

Recovery of diesel fuel from clays by supercritical fluid extraction—gas chromatography

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ABSTRACT

Supercritical fluid extraction (SFE) coupled with gas chromatography was used to analyze diesel fuel oil adsorbed on montmorillonite, kaolinite and illite clays. Adsorptive differences in the clays were reflected in the SFE desorption conditions required. However, in all instances the diesel hydrocarbon recovery was greater than 75% with an extraction precision of 2–3%. The short extraction times of 20 min and the other benefits of SFE make this method attractive over classical methods used to extract diesel oil quantitatively from soils.

INTRODUCTION

Supercritical fluid extraction (SFE) promises to provide rapid, automated extractions of organic analytes from various matrices without the use of hazardous solvents. These benefits suggest that SFE may be an attractive alternative to solvent extraction techniques which require large volumes of such solvents (*e.g.*, Soxhlet extraction and sonication). However, unlike the commonly used Soxhlet extraction and sonication procedures, the SFE conditions required for quantitative recovery are particularly dependent on the analyte and its matrix, and also on how the analyte is incorporated in the matrix.

Soil and associated groundwater contamination resulting from diesel oil spills and leaks from underground storage tanks are pressing environmental issues [1–3]. Because of its advantage, SFE was in-

vestigated as an alternative method to remove hydrocarbon contaminants from soil samples. As a first step in developing this method, the recovery of diesel fuel from clay was studied because clay is one of the major adsorptive fractions of soils. The three clays that were studied, each being a relatively well characterized material, were also used as model matrices to investigate SFE recovery processes.

Clay minerals are composed of layered aluminosilicate sheets which are bound to each other by van der Waals and electrostatic forces. Typically, the clays possess anionic charge on the surfaces of the sheets and to a small extent at edges of the clay particle surfaces. This charge is the result of isomorphous substitution throughout the clay lattice structure and is compensated for by the sorption of exchangeable cations. The nature of the cation (valence, size, energy of hydration, etc.) is important in defining the structure and stability of the interlayer which, in turn, affects the sorptive ability of the clay. Interaction of organic molecules with clay occurs either through weak physical adsorption or through actual penetration and intercalation in the interlayers, or basal spacings, of the clay matrix [4,5].

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The recovery of diesel oil from illite, kaolinite and montmorillonite (sodium and calcium forms) was studied. By using these clays, commonly found in North American soil, it was possible to determine diesel recovery from clays having different basal spacings and counter ions. The effect of added water on the SFE recovery of diesel oil from sodium montmorillonite clay was also investigated.

EXPERIMENTAL

Preparation of diesel-contaminated clay samples

Montmorillonite (sodium and calcium forms), kaolinite and illite clays were obtained from Ward's Natural Science Establishment (Rochester, NY, USA). Each clay was ground using an agate mortar and pestle and then sieved through wire-mesh screens. The 40–60 mesh fraction of the clay was used for all of the experiments. National Institute of Standards and Technology Standard Reference Material (SRM) 1624, a distillate fuel oil comparable to a commercial diesel oil, was used to contaminate the samples. Although SRM 1624 was not certified for any organic analytes, it was chosen because it is a homogeneous liquid and is a readily available source for diesel fuel oil. Five types of samples were investigated: SRM 1624 spiked on to filter-paper, unspiked/uncoated clays (blanks), SRM 1624 spiked on to each clay and SRM 1624 coated on to each clay with and without added water. Three 1-g aliquots of each sample type were extracted.

Spiked filter paper samples. Spiked filter paper samples were prepared by placing a *ca.* 1-cm thick bed of 1.1-cm diameter discs of filter paper in the top portion of the extraction cell as described below, and then injecting a weighed amount (*ca.* 50 mg) of a 50% (w/w) solution of SRM 1624 in toluene into the middle of the filter paper bed.

Blank clay samples. Blank samples were prepared by extracting 1.0 g of each of the clays. The clay bed was placed between two pieces of filter paper in the top portion of the extraction cell.

Spiked clay samples. Spiked clay samples were prepared by positioning 1.0 g of clay, sandwiched between two discs of filter paper, in the top portion of the extraction cell. A weighed portion (*ca.* 20 mg) of SRM 1624 was then injected through the top

filter paper disc mid-way into the clay layer.

