	On-column
Injection port temperature	280°C
Carrier gas	Helium
Carrier flow-rate	1.0 ml/min constant flow
Retention gap	2 m uncoated 0.53 mm fused-silica
Column	60 m (5% phenyl) methylpolysiloxane, 0.25 mm I.D., 0.25 mm film thickness
Temperature program	35°C initial temperature; 5 min hold at initial temperature; 4°C/min ramp to 280°C final temperature; 10 min hold at final temperature
Detector	Flame ionization detection (FID)
Detector temperature	280°C
Data system	HP 3365
Data acquisition rate	20 Hz

column injection was required since less than ~ 0.6 μg total extracted diesel fuel was contained in each 1.0 μl injection volume. An automatic injection system and a PC-based data acquisition system permitted unattended operation.

2.6. Method of calibration and preparation of calibration solutions

Three separate diesel calibration solutions of approximately the same concentration were prepared gravimetrically from SRM 1624b in hexane. Biphenyl and anthracene internal standards were gravimetrically added to weighed aliquots of these solutions for each set of extracts analyzed. SFE and Soxhlet hydrocarbon extraction recoveries were calculated from the peak areas of the *n*-alkanes in the extracts normalized to the internal standard with the closest retention time. These areas were compared with those generated by directly injecting the calibration solutions of SRM 1624b.

3. Results and discussion

Measurement of the infrared absorbance at the 2900 cm^{-1} hydrocarbon C–H stretch is now widely used for qualitative detection of diesel fuel presence in soil extracts [10,13]. While this spectroscopic method is suitable for rapid screening of large numbers of samples, its inherent lack of specificity precludes quantification of individual hydrocarbon components present in any detected contamination. cGC with flame ionization detection (FID) provides quantitative measurement of individual diesel hydrocarbons, enabling identification of the possible source(s) of contamination. Individual hydrocarbon detection also enables quantitative characterization of extraction efficiencies as a function of volatility. Fig. 1 presents a typical chromatogram of SRM 1624b as recovered from soil.

Since we sought to characterize the absolute recoveries of specific analytes extracted from the soil samples (as opposed to the absolute amount of analyte in the original soil samples), internal standards were added to the samples after extraction but prior to any evaporation or transfer steps. Recoveries for individual components in the chromatographic

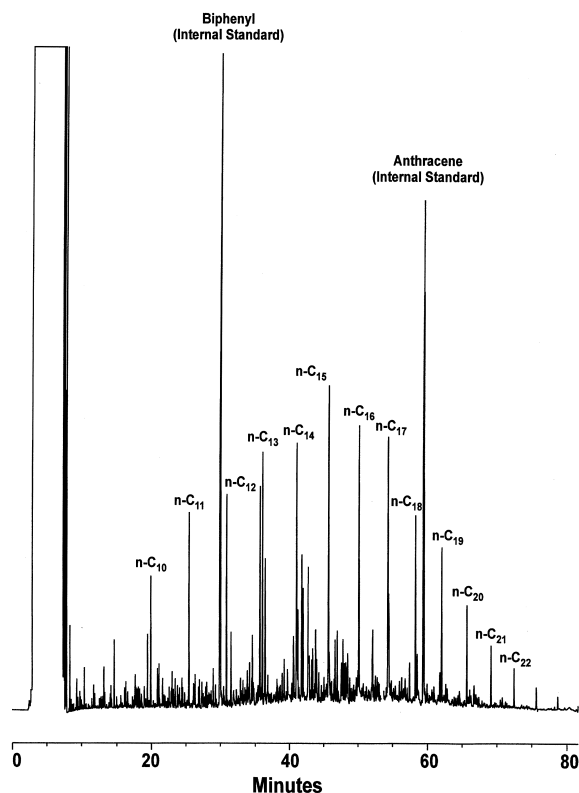


Fig. 1. Gas chromatogram of SRM 1624b sulfur in distillate (diesel) fuel oil after extraction from a representative soil.

analysis of both Soxhlet and SFE extracts may be calculated as:

$$\% \text{Recovery} = 100 \frac{(\text{Area}_{n\text{C}} / \text{Area}_{\text{I.S.}})_{\text{extract}}}{(\text{Area}_{n\text{C}} / \text{Area}_{\text{I.S.}})_{\text{standard}}} \times \frac{(\text{Weight}_{\text{standard}} / \text{Weight}_{\text{soil}})}{102.0} \quad (1)$$

where $\text{Area}_{n\text{C}}$ is the peak area of a selected *n*-alkane, $\text{Area}_{\text{I.S.}}$ is the area of the internal standard peak with the most similar retention time, $\text{Weight}_{\text{standard}}$ is the weight of diesel fuel in the standard calibration solution, $\text{Weight}_{\text{soil}}$ is the weight of soil extracted and 102.0 is the soil loading of SRM 1624b in $\mu\text{g/g}$.

