

# Extraction and analysis of diesel fuel by supercritical fluid extraction and microbore supercritical fluid chromatography

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## ABSTRACT

Supercritical fluid extraction was used to extract diesel fuel from soil. Extraction efficiency was greater than 90% regardless of the organic content of the soil and even after the soil had been aged for five days before analysis. Analysis of extracts by microbore supercritical fluid chromatography provided rapid characterization while GC–MS was used for analysis of residue levels.

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## INTRODUCTION

As environmental concerns grow, so does the need for rapid and reliable analytical methodology. One area of concern is contamination from underground storage tanks. In Massachusetts, where 80% of its municipalities rely on groundwater for their community drinking water [1], stringent penalties for polluters have been adopted under general law 21E [2].

Analytical methodology for extraction and analysis of soil for diesel fuel has largely been confined to extraction with dichloromethane [3], or alkalized methanol [4]. Both these techniques illustrate the problems associated with present environmental methods; (a) they are slow, requiring a minimum of two or more hours, and (b) they generate their own hazardous waste.

Further, the sample preparation step makes it virtually impossible to carry out the analytical procedure "on site". The increasing utilization of mobile laboratories has enhanced the demand

for methods which require little or no sample clean-up.

Supercritical fluid extraction (SFE) is increasingly becoming the technique of first choice for new environmental methodology. A general rule is that by increasing the pressure of the supercritical fluid, the solvating power of the fluid is increased [5]. This is a highly simplistic view of the dynamics of SFE and only appropriate for compounds sharing similar degrees of polarity to the fluid. For example carbon dioxide has a dipole moment of zero; increasing its density increases its ability to solubilize apolar analytes. This makes supercritical carbon dioxide an ideal vehicle for extraction of alkanes in fossil fuels from environmental matrices.

Supercritical fluid chromatography (SFC) has been recently somewhat overshadowed by SFE. Since the same equipment can often be used for both SFC and SFE, this technique combination presents an excellent tool for mobile laboratories where space is a premium.

Microbore column SFC presents several advantages over both capillary SFC and conventional packed column SFC [6]. Microbore offers

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the same advantages of packed column SFC over capillary column SFC [7], namely (a) a wide choice of stationary phases, (b) use of modifier gradients with organic solvents, and (c) use of less expensive grade carbon dioxide. However, microbore columns also boast advantages of capillary SFC, *i.e.*, being mobile phase linear velocities closer to optimum and less fluid consumption compared to standard packed SFC. Microbore SFC allows a simple 0.53  $\mu\text{m}$  O.D. fused-silica capillary to act as a restrictor and still maintain flow-rates between 0.5 and 1.5 ml/min, consequently not extinguishing the flame in the flame ionization detector at higher pressures. Microbore SFC has been used previously for analysis of pesticides [8].

This paper considers extraction of diesel fuel from soil, followed by analysis with either SFC or GC-MS. The extraction requires only a brief concentration step. SFC allows rapid on site analysis of soil contaminated by diesel spills while GC-MS analysis can be used for trace analysis. The effects of organic materials and water on the extraction efficiency are also explored.

## EXPERIMENTAL

### Reagents

Organic soil was potting soil purchased from Frank's Florist (Hadley, MA, USA). Low organic soil was collected at the University of Massachusetts (Amherst, MA, USA). Diesel fuel was automobile grade and purchased from Pride service station (Hadley, MA, USA). Dichloromethane was HPLC grade (Fisher Scientific, Springfield, NJ, USA) and liquid carbon dioxide was from Scott Specialty Gases (Plumsteadville, PA, USA).