Coated clay samples. A 10-g portion of the 40–60-mesh fraction of clay was weighed into a 250-ml round-bottomed flask. Approximately 260 mg of SRM 1624 were weighed into a 100-ml flask and diluted with 50 ml of a solution of 5% (v/v) methylene chloride in hexane. The diluted SRM solution and two solvent rinses were transferred into the 250-ml flask containing the clay. The flask was attached to a rotary evaporator and the solvent was removed in 20 min under a 25 mm water vacuum (3.3 kPa) at 40°C. The resulting material, a homogeneous-appearing, free-flowing powder, was stored in glass jars with Teflon-lined caps prior to extraction. Samples were found to be stable for 3 months at room temperature (20°C). Coated clay samples were prepared by placing a weighed portion (1.0 g) of the coated clay between filter papers in the top portion of the extraction cell.

Water wet-coated clay samples. The wet samples were prepared by injecting a weighed portion of distilled water (250 mg) into the bed of diesel-coated clay in the extraction cell.

Method of calibration and preparation of calibrant solutions

To evaluate the SFE recovery, the peak areas of the *n*-alkanes in the SFE extracts, normalized to the appropriate internal standard peak area, were compared with those generated by directly injecting a calibration solution of SRM 1624. Calibration solutions were prepared gravimetrically from SRM 1624 and a solution of internal standards, biphenyl and anthracene. Approximately 25 ml of SRM 1624 were drawn up into a 50-ml syringe. The syringe was weighed, and then its contents were injected into 2 ml of 5% (v/v) methylene chloride in hexane solution. The syringe was then reweighed, and the weight of SRM 1624 delivered was determined by difference. Because, in this study, the absolute recoveries of specific analytes extracted from the clay samples were to be measured (as opposed to the amount actually contained in the original clay samples), the internal standards were added to the samples after extraction.

SFE extraction procedure

Samples were extracted using an automated SFE instrument using SFE-grade carbondioxide. All 1-g

samples were extracted in 7.5 cm × 1.1 cm I.-D. stainless-steel extraction cells having an internal volume of 7 ml. After each sample had been loaded into the cell, the excess cell volume was filled by placing a 6 cm × 1.0 cm glass rod in the portion of the cell below the sample bed (Fig. 1). The extraction cells were sealed and the samples were extracted immediately to avoid evaporative losses. Samples were extracted using the conditions shown in Table I. After depressurization through an adjustable stainless-steel (SS) orifice, the extracted sample components were collected on an octyldecylsilane (ODS) trap and then eluted from the trap with two 1-ml portions of 5% (v/v) methylene chloride in hexane into 1.8-ml chromatography vials. The trap temperature was maintained at 10°C during analyte collection and at 40°C during analyte elution. After extraction, the two 1-ml trap eluates were combined with a weighed portion (440 mg) of a toluene solution containing the biphenyl and anthracene internal standards.

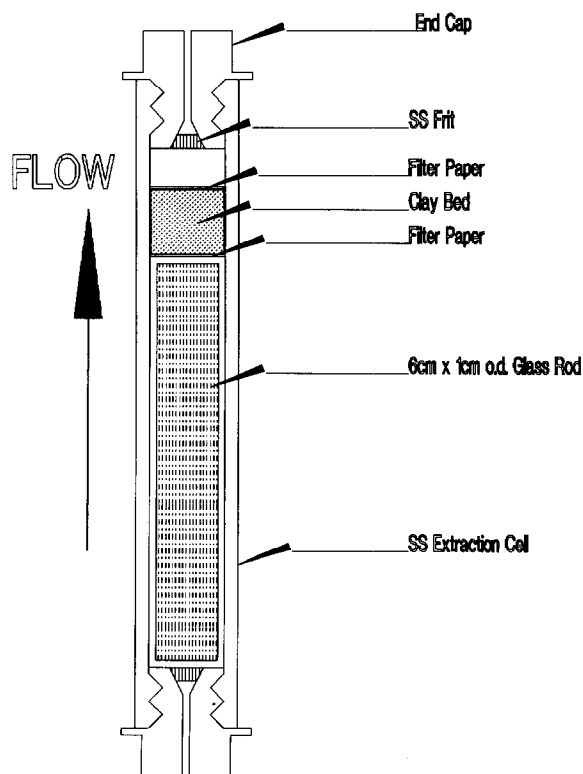


Fig. 1. Schematic diagram of extraction cell.