The initial SFE extracts of the coated soil samples exhibited recoveries for the even hydrocarbons (*n*-C₁₂ through *n*-C₂₂) of 105–110%. After solvent cleaning the extractor, blank extraction of an empty extraction thimble with 50 ml of supercritical CO₂

revealed a significant presence of these even *n*-alkanes in the extraction volume. These artifact hydrocarbons disappeared after replacing the CO₂ cylinder with the same suppliers SFE Grade CO₂ from a different production run.

Fig. 2A reports the average recoveries for both SFE and Soxhlet extraction for the *n*-alkanes from *n*-C₁₀ to *n*-C₂₀. Fig. 2B reports the among-sample heterogeneity standard deviation for the analyses, calculated as the standard deviation of the average of

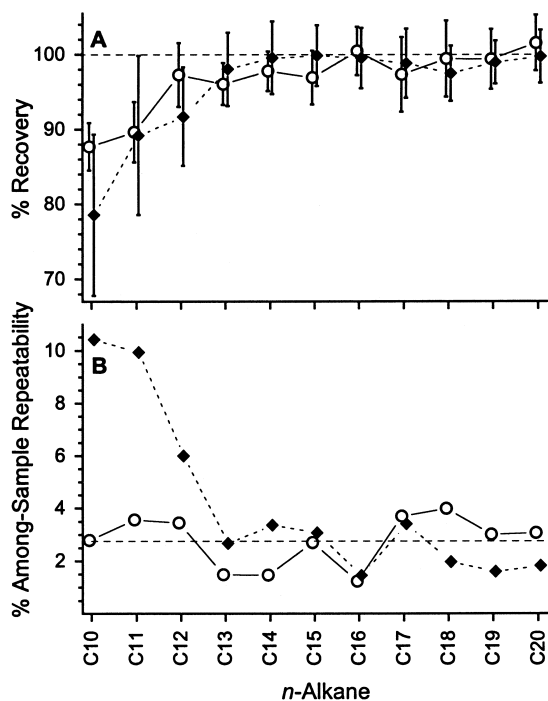


Fig. 2. Recovery efficiency and repeatability standard deviation for normal alkanes as a function of increasing carbon number. (A) Relative recoveries [100(weight recovered)/(weight loaded)] for SFE extraction are denoted as (○, solid line); those for Soxhlet extraction as (◆, dotted line). The bars denote the standard uncertainty, a combination of chromatographic variability and sample/extraction heterogeneity calculated from four replicate GC analyses each of five different soil extracts. The dashed line denotes the desired 100% recovery. (B) One standard deviation among-sample measurement repeatabilities for SFE extraction are denoted as (○, solid line), those for Soxhlet extraction as (◆, dotted line). These repeatability standard deviations were calculated from the average chromatographic values for each of five soil extracts. The dashed line denotes the expected total diesel measurement repeatability, calculated as the pooled individual repeatabilities for *n*-C₁₀ to *n*-C₂₀ SFE extracts and *n*-C₁₃ to *n*-C₂₀ values for Soxhlet extracts.

all replicate GC analyses of the same extract. While results of SFE and Soxhlet extraction methods are identical for the less volatile *n*-alkanes, SFE provides more complete and more uniform recovery of the *n*-C₁₀ through *n*-C₁₂ components. Pooling results for *n*-C₁₀ to *n*-C₂₀ alkane components of the SFE extracts with those for the Soxhlet *n*-C₁₄ to *n*-C₂₀ components, the expected relative repeatability standard deviation at the regulatory threshold (100 μg/g hydrocarbon in soil) is about 3%.

Suspecting that the low and variable Soxhlet results for the more volatile *n*-alkanes arose more from post-extraction sample handling rather than directly from extraction processes, 250 ml aliquots of methylene chloride were spiked with 60 μg of diesel fuel and prepared for analysis as if they were Soxhlet extracts. The same pattern of recovery and heterogeneity as a function of volatility was observed (data not shown).

We have recently achieved results for the Soxhlet extracts that almost equal our SFE results, using an automated turbo-evaporation apparatus that minimizes volatile losses. Nonetheless, some loss of the more volatile components seems unavoidable in both SFE and Soxhlet extracts. Thus, total diesel loading is more reliably estimated from hydrocarbons less volatile than *n*-C₁₃.

Each set of six SFE extractions required about 2.5 h (from sample weight determination to GC-ready extracts) and used 12 ml of organic solvent as well as 150 g CO₂. Each set of six Soxhlet extractions required 12 h and used a total of 1800 ml of solvent (methylene chloride and hexane).

4. Conclusions

SFE extraction with GC separation and FID detection can be successfully used to characterize soil contaminated with diesel fuel at 100 μg/g. An extraction blank is required for each CO₂ cylinder used, regardless of supplier specifications. SFE and Soxhlet extraction are equally efficient for *n*-alkanes no more volatile than *n*-C₁₃, with SFE providing more complete and more uniform results for the more volatile hydrocarbons. The superior results of SFE extraction are related more to the simpler, more automated sample handling than to intrinsic extrac-

tion efficiencies; both methods provide a relative repeatability standard deviation for total hydrocarbon load of less than 3%. SFE extraction of hydrocarbons from soil is thus as efficient as the reference Soxhlet method, while requiring less time and using much less organic solvent.

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