SUPERCRITICAL FLUID EXTRACTION
OF OIL SHALES

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The quantification of the part of organics that is not included in the structure of kerogen and can be extracted from oil shale matrix, is feasible by application of analytical supercritical fluid extraction (SFE) with CO_2 as an eluent. The extraction power for a certain type of compounds was evaluated and the selective extraction was achived in wide limits of pressure, temperature and modifiers used in SFE.

Study of the possibilities of extraction included, besides the speed-up of the analysis, also the determination of geochemically significant compounds (biomarkers like pristane and phytane as well as steranes and triterpanes) and of carbon number distribution of n-alkanes in extractable organic matter. A very good correlation with classical Soxhlet extraction data was achived.

Introduction

On looking for new methods of extraction and separation of complex natural mixtures from a solid matrix like rocks, the use of supercritical eluents is acquiring a greater 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 less laborious and time-consuming. The most widely used supercritical eluent in SFE is CO_2 that allows combining speed and safety of extraction in one system. At low temperatures (far below 100 °C) thermally labile compounds can be extracted by SFE without their decomposition. On the other hand, the solvent strength of a supercritical fluid can be easily controlled by the pressure, temperature and modifiers used for extraction. The successful choice of these conditions can lead to the selective extraction of substances from matrix.

A part of organics is not included in the kerogen structure and can be extracted from coal or oil shale matrix. This is like a mobile phase inside the macromolecular network. Quantification of this mobile phase would be an interesting application of analytical SFE. Study of the possibilities of extraction include also the determination of biomarkers (e.g. pristane and

phytane) and carbon number distribution in crude oils and source rocks [2]. The geochemical information on organic matter (OM) concerning the composition and relative distribution of *n*-alkanes and isoprenoids as well as steranes and triterpanes, which serve as biomarkers, is useful for elucidating the genesis of oil shale OM and the degree of itsmaturity.

From studies of solvent extracts of oil shales according to the methods [3] it is known that aliphatic and polycyclic hydrocarbons (steranes and triterpanes) appear in just the same thin-layer chromatographic fraction. The same would be expected from SFE. Comparison of SFE extracts with those obtained by routine methods would be valuable in deciding about advantages of methods to obtain geochemical information.

In this study, the samples of oil shales and their kerogene concentrates whose extracts represent complex organic mixtures are examined. For this kind of application of SFE it is important to get the data about the characteristics of extraction by supercritical CO_2 and to evaluate the range of extraction power for a certain type of compounds. The first step is to get some information about the differences between extracts from different oil shale samples. The aim is to speed up the procedures without losing geochemically significant compounds. The second step is the variation of extraction conditions in wide limits to achive the selective extraction.

Experimental

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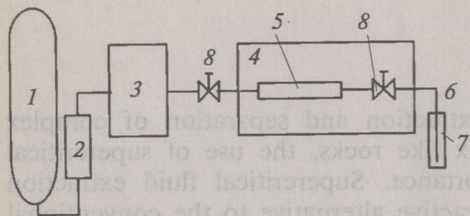

Fig. 1. Off-line SFE system schematic diagram. *1* - CO_2 tank, *2* - trap, *3* - pump, *4* - oven for extractor, *5* - extractor, *6* - restrictor, *7* - collector, *8* - on-off valves

An HPP4001 (Laboratorny Pristroje, Czechoslovakia) syringe pump with a maximum operating pressure of 450 atm was used to deliver fluids. The extraction cell was self-constructed using a recycled HPLC column (stainless steel) with 20 μm pore diameter frits. Fittings were placed on each end of the piece of stainless steel tube to produce a vessel with an internal volume of 1.5 ml (60 mm × 4.6 mm i.d.) for the sample.

