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SEPARATION OF OIL SHALE PHENOLS BY CAPILLARY ELECTROPHORESIS

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Estonian oil shale is characterized by relatively high content of oxygen and specific structure of organic matter that lead to the fact that its thermal decomposition products contain more phenols than other fuels. These oil shale phenols are also quite specific and consist mainly of resorcinol and its alkyl derivatives, but contain monobasic phenols, naphthols, and polybasic phenols as well. Up to now for separation of these phenols gas and liquid chromatography have been used. In this study for separation of oil shale phenols capillary electrophoresis (CE) was utilized. Two modes of CE viz. capillary zone electrophoresis and micellar electrokinetic chromatography (MEKC) were tested for separation of phenolic substances and it was demonstrated that using MEKC practically all phenols present in oil shale products could be separated.

Introduction

Estonian oil shale is characterised by relatively high content of oxygen that results in a variety of oxygen-containing organic substances being formed at thermal processing of Estonian oil shale. Unique and somewhat peculiar is the phenomenon that there are much phenolic substances among the oil shale retorting products soluble in water and that these phenols contain approximately 10 % monobasic phenols and 90 % dihydroxybenzene derivatives. The latter fact probably reflects the specific structure and composition of organic matter of Estonian oil shale.

Monobasic phenols are represented by phenol (hydroxybenzene) and its alkyl derivatives with small alkyl substituents (cresols, xylenols). Phenols with two hydroxyl groups consist mainly of resorcinol (1,3-dihydroxybenzene) and its alkyl derivatives (alkylresorcinols). Eight alkylresorcinols: R, 2-MR, 4-MR, 5-MR, 2,5-DMR, 4,5-DMR, 4-ER, 2-M-4-ER may be considered the main components of total oil shale phenols.

During the decades investigation of complex mixture of oil shale phenols was a challenge for many outstanding Estonian chemists (e.g. P. Kogerman, H. Raudsepp, A. Aarna, Ü. Lille, L. Mölder) and their colleagues. Neverthe-

less, at present this topic still deserves scientific and commercial interest especially with the advent of new methods and technologies that may reveal some new aspects of the problem.

Traditionally, analytical separation of phenols is performed using gas or liquid chromatography [1–6]. The objective of this study is to apply relatively new analytical method – capillary electrophoresis for separation of phenolic compounds present in Estonian oil shale retorting products.

Conventional capillary zone electrophoresis (CZE) is used for separation of charged molecules and is based on different mobilities of ionic species. Phenols are too weak acids to be sufficiently ionized in moderately basic buffer medium and in most cases they cannot be properly separated by CZE. For separation of neutral (uncharged) substances micellar electrokinetic chromatography (MEKC) may be applied by adding a surfactant to running buffer in concentration above its critical micelle concentration. As a result, surfactant micelles are being formed, and phenols are partitioned between aqueous buffer phase and hydrophobic micellar pseudo-phase. Differences in partition coefficients of analytes lead to different migration times and to separation of substances.

Experimental

Separation of phenols was performed in a home-made electrophoretic set-up that consisted of an adjustable up to +18 kV high-voltage power supply unit (International High Voltage Electronics, Inc.), a UV detector ISCO CV^4 and an uncoated quartz capillary (Polymicro Technologies) with ID 75 μm, total length 75 cm and length to the detection window 50 cm. In CZE experiments 0.02 M phosphate and borate buffers were used, and all MEKC separations were carried out utilizing phosphate buffer (pH = 7.5) containing sodium dodecyl sulfate (SDS) in the concentration of 50 mM. Detection was performed at 212 nm and detector signal was recorded by computer via ADC (Keithley) with frequency 4.2 Hz.

Phenols used in separations were obtained from several sources.

