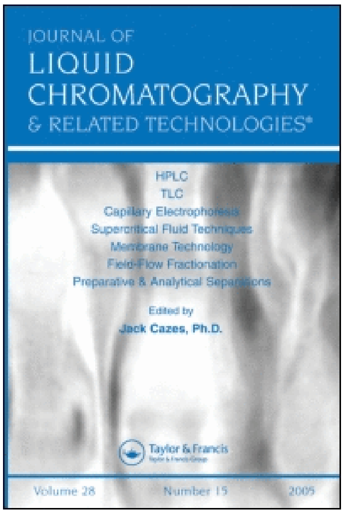

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Comparison of Modern Extraction Techniques in Analysis of Soil Contaminated with Fuel and Crude Oil Spills

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ABSTRACT

Supercritical fluid extraction (SFE) with CO_2 and pressurised fluid extraction (PFE) have been investigated for assays of soil samples contaminated with crude oil and compared with reference Soxhlet extractions using 1,1,2-trichlorotrifluoroethane (Ledon 113). Quantitative extraction of total petroleum hydrocarbons (TPH) by SFE was accomplished in 30 min at a pressure of 40 MPa and temperature of 100°C by using pure CO_2. For the PFE Ledon 113 as extractant, 100°C, 10 MPa, and two 5 min static steps were found as optimal conditions for quantitative extraction of petroleum hydrocarbons. To determine TPH in the extracts, Fourier transformation infrared spectrometry was used. Capillary gas chromatography with flame ionization detection provided information allowing one to differentiate the source of contamination of soil in the vicinity of an oil exploitation site.

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Key Words: Supercritical fluid extraction; Pressurised fluid extraction; Total petroleum hydrocarbons.

INTRODUCTION

The contamination of soil by crude oil or petroleum products may be attributed to various sources, which should be assessed before decontamination processes are started. Accidental spills and leaks of petroleum products during production, storage, and transportation represent potential environmental hazards. An extensive contamination of soil by crude oil spills is encountered in the vicinity of drill holes in an oil field.[1,2] In an investigated oil zone the case may be complicated by protrusion of the oil rock to the surface where an intensive biogenic alteration and oxidation of the degradation products of crude oil components takes place.[3,4] Such a secondary transformation brings about substantial changes in the composition of crude oil indicated by changed physico-chemical properties (density, viscosity, refractive index, etc.,) of the transformed crude oil, which at the surface temperature and pressure, resembles a tar-like, highly viscous liquid. An efficient mode of lifting such oil, which is used in a Centre of Oil Exploitation (COE) in Southern Moravia, Czech Republic, employs a combustion of oil in the deposit. The decreased viscosity of crude oil, caused by a high temperature, and the action of pressure of combustion products and also of compressed underground water, allow us to use a blowing method of oil exploitation.

Supercritical fluid extraction (SFE), is an extraction technique based on specific properties of a solvent above the critical point. The physical properties of supercritical fluids are favourable factors for the separation of substances from solid samples.[5] Details on thermodynamics of supercritical fluids can be found in the literature, showing that carbon dioxide is the most frequently used fluidum for SFE. For example, hydrocarbons and other lipophilic substances up to a molecular weight of $400\,\mathrm{g\,mol^{-1}}$ are easily extracted with CO_2 at a pressure below 30 MPa.[6–9]

Pressurised fluid extraction (PFE)[10] is based on an increased dissolving capacity of liquids at higher temperatures.[11] The extraction is realized above the atmospheric boiling point of the solvent, which is kept in the liquid state by an increased pressure,[12] thus, a diffusion rate is increased and, contrarily, viscosity and surface tension of the solvent are lowered.[13] These factors contribute to higher reaction kinetics of the extraction process. Thus, effective results of assays can be obtained in a relatively short time.