Soxhlet extraction procedure

Cellulose extraction thimbles were pre-extracted for 4 h in methylene chloride and charged with 1.0-g samples of diesel-coated montmorillonite clay. Triplicate samples were extracted for 6 h with 100 ml of methylene chloride. The resulting extracts were concentrated with argon to 0.5 ml using an automated evaporative concentrator. The concentrates were reconstituted to 2 ml with 5% (v/v) methylene chloride in hexane and the internal standards were added. Instead of adding internal standards before concentration, an evaporation blank was run. A weighed portion of the SRM 1624 was added to 100 ml of methylene chloride, which was then similarly concentrated and reconstituted to determine if any sample loss occurred during evaporation of the Soxhlet extracts.

Gas chromatographic (GC) analysis

The extracted diesel oil samples were analyzed using a gas chromatograph equipped with an auto-sampler and a flame ionization detector. The diesel analytes were separated on a 60 m × 0.25 mm I.D. immobilized methylsilicone column with a film thickness of 0.25 mm. The injection volume was 3 ml and the split ratio was 30:1. The carrier gas was helium at a flow-rate of 1 ml/min. The column oven was held at 100°C for 5 min, then programmed at 4°C/min to 280°C and held there for 5 min. The injector and detector temperatures were set at 280°C. Integration was performed using a PC-based data acquisition system. The reported recoveries represent the mean values of at least three individual GC analyses of each extract.

RESULTS AND DISCUSSION

The initial extraction and collection conditions [5 min, low pressure and temperature (P/T)] are shown in Table I and were determined by evaluating the recoveries of n -C₁₁ to n -C₂₂ Alkanes in SRM 1624 from the spiked filter paper samples. A chromatogram of SRM 1624 is shown in Fig. 2, and the results of the spiked filter paper studies are shown in Fig. 3. Quantitative extraction of SRM 1624 from the non-adsorptive filter paper matrix occurred after the passage of as few as 2.2 column volumes of carbon dioxide through the extraction cell. This observation suggests that once the ana-

TABLE I
SUPERCRITICAL FLUID EXTRACTION CONDITIONS

Parameter	5 min, low <i>P/T</i>	20 min, low <i>P/T</i>	20 min, high <i>P/T</i>
Extractant	CO ₂	CO ₂	CO ₂
Extractant density	0.8 g/ml	0.8 g/ml	0.8 g/ml
Extractant pressure	19.1 MPa (189 atm)	19.1 MPa (189 atm)	37.0 MPa (365 atm)
Extractant flow-rate	1 ml/min	1 ml/min	2 ml/min
Extraction temperature	45°C	45°C	80°C
Extraction time	5 min	20 min	20 min
Cell volumes swept	2.2	8.8	17.6

lytes are desorbed from the sample matrix, the extracted components are efficiently swept out of the cell without excessive mixing and are quantitatively retained on and then eluted from the ODS trap.

No organic material was found in extracts of the blank clay samples, and therefore the clay was used as received without further clean-up. Although the

5 min, low *P/T* extraction conditions provided greater than 95% recovery of each of the alkanes from the non-adsorptive filter paper, these conditions were not adequate for quantitative extraction from the spiked clay samples, being *ca.* 90% for C₁₄ to as low as 80% for C₂₂, indicating that physical and/or chemical interactions were occurring be-