An LC column oven with a maximum operating temperature of 100 °C was used to maintain a constant extraction temperature. The oven temperature was kept on the desired level and the extraction cell with a sample was held in it for a long time to stabilize the sample temperature

Fig. 2. GC chromatograms of oil shale sample extracts SFE with CO_2. *a* – Krasava oil shale, *b* – Anabar oil shale, *c* – Boltysh oil shale. Capillary column 25 m x 0.2 mm i.d., temperature programming rate 3 °C/min in the interval of 60–270 °C
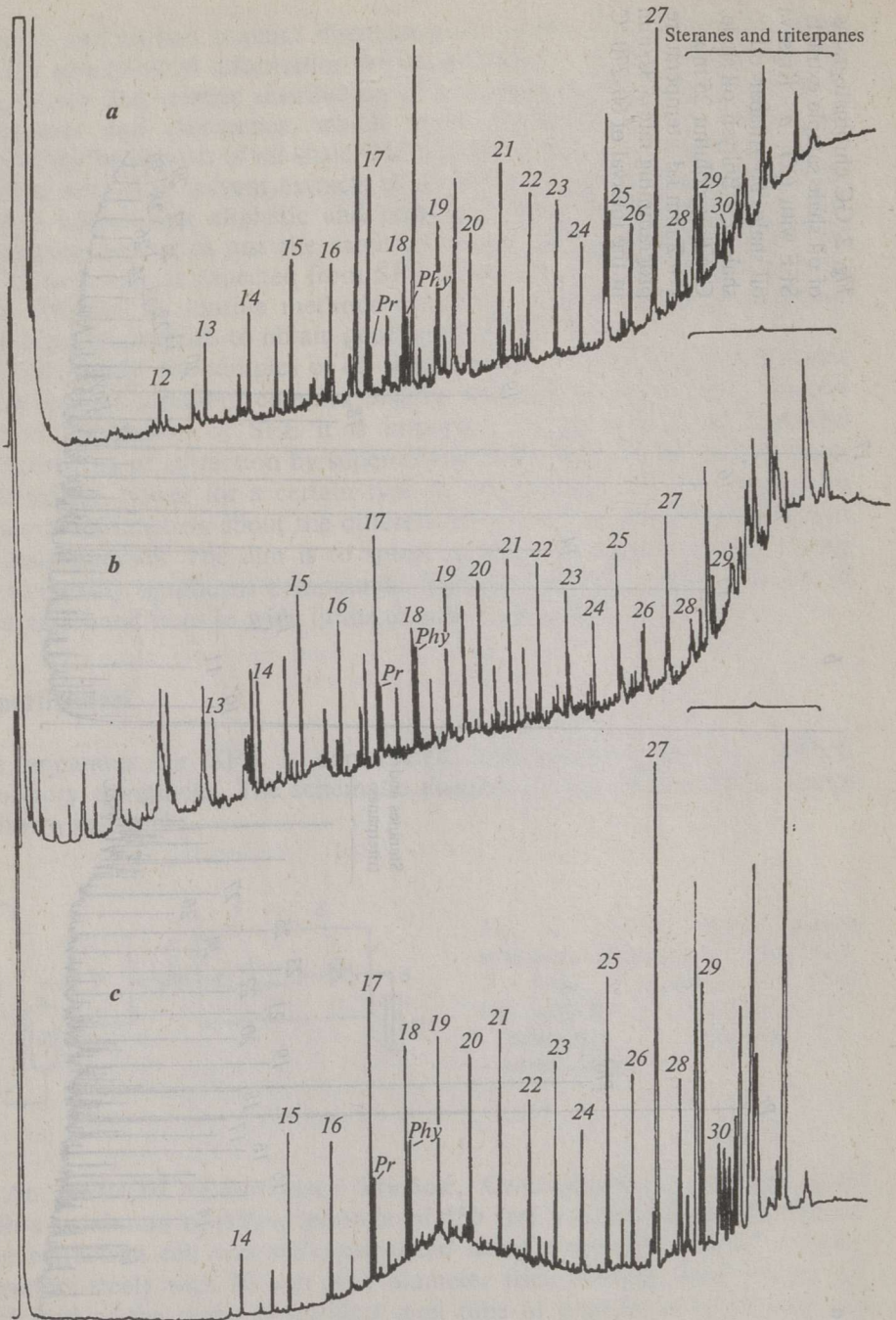
Steranes and triterpanes
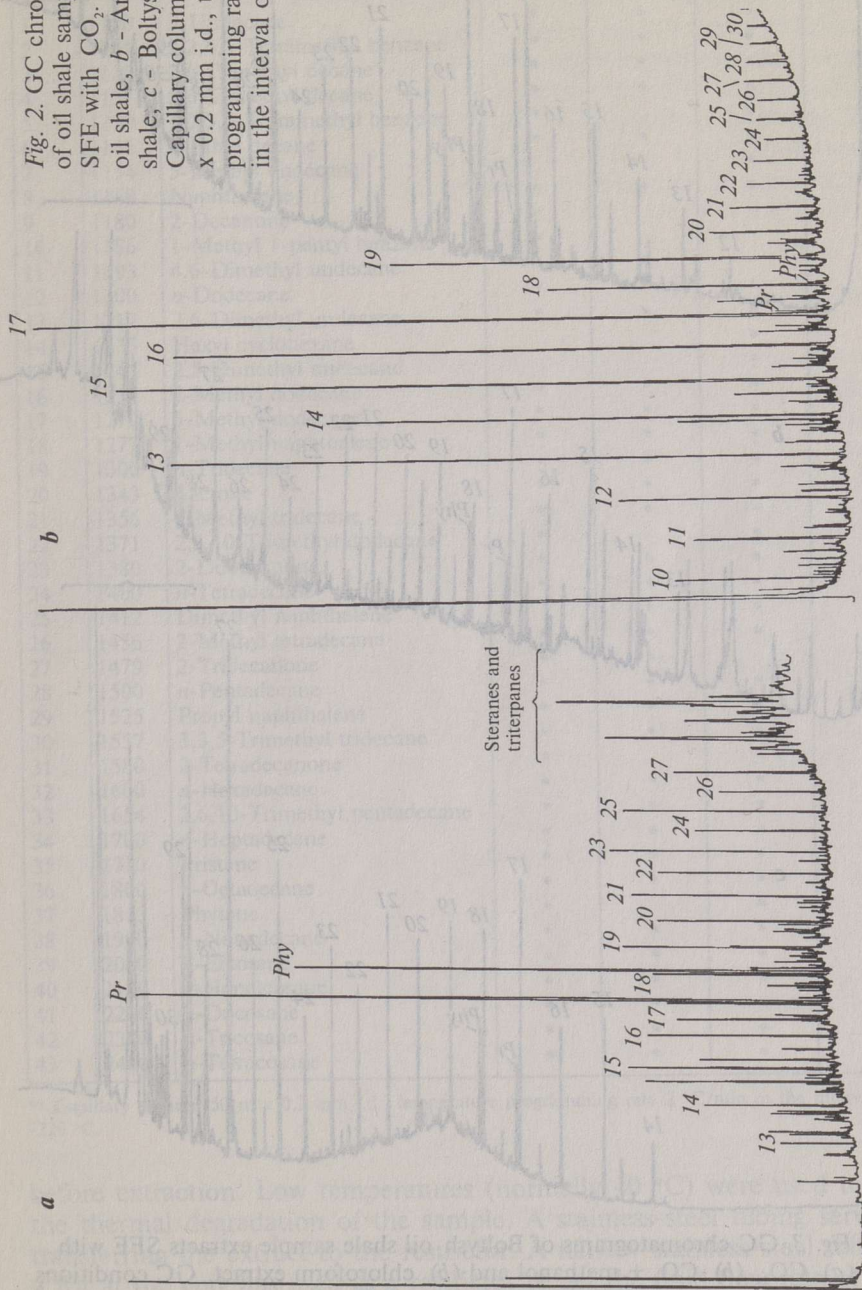
Fig. 3. GC chromatograms of Boltysh oil shale sample extracts SFE with
(*a*) CO_2, (*b*) CO_2 + methanol and (*b*) chloroform extract. GC conditions
see in the text and in Fig. 2