Phenolic substance	Abbreviation
Phenol (hydroxybenzene)	Ph
o-Cresol (2-methyphenol)	*o*-Cr
m-Cresol (3-methylphenol)	*m*-Cr
p-Cresol (4-methylphenol)	*p*-Cr
2,3-Xylenol (2,3-dimethylphenol)	2,3-X
2,4-Xylenol (2,4-dimethylphenol)	2,4-X
2,5-Xylenol (2,5-dimethylphenol)	2,5-X
2,6-Xylenol (2,6-dimethylphenol)	2,6-X
3,4-Xylenol (3,4-dimethylphenol)	3,4-X
2,3,4-Trimethylphenol	Tmph
2-*tret*-Buthylphenol	2-BPh
Catechol (1,2-dihydroxybenzene)	Cch

Phenolic substance	Abbreviation
Resorcinol (1,3-dihydroxybenzene)	R
2-Methylresorcinol	2-MR
4-Methylresorcinol	4-MR
5-Methylresorcinol	5-MR
2,5-Dimethylresorcinol	2,5-DMR
4,5-Dimethylresorcinol	4,5-DMR
2-Ethylresorcinol	2-ER
4-Ethylresorcinol	4-ER
5-Ethylresorcinol	5-ER
2-Ethyl-5-methylresorcinol	2-E-5-MR
4-Propylresorcinol	4-PR
Hydroquinone (1,4-dihydroxybenzene)	Hq
Pyrogallol (1,2,3-trihydroxybenzene)	Pyg
Phloroglucinol (1,3,5-trihydroxybenzene)	Phg
α-Naphthol	
β-Naphthol	

Some phenolic substances were commercial ones (Ph, R, phenols with one OH group, Cch, Hq, naphthols), some were isolated from oil shale thermal decomposition products (e.g. 5-MR, 2,5-DMR, 5-ER) and some were synthesized in the laboratory (2-MR, 4-MR, 4-ER, 4,5-DMR, 2-E-5-MR, 4-PR). Purity of phenols was not so important, for only separation was studied. In all experiments aqueous solutions of phenols with concentration around 10^{-4} M (each) were used as analyzed samples.

The following analysis procedure was used: before each run capillary was rinsed with 0.1 M NaOH solution, sample was introduced into the capillary electrokinetically during 7 s using analysis voltage (18 kV). In the course of analyses electric current was around 20 μA.

Results and Discussion

To be separated by CZE phenolic substances should be at least partly ionized in running buffer. Phenols have the ionization constants K_a about 10^{-10}

$$Ar{-}OH \rightleftharpoons Ar{-}O^- + H^+;\ K_a = [Ar{-}O^-][H^+]/[Ar{-}OH],$$

and according to the relationship

$$pK_a = pH + \log[Ar{-}OH]/[Ar{-}O^-]$$

one can evaluate that at pH = 7, 1/1000 of phenolic molecules is ionized, at pH = 8, 1/100 is dissociated, and at pH = 9 the ratio of $[Ar{-}O^-]/[Ar{-}OH]$ is 1/10. This means that at pH >8 some separation can be expected. CZE separation of the test mixture (aqueous solution of Ph, R and 5-MR) showed no separation at pH = 7 and partial separation at pH = 8.15 using phosphate buffer (Fig. 1,*a–c*). Similar separation was attained using borate buffer.

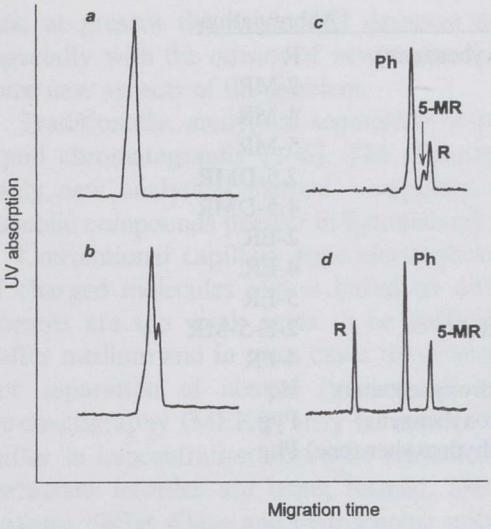

Fig. 1. Separation of test mixture consisting of Ph, R, 5-MR by CZE (*a-c*) and by MEKC (*d*). Conditions: phosphate buffer (*a*) pH = 7.0, (*b*) pH = 7.5, (*c*) pH = 8.15, (*d*) phosphate buffer containing 50 mM SDS, pH = 7.5

Interpretation of peak appearance order is not clear at the first glance. Negatively charged phenolate anions that are carried with buffer in the direction of cathode are additionally attracted towards the anode. So, they move more slowly than electroosmotic flow (EOF). Supposing that all phenolate anions have the same charge of –1, the smallest anion of hydroxybenzene with highest electrophoretic mobility should be last at the detector, and the anion of 5-MR (the biggest of three molecules in the test sample) should be the first one. But in reality it is not the case. It is probable that little differences in K_a values dramatically affect the order of peaks appearance. For example, pK_a values of Ph and R are 9.99 and 9.44, respectively, and conesquently phenol is less ionized and in its neutral state more quickly transported by EOF towards the cathode.