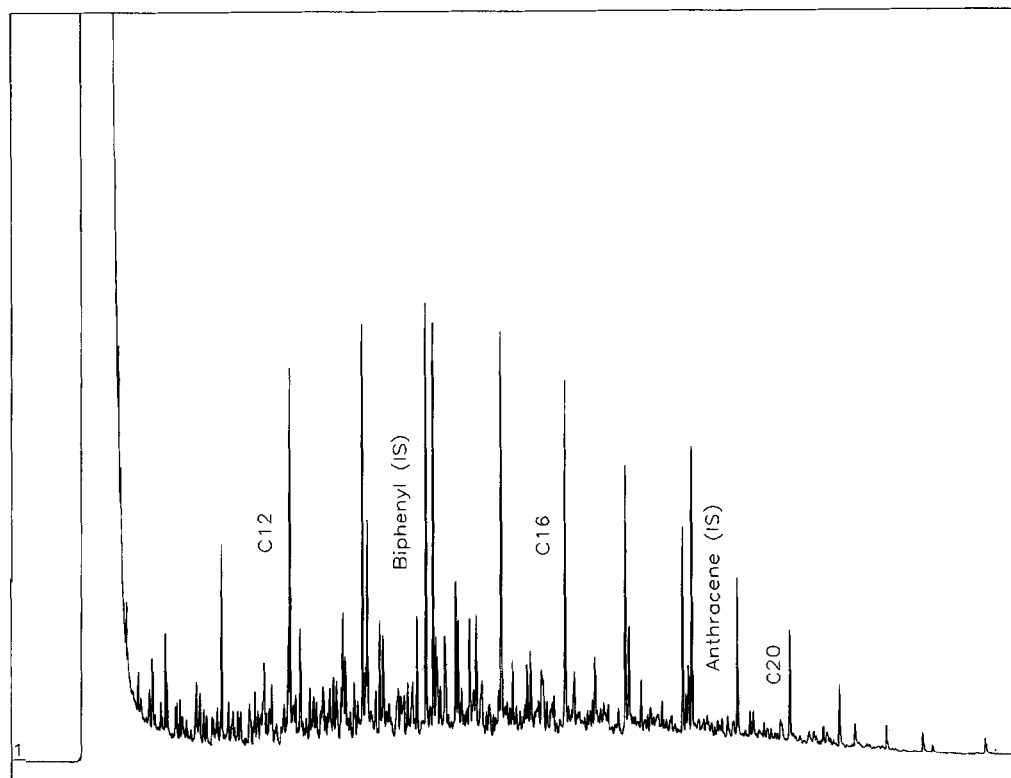


Fig. 2. GC of SRM 1624 diesel fuel oil. GC conditions: column, 60 m × 0.25 mm I.D. DB-5 with 0.25- μ m film thickness; carrier gas, helium (1 ml/min); split ratio, 30:1; column temperature, 100°C for 5 min, increased at 4°C/min to 280°C; held for 5 min; flame ionization detection.

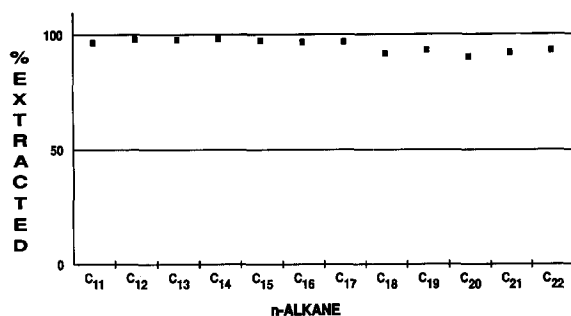


Fig. 3. Recoveries of *n*-alkanes in SRM 1624 from spiked filter paper following supercritical fluid extraction. CO₂: 0.8 g/ml at 1.0 ml/min. Conditions: 19.1 MPa (189 atm) and 45°C for 5 min.

tween the alkanes and the clay matrix. However, essentially quantitative recovery (>95%) of each of the sample components from each of the adsorptive clay matrices was achieved by increasing the number of column volumes of carbon dioxide swept through the extraction cell using 20-min extraction times (see Table I).

The 20 min, low *P/T* conditions were used to extract the illite and kaolinite clays. The recovery results are shown in Fig. 4. Recoveries >95% were achieved for each of the alkanes in SRM 1624 from the spiked illite and kaolinite samples. The apparent low recoveries of *n*-C₁₁ to *n*-C₁₃ alkanes in the coat-

TABLE II
CLAY PROPERTIES [4,7,10]

Clay	Basal spacing (nm)	Average surface area (m ² /kg)
Illite	1.0	100
Kaolinite	0.7	10
Montmorillonite	1.8	800

ed samples were shown by the Soxhlet experiments to be evaporative losses that occurred during coating of this material and were found not to be due to inefficient SFE extraction. Because of these losses, the maximum recovery and the mean replicate deviation reported for each experiment apply only to *n*-C₁₄ to *n*-C₂₂ alkanes. The high recoveries from both the spiked and coated samples indicate a weak alkane–clay interaction. Both illite and kaolinite possess strong interlayer bonding of the silicate sheets (Table II), as reflected by their basal spacings. As a result, penetration and adsorption of the alkanes by the clay matrices would be expected to be difficult [6].