Table 1. **Identified Compounds in the Oil Shale Concentrate Extracts*[1]**

No.	RI	Compound	Kashpir	Dictyo-nema	Kuker-site	Kender-lyk
1	1100	n-Undecane	*	*	*	*
2	1104	1,2,4,5-Tetramethyl benzene	*	*	*	
3	1120	2,6-Dimethyl decane	*	*	*	
4	1131	5,6-Dimethyl decane	*	*	*	
5	1139	1,2,3,4-Tetramethyl benzene	*		*	
6	1146	4-Ethyl decane	*		*	
7	1154	5-Methyl undecane		*	*	
8	1168	Naphthalene	*	*	*	*
9	1180	2-Decanone	*			
10	1186	1-Methyl 1-pentyl benzene	*			
11	1193	4,6-Dimethyl undecane		*		
12	1200	n-Dodecane	*	*	*	*
13	1217	2,6-Dimethyl undecane	*	*	*	
14	1235	Hexyl cyclohexane			*	
15	1245	2,5-Dimethyl undecane			*	
16	1257	2-Methyl dodecane	*	*	*	
17	1272	3-Methyl dodecane	*	*	*	
18	1277	1-Methyl naphthalene	*	*	*	
19	1300	n-Tridecane	*	*	*	*
20	1343	Lactone	*	*	*	
21	1356	2-Methyl tridecane	*	*	*	
22	1371	2,6,10-Trimethyl dodecane	*		*	
23	1380	2-Dodecanone	*	*	*	
24	1400	n-Tetradecane	*	*	*	*
25	1412	Dimethyl naphthalene		*	*	
26	1456	2-Methyl tetradecane	*	*	*	
27	1479	2-Tridecanone	*	*	*	
28	1500	n-Pentadecane	*	*	*	
29	1525	Propyl naphthalene	*	*	*	
30	1557	3,3,5-Trimethyl tridecane	*	*	*	
31	1580	2-Tetradecanone	*		*	
32	1600	n-Hexadecane	*	*	*	*
33	1654	2,6,10-Trimethyl pentadecane	*	*	*	
34	1700	n-Heptadecane	*	*	*	*
35	1710	Pristane	*	*	*	
36	1800	n-Octadecane	*	*	*	*
37	1813	Phytane	*		*	*
38	1900	n-Nonadecane	*	*	*	*
39	2000	n-Eicosane	*	*	*	*
40	2100	n-Heneicosane	*	*	*	*
41	2200	n-Docosane	*	*	*	*
42	2300	n-Tricosane	*	*	*	*
43	2400	n-Tetracosane	*	*	*	*

*[1] Capillary column 50 m × 0.2 mm i.d., temperature programming rate 2 °C/min in the interval of 50--220 °C.

before extraction. Low temperatures (normally 40 °C) were used to avoid the thermal degradation of the sample. A stainless-steel tubing served for transferring the extract to the restrictor. A narrow stainless-steel tube with a frit at the end was used as a restrictor to get the fluid flow rate of 0.5 to 1.5 ml/min. The expanded extract from the frit restrictor was collected into 2 ml of hexane or chloroform. In this study, the SF extraction was carried out in a dynamic extraction mode. A typical extraction time was

30 min. To increase the solvent power, a binary fluid system carbon dioxide with methanol (5 % by weight of oil shale) was used.

The chromatograms of collected extracts in hexane or chloroform are estimated on separate chromatographs. The Chrom 5 (Laboratorny Pristroje, Czechoslovakia) gas chromatographs equipped with a flame ionization detector (FID), a splitter port (1 : 150) and fused silica capillary columns with the bonded phase OV-101 as a stationary phase, were used for GC analysis. Helium was used as the carrier gas. For other conditions of GC analysis see Table 1 and Fig. 2.