Application of MEKC with SDS-phosphate buffer led to crucial improvement of separation (Fig. 1,*d*), efficiency calculated from the peaks of naphthols was about 200,000 theoretical plates. Due to another principle of separation, the order of peak appearance also has been changed. Distribution of phenols between relatively slowly moving negative SDS micelles and aqueous buffer (characterised by partition coefficient) is mainly governed by the interaction of phenolic species with aqueous and micellar phases. The transit time of analyte t_r may be related to the partition coefficient $\boldsymbol{k'}$ (in analogy with the capacity factor used in chromatography) by equation

$$t_r = t_0(1 + \boldsymbol{k'})/(1 + (t_0/t_{mc})\boldsymbol{k'})$$

where t_0 and t_{mc} are migration times of neutral marker and micelle, and have the value between t_0 and t_{mc}.

Resorcinol with two hydroxyl groups is more hydrophilic compared with phenol and reaches the detector first. Owing to the methyl group that strongly interacts with hydrophobic micelle, 5-MR appears last.

To demonstrate high separation ability of MEKC, three mixtures of phenols have been prepared for analyses. Figure 2 illustrates the separation of phenolic compounds with only hydroxylic substituents.

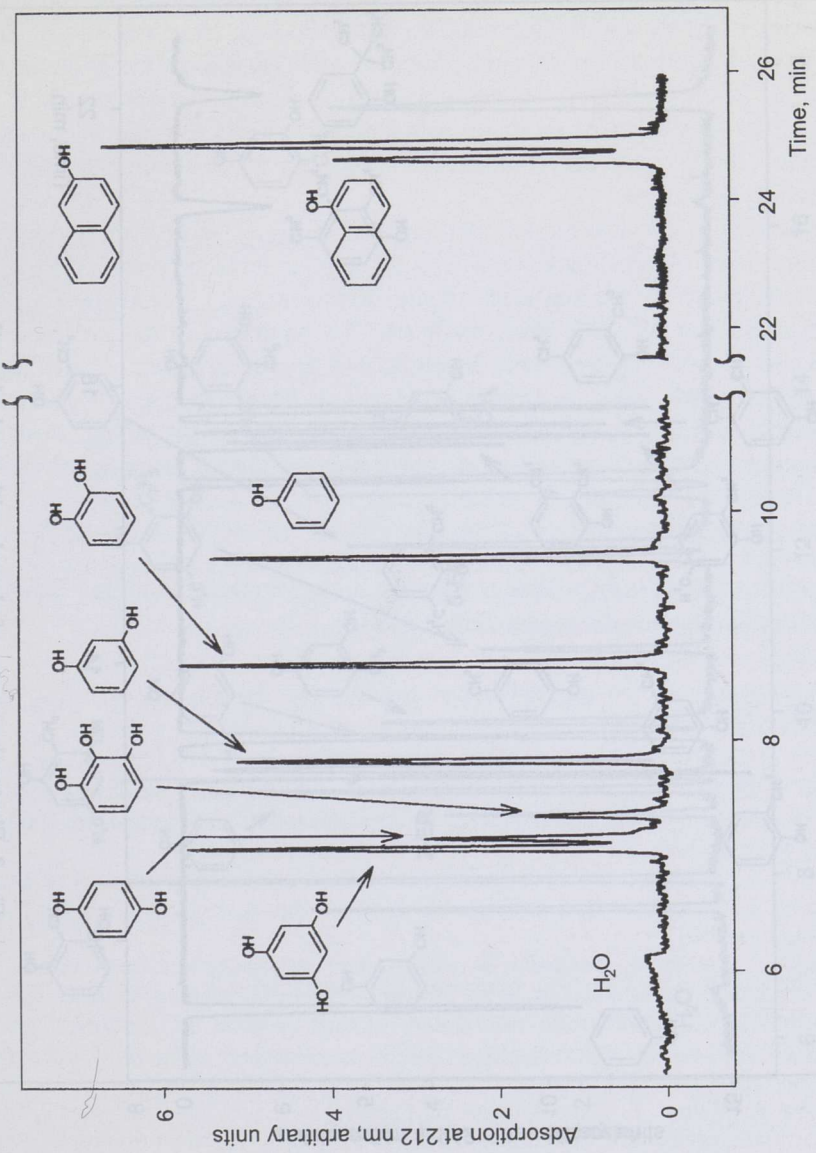

Fig. 2. Electropherogram of phenolic substances with hydroxylic substituents only