Results for the spiked and coated sodium montmorillonite clay are presented in Fig. 5. The recoveries of the alkanes from the spiked sodium mont-

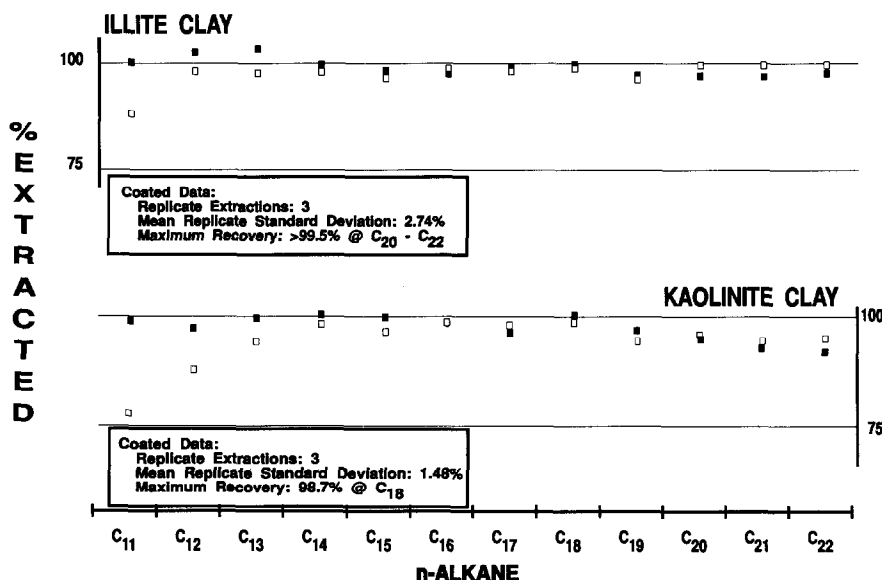


Fig. 4. Recoveries of *n*-alkanes in SRM 1624 from illite clay and kaolinite clay following supercritical fluid extraction. CO₂: 0.8 g/ml at 1.0 ml/min. Conditions: 19.1 MPa (189 atm) and 45°C for 20 min. ■ = spiked; □ = coated.

morillonite samples were significantly greater than those from the coated material. This effect is probably attributable to the extremely large internal surface area (approaching 750 m²/kg) accessible to the alkanes in this freely expandable clay. The large internal surface area is due to large basal spacings that result from weak interlayer bonding of the silicate sheets of the clay matrix [7]. Lower recoveries of the higher molecular weight alkanes extracted from the clay may be due to the greater Van der Waals sorption forces of these compounds with the clay matrix [8], the lower solubility of these species in the extracting fluid [9] and the lower diffusivities of these compounds through the clay matrix [10].

Additional samples of the coated sodium montmorillonite material were extracted using the 20 min, high *P/T* conditions (Table I). The number of cell volumes of carbon dioxide swept through the extraction cell was increased to 17.6 as its flow-rate was doubled. The extraction cell temperature was increased to 80°C while maintaining a constant density of 0.8 mg/ml, causing the extractant fluid pressure to increase to 37.0 MPa. The greater recoveries achieved using these conditions may result from the increased mobility of the alkanes and their increased solubility in the carbon dioxide. The recoveries for each of the analytes using the modified clay conditions are shown in Fig. 5.

As seen in Fig. 5, even under conditions near the pressure limit of the instrument, quantitative recovery of the higher-molecular-weight alkanes was not possible using pure carbon dioxide as the extractant. To determine if exhaustive extraction of all of the alkanes could be achieved, 1-g samples of montmorillonite clay coated with SRM 1624 were extracted using a classical Soxhlet apparatus. The Soxhlet extraction data, corrected for any evaporative losses are shown in Fig. 6. The results of the Soxhlet extraction study indicate that the SRM material was not irreversibly adsorbed and could be recovered. The Soxhlet extraction results also confirmed that the losses of *n*-C₁₁ to *n*-C₁₃ alkanes occurred during preparation and not extraction. There was significantly greater imprecision (8–9%) of the “recovered” low-molecular-weight alkanes that may have been caused by irreproducible losses in the Soxhlet extraction process and the final evaporative concentration step. Because the imprecision of the SFE recoveries for these alkanes was observed to be lower (2–3%), SFE appears to be a more precise method for extracting these volatile compounds.