In the present paper, the applications of alternative and more rapid methods of extraction of the total petroleum hydrocarbons (TPH) has been investigated for assays of soil samples contaminated with such altered crude oil. Common physico-chemical methods of analysis do not provide a basis to differentiate between the original and the heat affected crude oil; therefore, it was necessary to investigate, beside the FTIR spectrometry, also the applicability of gas chromatography with flame ionization detection (GC-FID), and a direct sample injection.

EXPERIMENTAL

Instrumentation

A commercial SE-1 apparatus (SEKO-K, p.l.c., Brno, Czech Republic) was used for SFE analyses. For PFE, an apparatus prototype (model FastEx 01) was designed in co-operation with the University of Pardubice and produced in a development laboratory of the Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Brno.

Spectral analysis of extracts[14] was carried out with Equinox 55 Fourier transformation infrared spectrometer (Bruker analytische Messtechnik, Germany). Chromatographic analysis was performed with the use of Mega 5300 gas chromatograph (Fisons—Carlo Erba, Milano, Italy) equipped with a flame-ionization detector and a capillary column.

Reagents and Samples

Ledon 113 (1,1,2-trichlorotrifluoroethane for IR spectrometry, Merck) was used for the extraction with Soxhlet apparatus[15] and in the SFE and PFE experiments. Carbon dioxide of purity 4.5 (sum of hydrocarbons <2 ppm, Linde Werk. Tech. Gase, Germany) served as an extraction medium for SFE. Nitrogen gas of purity 4.0 (Linde Technoplyn, Prague, Czech Republic) was used as pneumatic pump driven gas with SFE, and as a carrier gas in gas chromatography, as well as in expelling the PFE extracts. Methanol for HPLC (J.T.Baker, Deventer, The Netherlands) was used as a modificator for SFE. Diesel oil, type NM4 (Česká rafinérská a.s., Litvínov, Czech Republic) was chosen as a standard substance for the determination of TPH.

For assessment of oil contamination, three types of samples of soil were taken from a COE site:

Sample A to represent combustion products burst to ground level. The base matrix of the sample is represented by gravel sand with a high proportion of well-formed grains in the range of 10^{-1}–100 mm diameter.

Sample B representing sampling from a depth of 3 m under the ground level. This sample was similar to that of type A, but the base matrix was more fine-grained.

Sample C representing a mixed sample. This sample, with a matrix resembling clayish soil, was taken from a muck pile of contaminated soil cleared away from different places and depths of the site. This type of sample was chosen to assess the effect of different types of mineral matrix on the degree of extraction of contaminating components.

A high level of oil contamination of the samples with a sandy or gravel matrix was noticeable, even visually, as they nearly resembled a sort of asphaltic bitumen material used for road surface. All extracted samples of soil did not contain any moisture (a dry basis was more than 98% for all cases), thus, it was not necessary to add any dessicant (e.g. an anhydrous Na_2SO_4) and untreated samples were taken directly for the analysis.

Extraction Conditions

Soxhlet Extraction

The extractions by a 100 mL Soxhlet apparatus were carried out for a period of 12 hours with the use of Ledon 113 as extraction solvent. An amount of 1 g samples A and B and a mass of 5 g the sample C, respectively, were taken for the analysis. The extracts were then evaporated in order to concentrate the analyte concentration, transferred to a 25 mL standard flask, and diluted with Ledon 113 to the mark.

Supercritical Fluid Extraction

For SFE a sample of 0.5 g was transferred to a 1 mL stainless steel cartridge and the extraction was performed under three different conditions according to the type of sample:

I. Sample A was extracted with CO_2 with addition of 5% of methanol as modifier, at a temperature of 50°C and pressure of 25 MPa. The extraction time was 45 min, of that 5 min in static and 40 min in dynamic mode. Then, all solvent was evaporated and Ledon 113 was added to make up a volume of 5 mL.

II. All three types of samples were extracted with a pure CO_2 at a temperature of 50°C and pressure of 25 MPa. The extraction time was 60 min (10 min in static and 50 min in dynamic mode).

