

SUPERCRITICAL FLUID EXTRACTION OF DIFFERENT OIL SHALE CONCENTRATES

Mihkel KOEL and Anne ORAV

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

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Abstract. Supercritical fluid extraction was performed on different oil shale samples giving characteristic extracts in very mild conditions. The distribution of *n*-alkanes in extracts is unique for every sample.

Key words: supercritical fluid extraction, oil shale, gas chromatography, *n*-alkanes.

INTRODUCTION

In the search for new methods in the extraction and separation of complex natural mixtures from a solid matrix like rocks, the use of supercritical eluents is assuming increasing importance. Supercritical fluid extraction (SFE) has been shown to be an attractive alternative to the conventional solvent extraction for a wide variety of analytes [1]. SFE is labour-saving and less time-consuming. The most widely used supercritical eluent in SFE is CO₂, allowing to combine, in one system, the speed and the safety of the extraction.

Part of the organics is not included in the structure of kerogen and can be extracted from oil shale matrix. It is like a mobile phase inside a macromolecular network. The quantification of this mobile phase will be an interesting application for SFE. The study of the extraction possibilities also includes the determination of biomarkers (i. e. pristane and phytane) and the carbon number distribution in the source rocks of crude oil [2]. For this kind of application, it is important to obtain data about the characteristics of extraction by supercritical CO₂, and to evaluate the range of extraction power for a certain type of compounds because of the relatively nonpolar nature of the fluid used. On the other hand, the solvent strength of a supercritical fluid can be easily controlled by the pressure and temperature used for extraction. The choice of these conditions can lead to the selective extraction of substances from matrix.

In this study, the target samples are oil shale concentrates whose extracts may be complex organic mixtures. The first step is to get an impression of the difference between extracts from different oil shale samples. The second step is to vary the extraction conditions to a large degree in order to achieve the selective extraction.

EXPERIMENTAL

SFE is constructed from suitable parts of the HPLC laboratory equipment. The off-line SFE system is shown in Fig. 1.

An HPP4001 (Laboratorni Pstroje, Czechoslovakia) syringe pump with a maximum operating pressure of 500 atm was used to deliver fluids. The self-constructed extraction cell used recycled HPLC column and fittings with a 20 μm pore diameter (stainless steel) frits. Fittings were placed on each end of the piece of stainless steel tubing to produce a vessel with an internal volume of 1.0 ml (60 mm \times 4.6 mm i. d.) which housed the sample.

A LC column oven with a maximum operating temperature of 100°C was used to maintain constant extraction temperature. The oven temperature was kept on the desired level and the extraction cell was held in it for a long time to stabilize the sample temperature before extraction. Low temperatures were used to avoid the thermal degradation of sample.

A stainless steel tubing transfer line carried the extract to the restrictor. The narrow stainless-steel tube with a pressed end was used as a restrictor to get the required fluid flow rate from 0.5 to 1.5 ml/min. The extract was collected by expansion from the restrictor capillary into 2 ml of hexane or chloroform. In this study, the SFE will be carried out in a dynamic extraction mode. The chromatograms of collected extracts in hexane or chloroform are estimated on a separate chromatograph.

A Chrom 5 (Laboratorni Pstroje, Czechoslovakia) gas chromatograph (GC) equipped with a flame ionization detector (FID), a splitter port (1:150) and a 50 m \times 0.20 mm i. d. fused silica capillary column with the bonded phase OV-101 as a stationary phase, was used for GC analysis. Helium was used as the carrier gas (the inlet pressure of 1.4 kG/cm² and a Hewlett-Packard 3390A reporting integrator was applied for chromatogram calculation). GC analyses were performed at an initial oven temperature of 50°C, followed by a linear increase to 220°C at 2°/min. The injector temperature was kept at 160°C. The detector temperature was kept at 250°C. The sample volume injected was 5–10 μl .