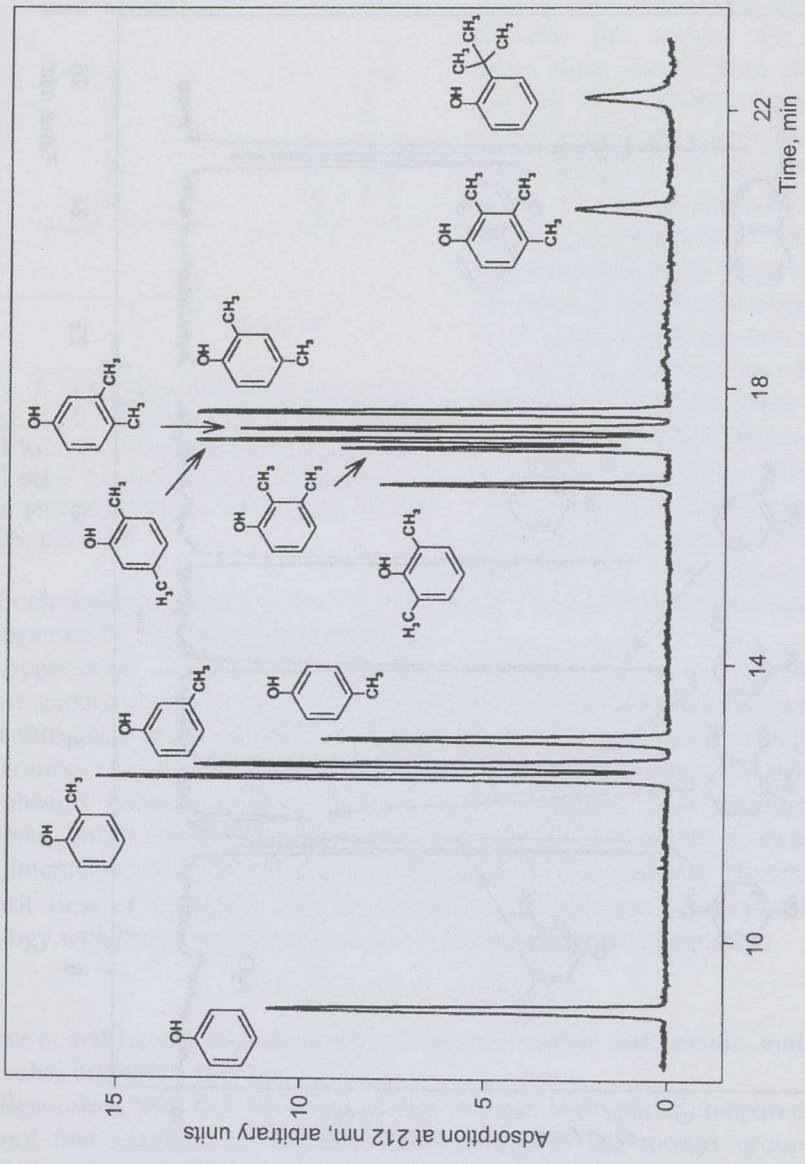

Fig. 3. Electropherogram of phenols with one hydroxylic group

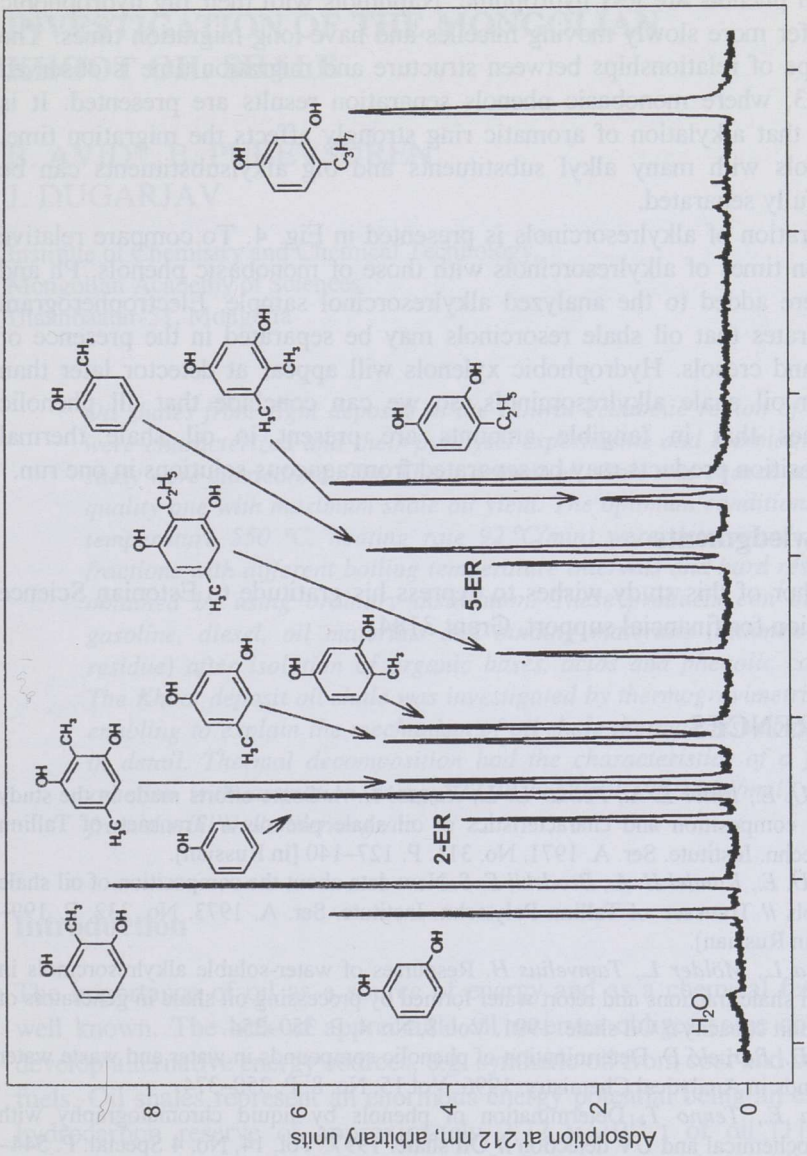

Fig. 4. Electropherogram of alkylated resorcinols. For comparison phenol and *o*-cresol have been added

As one can see, the migration time depends on the number and mutual position of OH groups in the molecule. In phloroglucinol and hydroquinone the OH groups are accessible for water molecules and H bonds retain phenols in the buffer phase. When hydroxyl groups are in *ortho* positions they cannot exert entirely their H-bonding ability because of steric hindrance and such phenols are less hydrophilic. Naphthols with their big hydrophobic part prefer more slowly moving micelles and have long migration times. The same type of relationships between structure and migration time is observed in Fig. 3, where monobasic phenols separation results are presented. It is obvious that alkylation of aromatic ring strongly affects the migration time, so phenols with many alkyl substituents and big alkylsubstituents can be successfully separated.

Separation of alkylresorcinols is presented in Fig. 4. To compare relative migration times of alkylresorcinols with those of monobasic phenols, Ph and *o*-Cr were added to the analyzed alkylresorcinol sample. Electropherogram demonstrates that oil shale resorcinols may be separated in the presence of phenol and cresols. Hydrophobic xylenols will appear at detector later than all main oil shale alkylresorcinols, so we can conclude that all phenolic substances that in tangible amounts are present in oil shale thermal decomposition products may be separated from aqueous solutions in one run.

Acknowledgments

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