III. All three types of samples were extracted with a pure CO_2 at a temperature of 100°C and pressure 40 MPa. The extraction time was 30 min (5 min in static and 25 min in dynamic mode). In all cases a quartz restrictor was used (inner diameter 25 μm, length 200 mm. The analytes were entrapped into approximately 3 mL of Ledon 113.

Pressurised Fluid Extraction

Extractions with Ledon 113 were performed under a temperature of 100°C and pressure of 10 MPa in two static 5 min periods. Ledon 113 was taken as an extractant. A sample mass of 0.5 g was transferred to a 11 mL stainless steel cartridge. The remaining free volume was filled with 1 mm size glass beads. The extract was entrapped into one collection vial. After extraction was completed, the remaining solvent in the extractor was expelled in 30 s with pressurised nitrogen, and the resulting volume of the extract was made up to 16 mL with Ledon 113.

Analysis of Extracts

FTIR measurements were performed in a quartz cell of a 10 mm optical path-length with the use of 32 scans, when a resolution of 4 cm^{-1} was achieved. Quantitative analysis of TPH was based on calibration dependence of the peak area measured from 3100 to 2700 cm^{-1} in a concentration range of 0–0.6 mg mL^{-1} of diesel oil, chosen as a standard substance, in Ledon 113.

Chromatographic analysis was performed with the use of a GC capillary column Spira K155 type (100% methylpolysiloxane), with a length of 27 m, internal diameter 0.2 mm, and a film thickness of 0.3 μm (Lachema, Brno, Czech Republic). A temperature programme involved a starting temperature of 50°C with an increase of 5°C min^{-1} up to 290°C; then, after an isothermal mode of 10 min followed by a temperature increase of 10°C min^{-1} up to 295°C, and a final 5 min isothermal period. The injection temperature was 290°C, when heating the detector to a temperature of 300°C. The flow rate of carrier nitrogen gas was 2.25 mL min^{-1}, with a split ratio of 1 : 20.>

RESULTS AND DISCUSSION

Soxhlet Extraction

Extraction conditions mentioned in the experimental section were considered adequate, according to the previous experience with samples of similar nature.[16] The extraction recovery expressed as the total amount of petroleum hydrocarbons with the use of FTIR spectrometry was, thus, considered as a basis for comparison of effectiveness with the other extraction techniques. Ledon 113 was selected as an extractant, though a more polar solvent or a suitable azeotropic mixture might be more convenient with respect to the expected nature of contamination. The quantitative method of choice, i.e., the FTIR spectrometry, had lead to the final decision that the presence of stretch vibrations of $-CH_3$,$-CH_2$ and aromatic groups in some other extractant might influence, negatively, the TPH determination. The results of Soxhlet extractions of the samples analysed are listed in Table 1.

Supercritical Fluid Extraction

This technique allows modifying the experimental conditions for the extraction, i.e., to adjust the temperature, pressure, and a flow rate of supercritical fluid, or to add a suitable modifier in order to achieve an optimum for the extraction of a given kind of contaminating substance. Thus, satisfactory results of assays can be obtained in a relatively short time.

The extraction recovery was determined by means of FTIR spectrometry. When 5% of methanol was added as the modifier, it was necessary to evaporate the solvent together with the modifier at laboratory temperature, because the presence of the functional groups $-CH_3$ and of $-OH$ would contribute to a positive error of the FTIR measurements; after the evaporation step a pure solvent was added to make up the difference.

Table 1. Comparison of the SFE and PFE techniques with Soxhlet extraction in assays of total oil contamination of soil.