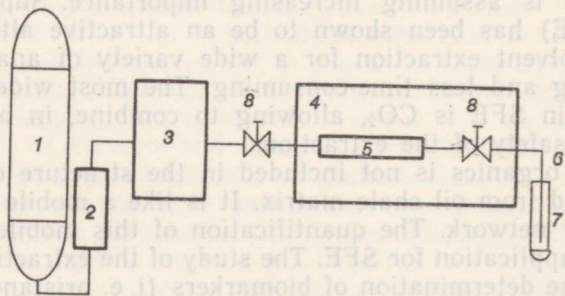


Fig. 1. Schematic diagram of the supercritical fluid extraction apparatus: 1 — fluid cylinder, 2 — activated charcoal and molecular sieve trap, 3 — syringe pump, 4 — oven, 5 — extraction vessel, 6 — restrictor, 7 — extract collection vial, 8 — on-off valve.

MATERIALS

Industrial grade CO₂ (purchased from Eesti AGA Ltd.) with no oily constituents was employed for extraction analysis. Control experiments showed no contaminated peaks in the range of interest. In experiments, the extraction with liquid CO₂ was performed with a flow rate of 1 ml/min for 30 min.

All the solvents used were chromatographic grade (Reakhim, Kharkov, Ukraine).

The samples under study represent different types of shales originating from different areas of Estonia (Dictyonema and Kukersite), Kazakhstan (Kenderlyk) and Russia, the middle reaches of the Volga (Kashpir). Kukersite (93.2% of organic matter) and Kenderlyk shale (56.0% of organic matter) originate predominantly from the lipid fraction of the initial sediments. The organic part of Dictyonema shale (59.9% of organic matter), a typical "black" shale, is of a very complex nature with its specific transformation ways of initial material. Kashpir shale (87.6% of organic matter) is a representative of high-sulphur shales. More detailed data about the parameters of these shales are available in [3].

The quantitative composition of the extracts was determined by using the internal standard method, 1-tetradecene (>98%) serving as standard.

DISCUSSION

SFE was the method of choice for sample preparation due to the highly interactable nature of the sample matrix and the increased speed in comparison with traditional liquid extraction, and the non-use of organic solvents.

Preliminary analysis of the SFE extracts from all samples showed that no additional sample preparation (except for the addition of the internal standard) was required after SFE.

The complex nature of the extract is demonstrated by the large number of peaks in the FID-generated chromatogram of the extract. Chromatograms for different oil shale samples (Fig. 2, *a—d*) differ in the amount of peaks and in the relative height of the same peaks. The mass balance of extracts on four shales is given in the Table.

The data show that the total amount of compounds extracted and their *n*-alkane content are different for the oil shale samples studied, being highest for Kukersite and lowest for Kenderlyk shale. The distribution curves of *n*-alkanes in extracts (Fig. 3) are similar for Kukersite and Dictyonema (maximum points are at C₁₀ and C₁₁). The Kenderlyk and Kashpir oil shale extracts show the maximum points of these curves to be at C₁₅ alkane.

GC analysis showed the presence of mainly branched and normal alkanes. A detailed description of the results of the identification of components in SFE extracts of oil shale samples will be presented in the next paper. It may be said, even now, that the SFE extract is an additional source for the identification of the origin of oil shale. The extraction efficiency increased with increasing the extraction temperature from 45 to 85°C and changed the nature of the extract. The trends in extraction efficiencies, while changing the extraction temperature, appear to be highly dependent on sample matrix.

CONCLUSIONS

The SFE studies have demonstrated the applicability of supercritical fluids for the extraction from sedimental rocks. They have confirmed the fact that oil shales are unique for giving extracts in very mild conditions. This latter feature may be used for the discrimination/the identification of different samples.