Hewlett-Packard 3390A reporting integrator was applied for the chromatogram calculation. Soxhlet extraction was carried out under the conditions given in [4].

Materials

Industrial grade CO_2 (purchased from Eesti AGA Ltd.) with no oily constituents was employed for extraction analysis. Control experiments did not show any peaks of contamination in the range of interest. All the solvents used were of chromatographic grade (Reakhim, Kharkov, the Ukraine).

The samples under study represent different types of shales originating from different areas of Estonia (Low Ordovician Dictyonema shale and Middle Ordovician kukersite), Kazakhstan (Permian-Carbon Kenderlyk oil shale) , Russia (Jurasic Kashpir oil shale from the middle reaches of the Volga and Low Silurian Anabar oil shale from Siberia), the Ukraine (Eocene Boltysh oil shale) and Bulgaria (Paleogene Krasava oil shale).

Kukersite, Anabar and Kenderlyk oil shales originate preponderantly from the lipoid fraction of the initial sediments. The organic part of Dictyonema shale, a typical "black" shale, has a very complex nature reflecting the transformation ways of the initial material. Kashpir oil shale is a representative of high-sulfur oil shales. More detailed data about the parameters of these shales are available in [5, 6], and about the genesis of Krasava oil shale - in [7].

Prior to extraction the samples were ground to the 0.02 mm size. The quantitative composition of the extracts from oil shale concentrates was determined by using the internal standard method, 1-tetradecene (>98 %) serving as a standard.

Results and Discussion

The method of SFE was choosen for sample preparation due to the highly interactable nature of the sample matrix, increased speed of the method in comparison with traditional liquid extraction, and no need for organic solvents. Preliminary analysis of the SFE extracts from all samples showed that no additional step in sample preparation (except for an addition of the internal standard) for further analysis was required after SFE.

The complex nature of the extract is demonstrated by the large number of peaks in the FID-generated gas chromatogram of the extract.

Chromatograms for different oil shale concentrates (Figs. 2 and 3) differ in the amount and the relative height of the peaks.

GC analysis showed that there are mainly normal and branched alkanes present in these extracts. The identified compounds are listed in Table 1 (column with bonded OV-101 50 m × 0.2 mm i.d., the temperature 50--250 °C with the rate 2 °C/min, carrier gas, He, pressure 1.4 kG/cm^2). Identification of chromatogram peaks was carried out by their retention indices (RI) and confirmed by mass-spectrometric data. The programmed temperature RI was used as the most reliable and widely used one. It was calculated by the equation:

$$RI = 100 \frac{\lg t_{R(x)} - \lg t_{R(z)}}{\lg t_{R(z+1)} - \lg t_{R(z)}} + 100z,$$

where $t_{R(x)}$ - retention time;

      x - subindex for the substance of interest;

      $z, z+1$ - subindices for n-alkanes emerging before and after the substance x and having the number of carbon atoms z and $z+1$.

Although the compositions of the extracts are very complex, some similarities can be seen, and a number of compounds occur in all chromatograms of extracts of different oil shales. It allows us to consider the SFE extract an additional source for identification of the origin of oil shale. The data show that the total amount of compounds extracted and their n-alkane content are different for the oil shale samples studied.

It is interesting to compare the distribution curves of n-alkanes in extracts from the native oil shales. For chloroform extract and SFE with carbon dioxide they are similar being even identical for Anabar oil shale (Fig. 4). n-Alkane distribution in SFE with modifier (carbon dioxide + + methanol) is rather different, nevertheless n-alkane carbon predominance indexes (CPI) in extracts compared do not differ considerably (Table 3). As for the yields of extractables in general, yields of SFE extracts from oil shales with a high clay mineral content of inorganic matrixes are not as high as those of Soxhlet extracts and are only approximately similar to those of hydrocarbon fraction from Soxhlet chloroform extracts (Table 2).