Spiked and coated samples of the calcium form of montmorillonite were also studied further to investigate matrix effects with respect to diesel fuel recovery. Although calcium montmorillonite clay is

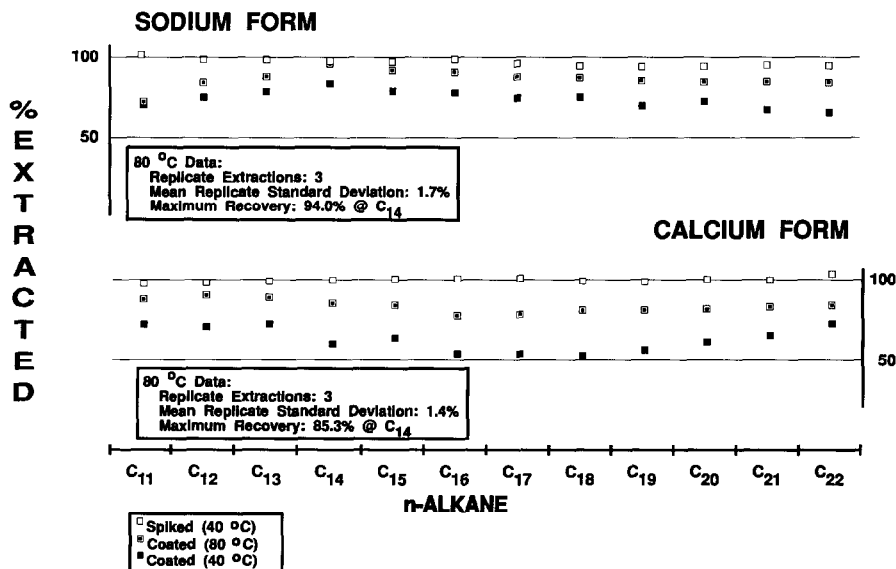


Fig. 5. Recoveries of *n*-alkanes in SRM 1624 from sodium montmorillonite clay and calcium montmorillonite clay following supercritical fluid extraction. CO₂: 0.8 g/ml at 2.0 ml/min. Conditions: 37.0 MPa (365 atm) and 80°C for 20 min.

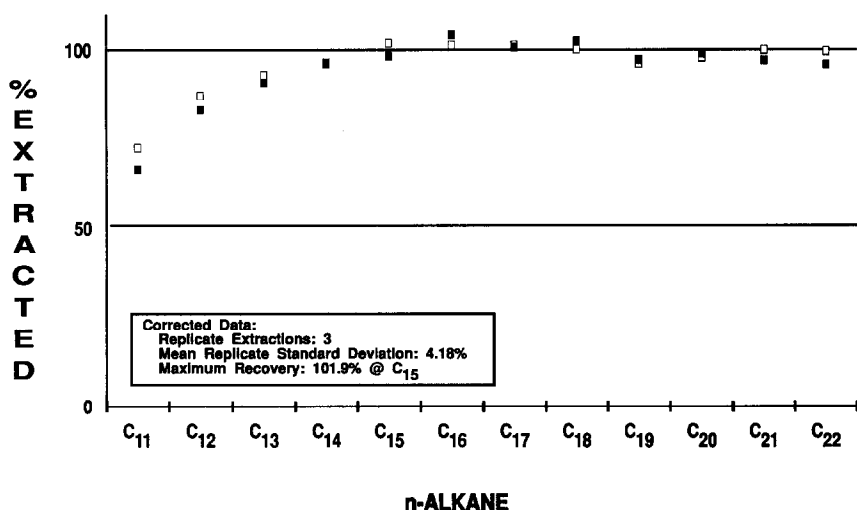


Fig. 6. Recoveries of *n*-alkanes in SRM 1624 from sodium montmorillonite clay following Soxhlet extraction (6h, methylene chloride). □ = Corrected for losses due to evaporative concentration; ■ uncorrected.

not as readily expanded by solvents as the sodium form of the clay [11], the calcium form, because of the greater energy of hydration of the calcium ion, is more adsorptive than its sodium counterpart [12]. SFE extraction recoveries were lower for the calcium form than those for the sodium form of the clay, as shown in Fig. 5. Unlike the other clay materials that were studied where the alkane recovery tended to decrease with increasing molecular weight, the recovery data for the calcium montmorillonite clay

exhibited a parabolic trend with respect to carbon number such that the mid-range alkanes were most strongly retained. This suggests that a size-exclusion effect, possibly due to the more structured interlayers in the calcium montmorillonite clay matrix [13], in addition to adsorption effects may influence the interaction of the diesel fuel with the clay matrix.