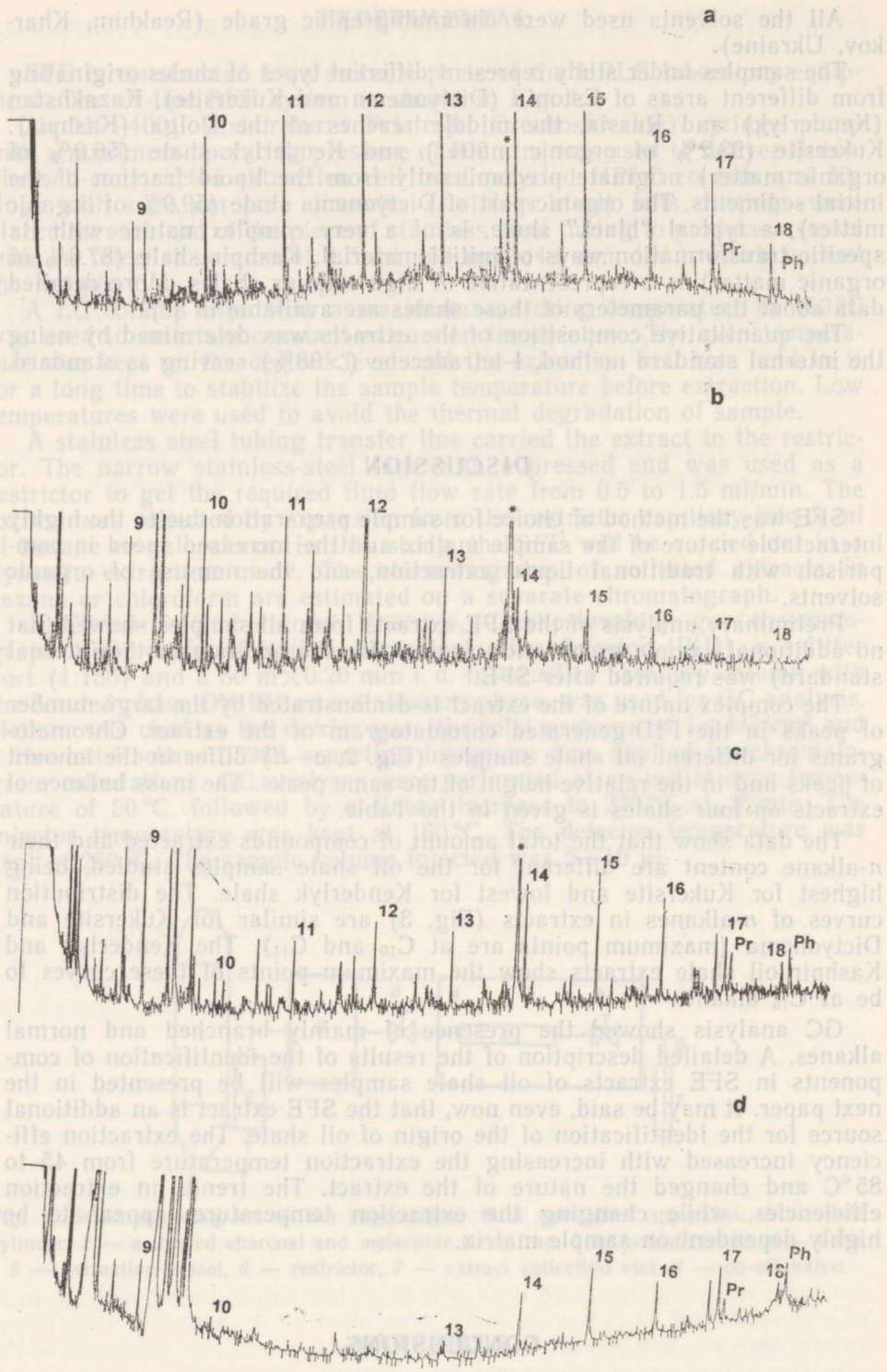


Fig. 2. Chromatograms of the extracts of different oil shale samples: a — Kukersite, b — Dictyonema, c — Kashpir, d — Kenderlyk. Conditions of extraction: 0.3 g powdered sample at temperature 85°C and pressure 40 Mpa; extracting time 0.5 h at fluid rate 0.5 ml/min. Conditions of chromatographic analysis see in text.