Sample	Soxhlet[a] ($mg\,g^{-1}$)	SFE (II)[b] ($mg\,g^{-1}$)	SFE(III)[c] ($mg\,g^{-1}$)	PFE[d] ($mg\,g^{-1}$)
A	32.80 ± 0.59	28.75 ± 1.00	33.40 ± 1.27	36.09 ± 1.48
B	32.45 ± 0.58	22.92 ± 0.80	31.93 ± 1.21	34.37 ± 1.41
C	31.83 ± 0.57	26.64 ± 0.93	31.02 ± 1.18	33.85 ± 1.39

[a] Extraction time 12 h, Ledon 113, sample mass 1 g (5 g for sample C), n = 5.
[b] Supercritical CO_2 at 50°C and 25 MPa, extraction time 60 min (10 min in static, 50 min in dynamic mode), sample mass 0.5 g, collection into Ledon 113, n = 10.
[c] Supercritical CO_2 at 100°C and 40 MPa, extraction time 30 min (5 min in static, 25 min in dynamic mode), sample mass 0.5 g, collection into Ledon 113, n = 10.
[d] 100°C, 10 MPa, two static 5 min steps, Ledon 113, sample mass 0.5 g, n = 10.

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Table 2 makes a comparison of the results of SFE for sample A under all the three extraction conditions (cf. the experimental part). As can be seen, the best recovery was achieved with procedure III. A comparison of this SFE mode with the other extraction techniques is then made in Table 1. The evaporation step before the FTIR analysis may cause a loss of low-boiling fraction of hydrocarbons.[3,4] Thus, the use of methanol as modifier was of little advantage. In the case of FTIR, it would be more suitable to eliminate the use of methanol as modifier, even if the extraction time is to be extended or a higher working pressure applied.

Pressurised Fluid Extraction

In consideration of the analytical detection used and the conditions allowing comparison of results with those of the Soxhlet extraction, Ledon 113 was chosen as an extraction solvent, even for this technique. Individual experimental parameters were optimized, including the temperature effect in the range of 80–120°C. The temperature of 100°C was found as most suitable because of considerable losses of volatile components at higher temperatures, a pressure of 10 MPa as satisfactory, as the effect of this parameter was found to be insignificant.

Time of the extraction then represented another experimental parameter to be optimized: a sample was extracted for several subsequent 5 min periods and from each step the extract was collected and analysed separately. The best recovery was obtained for the first step, whereas the third one was practically free of any petroleum hydrocarbons. Therefore, only two steps of 5 min were chosen involving an entrapment into a single collecting vessel.

Table 2. Comparison of amounts of TPH extracted from sample A by SFE for three different experimental modes (sample mass 0.5 g, collected into Ledon 113).

Extraction mode	SFE (I)[a]	SFE (II)[b]	SFE (III)[c]
Extraction amount (mg g^{-1})	28.75 ± 1.01	33.40 ± 1.27	27.30 ± 1.04

[a] Supercritical CO_2 at 50°C and 25 MPa, extraction time 60 min (10 min in static, 50 min in dynamic mode, sample mass 0.5 g, collection into Ledon 113, $n = 10$.

[b] Supercritical CO_2 at 100°C and 40 MPa, extraction time 30 min (5 min in static, 25 min in dynamic mode), sample mass 0.5 g, collection into Ledon 113, $n = 10$.

[c] Supercritical CO_2 with 5% of methanol at 50°C and 25 MPa, extraction time 45 min (5 min in static, 40 min in dynamic mode), collection into Ledon 113, $n = 10$.

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The results of the determination of TPH by PFE are listed again in Table 1 (for all types of the analysed samples).

Detection of Sources of Contamination

The gas chromatograms shown in Figs. 1–4 indicate that both qualitative identification and quantitative evaluation of the individual components were beyond the scope of the chromatographic technique used. A more detailed identification was practically impossible without coupling with mass spectrometry. However, the chromatograms could, at least, serve to compare the overall character of extracts from the individual oil contaminated soils. To a certain extent, they may also be used to reveal a source of the contamination.