The lowest yield of the SFE extract is characteristic of Krasava oil shale

Table 2. **Yields of Oil Shale Extracts (mg/g of oil shale)**

Oil shale	SFE , CO$_2$	SFE, CO$_2$+methanol	Soxhlet, chloroform	Hydrocarbon fraction of chloroform extract
Dictyonema	0.8	n.d.**	2.9	0.5
Kukersite*	1.8	3.7	1.6	0.2
Boltysh	1.2	2.5	6.2	0.7
Krasava	1.3	2.7	16.6	3.7
Anabar	1.6	n.d.	9.0	3.8

* Extraction time 60 min.
** n.d. - not determined.

Table 3. **Geochemical Data for Extractable OM of Oil Shales**

Data	Boltysh			Krasava			Anabar	
	CO_2	CO_2+ +MeOH	Sox	CO_2	CO_2+ +MeOH	Sox	CO_2	Sox
CPI of n-alkanes	1.36	1.33	1.39	1.17	1.06	1.20	1.46	1.57
Pristane/Phytane	0.68	0.76	0.80	1.84	2.00	2.33	3.71	4.10
Pr+Phy/ /n-C_{17}+n-C_{18}	0.36	0.40	0.56	3.55	3.51	4.65	0.10	0.22
Pr/n-C_{17}	0.23	0.27	0.43	5.03	4.86	5.47	0.07	0.23
Phy/n-C_{18}	0.56	0.62	0.75	2.40	2.25	3.56	0.09	0.20

F o o t n o t e . CO_2 - SFE with carbon dioxide; CO_2 +MeOH - SFE with carbon dioxide modified with methanol; Sox - Soxhlet extraction with chloroform.

with predominantly the zeolite (analcime) mineral matrix. Kukersite, having predominantly the carbonate mineral matrix, behaves differently from oil shales with clay mineral matter during SFE. The extract yield of SFE is comparable with that of Soxhlet extraction. It confirms the fact found in extraction of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAHs) from soil and sediments [8]: the matrix type has a pronounced effect on the extractability of an analyte, as well as on the characteristics of the analyte. Evidently, the most appreciable differences in n-alkane distribution and CPI (Table 3) in chloroform extract and SFE-s of Krasava oil shale occur on account of its mineral matrix type.

Using methanol as a modifier of carbon dioxide allows to double the yield of SFE extract from Kukersite and other samples. Here also the effect of a modifier on SFE efficiency is higly matrix- and analyte-dependent as mentioned earlier [9].

Capillary GC analysis of SFE extracts from the oil shales under study shows their composition to be similar to that of the hydrocarbon fraction
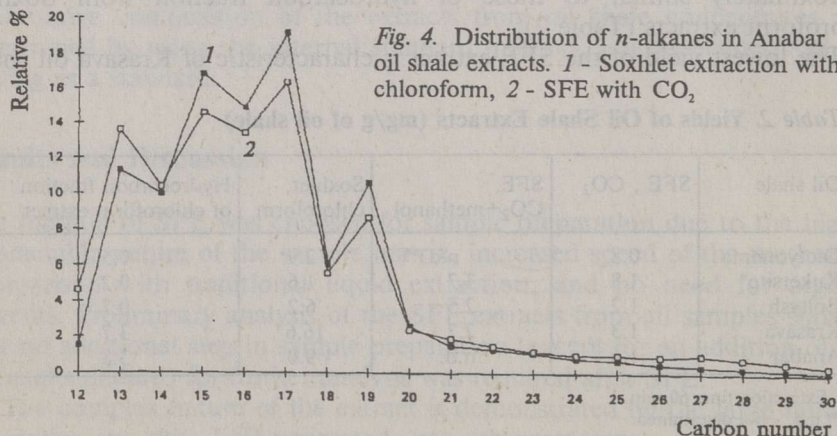

Fig. 4. Distribution of n-alkanes in Anabar oil shale extracts. *1* - Soxhlet extraction with chloroform, *2* - SFE with CO_2

of Soxhlet chloroform extracts (Fig. 3). Analogous similarity would be expected also for other parameters. Indeed, such geochemical data on organics as CPI of *n*-alkanes and the pristane-to-phytane ratio for SFE extracts and Soxhlet extracts are very close. Table 3 represents these data for three shale samples.