### Supercritical fluid extractions

Aliquots of 1 to 2 g of 40/60 mesh sieved soil were spiked with various amounts of diesel fuel. The fuel spikes were delivered in 50  $\mu\text{l}$  of dichloromethane, the solvent was allowed to evaporate and the samples were placed in an empty 15 cm  $\times$  4 mm I.D. liquid chromatography column for extraction. The apparatus (Fig. 1), was a Suprex Model 200A supercritical fluid

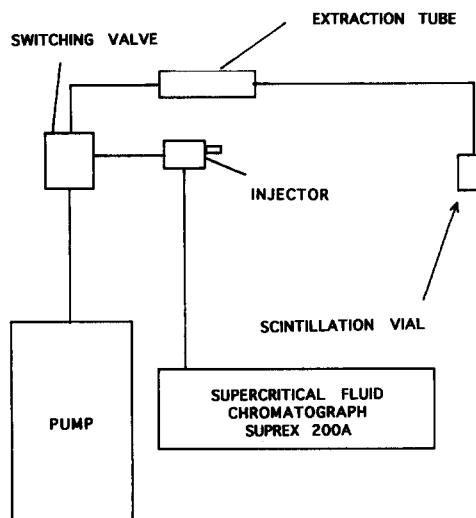


Fig. 1. Block diagram of SFE-SFC apparatus. A switching valve diverted the mobile phase to either the extraction vessel or the chromatograph.

chromatograph which had been modified so that extractions could alternately be carried out with chromatographic separations [9]. Samples were extracted for 10 min at 290 atm  $\text{CO}_2$  (1 atm =  $1.01 \cdot 10^5$  Pa) and ambient temperature (23–25°C) and collected in 10 ml dichloromethane. The dichloromethane extract was then reduced to 0.5 ml for analysis. Since the extraction was carried out below the critical temperature for carbon dioxide (31°C), it did not utilize a true supercritical fluid but rather a material in a dynamic gas-liquid equilibrium (*i.e.*, a “supercritical-like” fluid).

In some cases the soils were extracted moments after spiking while in others the spikes were aged for 5 days in the dark under ambient conditions.

### Supercritical fluid chromatography

A Suprex Model 200A supercritical fluid chromatograph equipped with a flame ionization detector was used. The unmodified carbon dioxide mobile phase was pressure programmed from 80 atm (3 min) to 165 atm at 5.7 atm/min then to 200 atm at 11.7 atm/min. The carbon dioxide effluent was restricted with 0.53 mm O.D. inert fused silica tubing to give a flow-rate of approximately 200 ml/min at ambient pressure for a pump head pressure of 80 atm. The oven con-

tained a 250 mm × 1 mm I.D. microbore Hyper-sil ENV column (Keystone Scientific, Bellefonte, PA, USA) and was maintained at 100°C. The flame ionization detector was operated at 250°C with hydrogen at 30 ml/min and air at 180 ml/min. Diesel fuel recoveries were quantitated by peak height against a one-point standard corresponding to 100% recovery. Comparison of random samples against a three-point curve gave equivalent recovery values to those obtained against the single standard.

#### Gas chromatography–mass spectrometry

Extracts analyzed by GC–MS utilized an HP 5890 equipped with an HP 5970A mass selective detector (Hewlett-Packard, Avondale, PA, USA). The 60-m DB-1 column (J & W Scientific, Folsom, CA, USA) was temperature programmed from 100°C (1) to 250°C (2) at 10°C/min. The injector and interface zones were maintained at 50°C and 280°C, respectively. Data acquisition was by single ion monitoring (SIM) for ion masses 57, 71, 85, 99, 113, 127, 140 and 155. Quantitation was by peak area against a reference standard equal to 100% recovery.

#### RESULTS

The soil utilized was arbitrarily classified as either 'high organic' or 'low organic' for the purpose of these experiments. High organic soil contained approximately 11% organic carbon while low organic soil was determined to contain about 3% organic carbon (Table I). All soil was dried at 100°C for 24 hr before use. SFE provided an effective means for extraction with recoveries greater than 90% (Table I). The presence of organic matter did not appreciably affect diesel fuel recoveries, not did aging the spikes for one week. Addition of water, however, reduced recoveries.