Practically identical chromatograms were obtained by GC analysis of the extracts from soil samples with the use of both Soxhlet (see Figs. 1, 2) and PFE technique. The chromatograms of the SFE extracts obtained with supercritical carbon dioxide were clearly different (cf. Figs. 3, 4). The extraction technique used allowed entrapping the analytes into a small volume of the solvent chosen, i.e., Ledon 113. The resulting extract was then sufficiently concentrated for a subsequent GC analysis. Evaporation of the solvent, which is a necessary but risky step of the classical Soxhlet extraction when low boiling point fractions are present, is thus avoided. Figure 3 documents a conspicuous group of peaks eluted approximately between 10 to 16 min. Appearance of these peaks within the same retention time interval is also indicated in a chromatogram showing sample B taken from a depth of 3 m (cf. Fig. 4). A full identification of these peaks was not successful for a lack of necessary standard compounds. Had no similar group of peaks been found either in

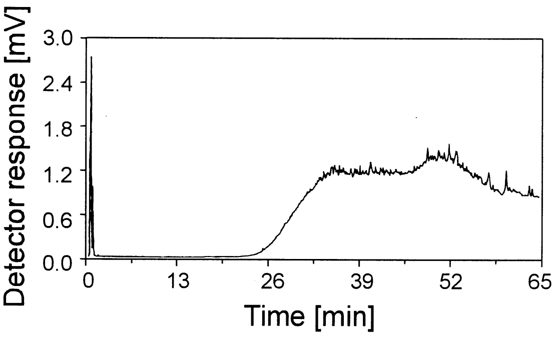

Figure 1. GC chromatogram of a Soxhlet extract from sample A.

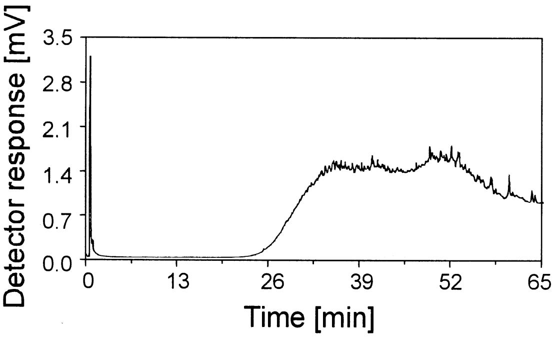

Figure 2. GC chromatogram of a Soxhlet extract from sample B.

the original or the heat affected crude oil, it was assumed that these peaks represent a migration wave front of the combustion products. At a temperature of 700°C and in vicinity of the collector of burning oil, a heat cracking of oil components takes place to form a mixture of compounds, with the boiling points about 100°C containing shorter, various branched alkanes and, possibly in a smaller amount, even alkenes and alkynes.

The present study has shown that local crude oil is of complex nature, which complicates defining a source of oil contamination in the vicinity of the oil field. Standard methods used in our laboratory could not provide results allowing a serious interpretation. Common physico-chemical analyses brought no proof of a difference between the two kinds of oil. Even infrared spectroscopy did not reveal the origin of oil contamination, though it was surely possible to differentiate between the samples of original and heat

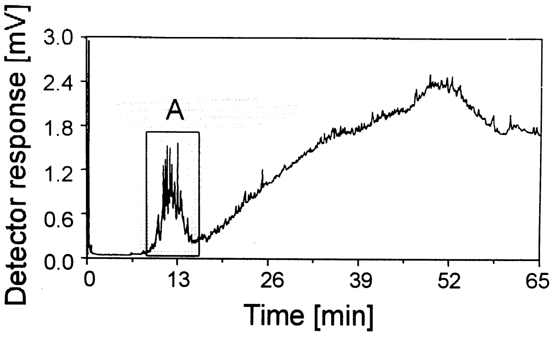

Figure 3. GC chromatogram of an extract by SFE from sample A. A—Probable migration wave front of light combustion products.