A comparison of the amounts of *n*-alkanes and the total yields from oil shale samples by supercritical fluid extraction, mg/g of rock

	Kukersite	Dictyonema	Kashpir	Kenderlyk
<i>n</i> -alkanes	0.47	0.039	0.032	0.11
% from total	40.5	10.8	17.0	5.2
Total yield	6.87	2.2	1.13	2.03

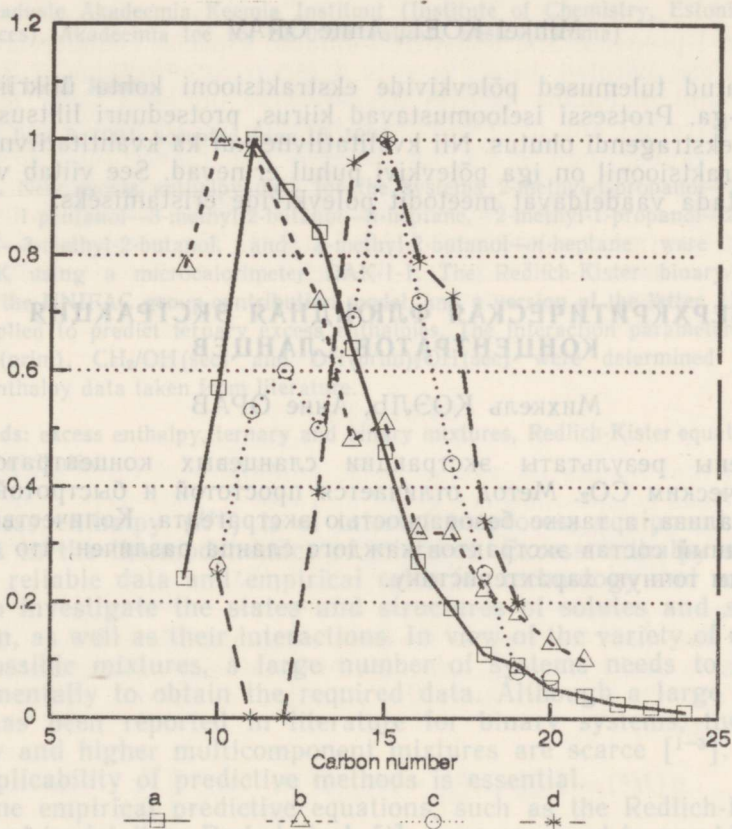


Fig. 3. Distribution of *n*-alkanes by carbon number in the extract of different oil shale samples: a — Kukersite, b — Dictyonema, c — Kashpir, d — Kenderlyk.

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REFERENCES

1. Hawthorne, S. B. Analytical-scale supercritical fluid extraction. — *Anal. Chem.*, 1990, 62, 633A—636A.
2. Monin, J. C., Barth, P., Perrut, M., Espitalie, M., Durand, B. Extraction of hydrocarbons from sedimentary rocks by supercritical carbon dioxide. — *Org. Geochem.*, 1988, 13, 4—6, 1079—1086.
3. Уров К. Э., Сумберг А. И. Характеристика горючих сланцев. Валгус, Таллинн, 1992.

PÕLEVKIVI KONTSENTRAATIDE EKSTRAKTSIOON ÜLIKRIITILISES OLEKUS ELUENDIGA

Mihkel KOEL, Anne ORAV

On esitatud tulemused põlevkivide ekstraktsiooni kohta ülikriitilises olekus CO₂-ga. Protsessi iseloomustavad kiirus, protseduuri lihtsus ning kasutatava ekstragendi ohutus. Nii kvalitatiivne kui ka kvantitatiivne väljatulek ekstraktsioonil on iga põlevkivi puhul erinevad. See viitab võimalusele kasutada vaadeldavat meetodit põlevkivide eristamiseks.

СВЕРХКРИТИЧЕСКАЯ ФЛЮИДНАЯ ЭКСТРАКЦИЯ КОНЦЕНТРАТОВ СЛАНЦЕВ

Михкель КОЭЛЬ, Анне ОРАВ

Приведены результаты экстракции сланцевых концентратов со сверхкритическим CO₂. Метод отличается простотой и быстротой проведения анализа, а также безопасностью экстрагента. Количественный и качественный состав экстрактов каждого сланца различен, что позволяет дать им точную характеристику.

Fig. 3. Distribution of n-alkanes by carbon number in the extract of different oil shale samples: a — Kärstale, b — Kärstale, c — Kärstale, d — Kärstale.

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