Sodium montmorillonite samples, with added water, were also analyzed using the 20 min, high

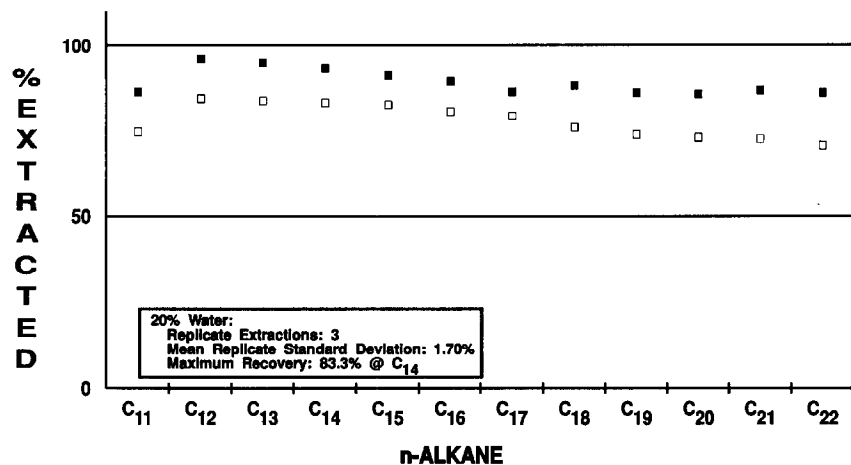


Fig. 7. Recoveries of *n*-alkanes in SRM 1624 from water-wet sodium montmorillonite clay following supercritical fluid extraction. CO₂: 0.8 g/ml at 2.0 ml/min. Conditions: 37.0 MPa (365 atm) and 80°C for 20 min. ■ = Coated, no added water; □ = coated, 25% added water.

P/T conditions. The recoveries for all of the alkanes were lower than those from dry diesel-coated clay, as shown in Fig. 7. When the clay matrix is swollen by the presence of water, the mass transfer of the analytes out of the matrix can be reduced. Addition of water can act to trap analytes physically within channels in the clay particles. Chemical changes, such as intra-cation exchange reactions, can also occur which affect the basal spacings within the clay by creating cavities that can cause the collapse of all or part of the lattice structure of the clay [7]. Further, the water film may also reduce the surface area available for penetration of the extractant.

As a result of this study, it was found that recovery of the n -alkanes from the clay matrices depended on the nature of the alkane and the matrix. While clays were used as model matrices to evaluate diesel recovery, the aim was to apply these results to the study of diesel-contaminated soil. Preliminary investigation of diesel-contaminated soils indicate that, while the highly adsorptive pure clays readily sorb and retain the diesel material, soils were quantitatively extracted using the 20 min, high P/T extraction conditions.

CONCLUSIONS

The SFE technique was easy to perform, rapid and required small amounts of solvents. We found that, unlike in the more accepted Soxhlet extraction and sonication procedures, the SFE extraction conditions must be optimized for the analyte and the matrix in order to achieve quantitative extractions. The SFE results showed that diesel oil recovery is influenced by the adsorptive behaviour of the individual clay matrix. The large internal surface areas of both of the montmorillonite clays enabled them to adsorb and retain more diesel material than the illite and kaolinite clays. Similarly, calcium montmorillonite retained more material than sodium montmorillonite. The recovery of the diesel oil was reduced when water was added to coated sodium montmorillonite clay, possibly because of changes in the matrix that may trap some of the adsorbed diesel, making it inaccessible to the extracting fluid.

In all instances, the recovery was improved by increasing the length, temperature and pressure of the extraction.

As the result of the study, a reliable SFE–GC method was developed that can be used successfully to extract diesel oil from illite and kaolinite clay, and also from the highly adsorptive sodium montmorillonite (wet or dry) and calcium montmorillonite clays. In all instances, diesel fuel recoveries were > 75% with a precision of 2–3%, making this method a candidate for survey analysis.

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