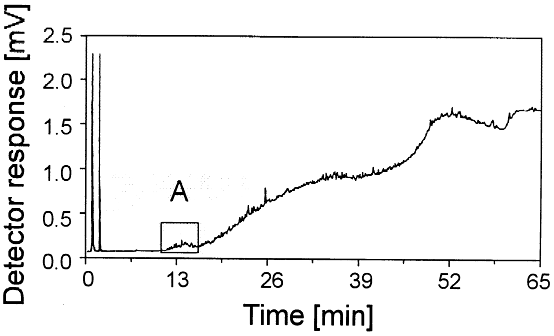

Figure 4. GC chromatogram of an extract by SFE from sample B. A—Slight appearance of combustion products indicating migration wave.

affected oil, owing to a different ratio of intensity between symetric and antisymetric vibrations of the function groups $—CH_2—$ and $—CH_3$ of alkanes.

A possible solution of the problem was suggested by the results of capillary GC. The GC analyses of supercritical fluid extracts have substantiated an assumption that the contamination of soil was caused by a leakage of crude oil and the products of oil combustion through a horizon of sealing clay back drop, eventually through a breakage limiting the oil deposit. This assumption was also partially supported by analyses of water samples taken near the assumed limiting dislocation. Not even one of the assays of water samples corresponded to the composition of underground water of the site under common conditions.

Extraction Methods and Their Comparison with Respect to Operational Costs

A high purchase cost of commercially available instruments represents a serious drawback for the introduction of these modern extraction techniques to the practice. At present, a price in the range of 350,000 CZK is typical for an apparatus, for both SFE and PFE, which would comply with the technical requirements necessary to provide reproducible recovery, comparable with the Soxhlet extraction of contaminating crude oil in assays of soil samples. However, the operating expenses with these techniques are considerably lower than those of classical Soxhlet extraction. Figure 5 illustrates that the introduction of modern extraction techniques is advantageous in laboratories

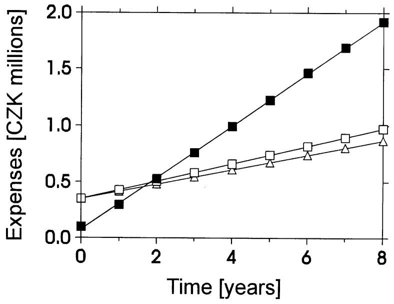

Figure 5. Comparison of operational costs for the techniques SFE and PFE with those of Soxhlet extraction. ■—Soxhlet extraction; □—SFE; △—PFE.

processing a large series of samples. If about 500 samples are to be analysed per year, the expenses are compensated approximately within two years. In the future, however, if prices increase, not only for the solvents but also for energy and water, a considerable shortening of the extraction time to several minutes will certainly be a point to consider. The extract is directly obtained in a concentrated form, which is of great advantage for the application of chromatographic methods.

CONCLUSIONS

Experience gained during the present study allowed us to estimate the advantages of both SFE and PFE in assays of oil-contaminated soils. These extraction techniques have shown some promise, as they may replace the classical Soxhlet extraction, namely in laboratories dealing with large series of solid samples (or in such situations when the results of extraction should be as rapid as possible). Another important aspect is a reduced consumption of solvents harmful to the environment.

The application of PFE technique is more convenient in comparison with SFE, as it is not limited only to the extraction of substances of low polarity, but the selectivity of this technique is lower than that utilising supercritical carbon dioxide. Although, SFE is applicable solely to isolate nonpolar analytes, it represents a careful extraction technique capable to achieve an adequate selectivity at suitable conditions chosen.

Application of the above-given techniques results in an advantageous reduction of the extraction time, from an order of hours to tens of minutes

(SFE) or even several minutes (PFE), with recoveries comparable to those achieved in classical extraction methods.

The applications of FTIR spectroscopy and capillary GC-FID were also explored for the detection of sources of oil contamination of soil in the vicinity of a site of oil exploitation. The combination of the SFE technique performed under optimised, and in combination with capillary GC-FID, has been found to be suitable as providing some interesting information.

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