The pristane-to-n-C_{17} and phytane-to-n-C_{18} ratios are considerably lower when only carbon dioxide is used as a supercritical fluid. This is indicative of the selective extraction of *n*-alkanes. Chromatograms show SFE extracts to contain lower concentration of polycyclic biomarkers (steranes and triterpanes) than one can detect in Soxhlet extracts (Fig. 3). Modifying carbon dioxide with methanol enables us to increase the concentration of isoprenoids and polycyclic hydrocarbons in SFE extracts (Table 3; Fig. 3*b*).

Further GC-MS studies are required to compare the stereoisomeric composition of the steranes and triterpanes present in SFE and Soxhlet extracts of oil shales.

Conclusions

The SFE studies have demonstrated the adaptability of the supercritical fluid for extraction of sedimentary rocks and have comfirmed the fact that oil shales are unique as for extracts obtained in very mild conditions, and this may be one feature for discrimination/identification of different samples. The efficiency of SFE depends on the composition of the mineral matrix of oil shale.

The geochemical information on OM concerning the composition and relative distribution of *n*-alkanes as well as the pristane-to-phytane ratio does not vary significantly when SFE of oil shale is used instead of Soxhlet extraction. Nevertheless, the ratios of pristane and phytane to the nearest homologues of *n*-alkanes (n-C_{17} and n-C_{18}) are lower than those of Soxhlet extracts. The absolute content of isoprenoid and polycyclic hydrocarbons in SFE extracts may be increased by using a more polar binary fluid system - carbon dioxide-methanol.

Acknowledgments

REFERENCES

1. *Hawthrone, S. B.* Analytical-scale supercritical fluid extraction // Anal. Chem. 1990. Vol. 62. P. 633A-642A.

2. *Monin, J. C., Barth, D., Perrut, M., Espitale, M., Durand, B.* Extraction of hydrocarbons from sedimentary rocks by supercritical carbon dioxide // Org. Geochem. 1988. Vol. 13, No. 4-6. P. 1079-1086.

3. *Klesment, I.* Application of chromatographic methods in biogeochemical investigations // J. Chromatogr. 1974. Vol. 31, No. 2. P. 705-713.

4. *Pobul, L., Klesment, I., Kuusik, M.* Investigation of the organic matter of Kenderlyk // Proc. Estonian Acad. Sci. Chem. 1982. Vol. 31, No. 1. P. 25-32.

5. *Urov, K., Sumberg, A.* Characteristics of Oil Shales (in Russian). - Tallinn, 1992.

6. *Bondar, E. B., Bityukov, M. M., Kuusik, M. G.* Peculiarities of oil shale deposition in the Silurian. 1. Characterization of Anabar oil shale (Low Landovery) and its extracts composition // Oil Shale. 1990. Vol. 7, No. 3-4. P. 193-205.

7. *Bondar, E. B., Kuusik, M. G.* On the origin of Krasava oil shale (Bulgaria) organic matter // Oil Shale. 1988. Vol. 5, No. 4. P. 337-347.

8. *Burford, M. D., Hawthrone, S. B., Miller, J.* Extraction rates of spiked versus native PAHs from heterogeneous environmental samples using supercritical fluid extraction and sonication in methylene chloride // Anal. Chem. 1993. Vol. 65, No. 11. P. 1497-1505.

9. *Langenfeld, J. J., Hawthrone, S. B., Miller, D. J., Pawliszyn, J.* Role of Modifiers for analytical-scale supercritical fluid extraction of environmental samples // Anal. Chem. 1994. Vol. 66, No. 6. P. 909-916.