Microbore SFC provided rapid and reproducible diesel fuel chromatograms (Fig. 2A) and gives an excellent means for spill identification. The unmodified carbon dioxide eluent did not extract extraneous materials from either type of soil (Fig. 2B). Sensitivity limitations of the FID and SFC capacity limitations (low injection vol-

TABLE I

RECOVERY OF DIESEL FUEL FROM VARIOUS MATRICES

Soil type <sup>a</sup>	Aging period (days)	% Recovery ± S.D. <sup>b</sup>
Low organic	0	97 ± 10
High organic	0	108 ± 4
Low organic	5	96 ± 10
High organic	5	108 ± 1
Low organic + water <sup>c</sup>	0	61 ± 2
High organic <sup>d</sup>	0	102 ± 3
High organic <sup>d</sup>	5	92 ± 10

<sup>a</sup> As defined in text, low organic soil contains 3% organic carbon while high organic soil contains 11% organic carbon.

<sup>b</sup> Recoveries are an average of 2 spikes with standard deviation. Unless otherwise specified, spikes were 43 mg total diesel fuel per 2 g soil (roughly 2%, w/w) and were determined by SFC.

<sup>c</sup> Soil was adjusted to be 10% (w/w) aqueous.

<sup>d</sup> These values were obtained by GC–MS for 30 ppm (w/w) soil spikes.

umes) limit the technique to ppt (w/w) detection limits. However with spills where concentrations of this magnitude exist, identification is simple and rapid even after sample aging (Fig. 3).

GC–MS analysis of diesel fuel gives a typical

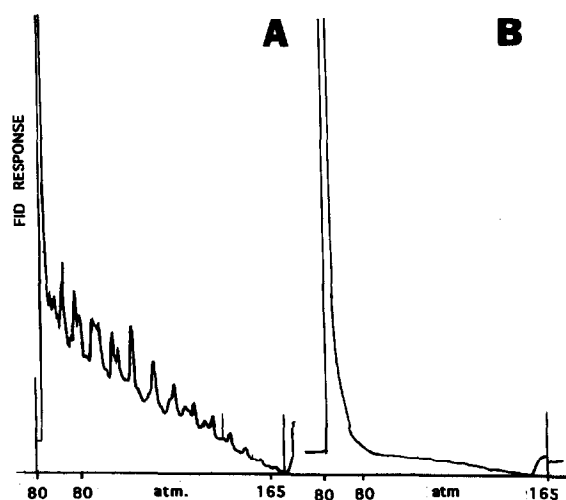


Fig. 2. Analysis of diesel fuel by SFC. (A) A 100- $\mu$ l injection of an 86 mg/ml diesel fuel standard. SFC conditions as given in text. (B) A 100- $\mu$ l injection of blank high organic soil extract. The 10-ml extraction was reduced to 0.5 ml for analysis.

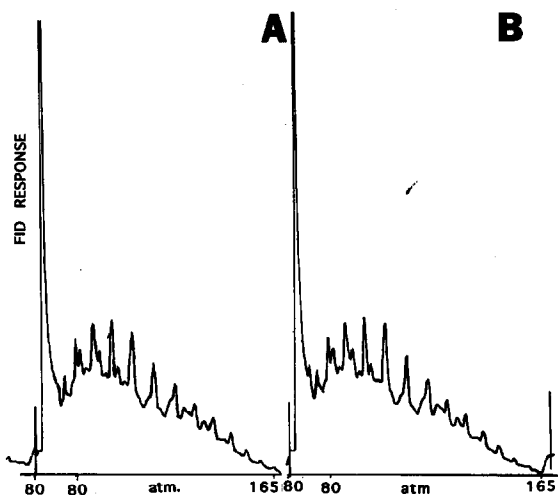


Fig. 3. Analysis of soil spikes by SFC. (A) A 100-nl injection of high organic soil spike. Sample was extracted within minutes of spiking. A 2-g soil sample was spiked with 43 mg diesel fuel. The 10-ml extract was reduced to 0.5 ml for analysis. (B) A 100-nl injection of high organic spike aged 5 days before analysis. Concentrations the same as those for A.

hydrocarbon profile (Fig. 4) and this technique enhanced detection significantly compared to SFC, with limits of 1–10 ppm being easily obtainable. Fig. 5 is an example of a SIM-GC-MS analysis of a 30-ppm soil spike extract. Mass spectrometry showed that analyte recoveries of residue level diesel contamination were similar to values obtained from spill level recoveries.

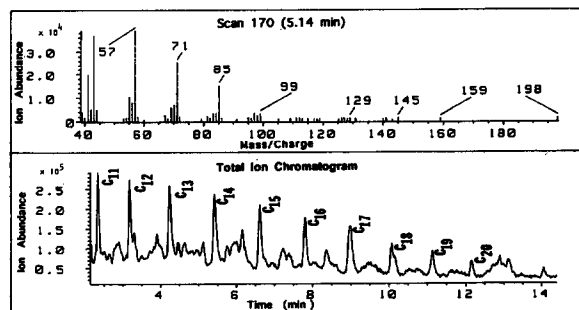


Fig. 4. Total ion chromatogram of 1 mg/ml diesel fuel standard. Chromatographic conditions as given in text, 2  $\mu$ l injected in the splitless mode. Peaks are identified by carbon number on chromatogram.

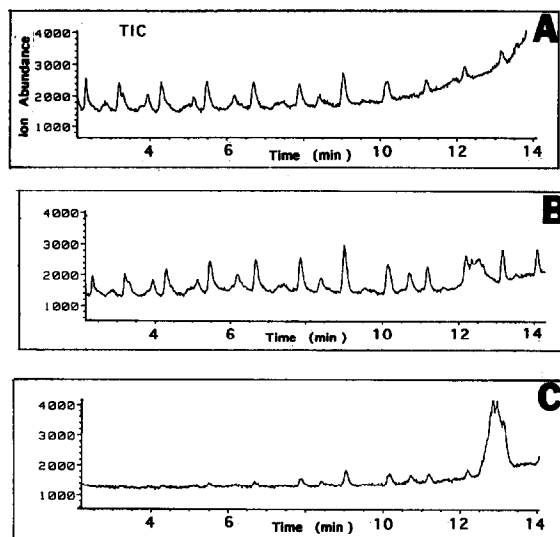


Fig. 5. Single ion monitoring chromatograms of 30 ppm soil spikes. Ions monitored are listed in text. (A) Extracted ion profile of a 2- $\mu$ l injection of a 120  $\mu$ g/ml standard. (B) Ion profile of a 30-ppm high organic soil spike recovery which was extracted moments after spiking. Final extract volume was 0.5 ml to give an expected concentration of 60  $\mu$ g/0.5 ml. An aliquot of 2  $\mu$ l was injected. (C) Ion profile of 2 g high organic soil which was not spiked with diesel fuel.

## DISCUSSION

SFE is a simple yet powerful tool for extraction of diesel fuel from soils. The selectivity of unmodified supercritical carbon dioxide for apolar compounds provides an excellent medium for extraction of the alkane series from petroleum fuels. The fact that effectiveness is not diminished as organic content is increased shows that even high levels of polar or slightly polar materials are not easily swept into the supercritical effluent. This dimension provides exciting prospects for designing clean-up steps with modified and unmodified carbon dioxide. The decrease in efficiency in the presence of water has been previously noted [10]. In solid phase extraction, large aqueous samples eventually form a hydrophobic envelope about the absorbing surface [11]; an analogous situation may be occurring here. Since water has such a dramatic effect of supercritical recoveries, addition of drying agents

such as Celite or sodium sulfate may enhance recoveries.

The utilization of SFC provides the analyst with a rapid (less than 1 hour from receipt of sample) and efficient means of on-site analyses. The use of microbore columns allows the chemist more flexibility with restrictors *vs.* standard packed columns and greater column capacity and ruggedness *vs.* capillary columns, which tend to become brittle in the presence of cold supercritical carbon dioxide.

#### ACKNOWLEDGEMENTS

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