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INVESTIGATION OF OIL SHALES BY THERMOCHROMATOGRAPHY

Abstract

The thermal decomposition of different oil shale types has been studied by thermochromatography in the temperature interval 150 to 550 °C at a heating rate of 7 °C/min. The maximum evolution of the thermolysis products has been observed to be at about 430 °C. The amounts of various products have been estimated by the integral of the corresponding chromatographic peaks.

Introduction

Pyrolysis-mass spectrometry is a widely used technique for study the structure of solid fuels organic matter [1]. Provided an experiment carried out properly, this technique enables us to get characteristic fragments of macromolecules. But in practice the experimental conditions are often far from ideal and different problems of interfacing arise. Gas chromatography as a simpler technique has been used to study pyrolysis products despite of chromatographic filtering problems. Another problem arises with complex samples, like coal or oil shale. In this case it is very difficult to establish correct correlations between the composition of pyrolysis products and the chemical structure of initial macromolecules. But analytical results from pyrolysis-gas chromatography are most useful for other studies.

Thermochromatography (ThGC) can be defined as temperature-programmed pyrolysis coupled with time-resolved fast gas chromatographic analysis of the evolving products. This technique provides simultaneously quantitative data as a function of sample decomposition rate and its products evolution in temperature.

In this work, different oil shale samples were investigated by ThGC. The aim was to study possibilities of ThGC and achieve a better understanding of the thermal decomposition process. The results obtained were compared with the data on the conventional thermal decomposition of the same set of oil shale samples.

Experimental

In this study, the home-made ThGC equipment provided with computerized data acquisition and processing was used (Fig. 1). The low amounts of sample (1—10 mg) were heated in a quartz vial from 150 to 550 °C at a heating rate of 7 °C/min. High-purity nitrogen was used as a carrier gas through the reactor and the chromatographic column, the flow rate being 30 and 10 ml/min respectively. A packed chromatographic column was used (packed with Cromosorb W coated with 10 % Apiezon L) and its temperature was kept isothermally at 200 °C. Chromatographic peak areas were measured as a function of temperature.

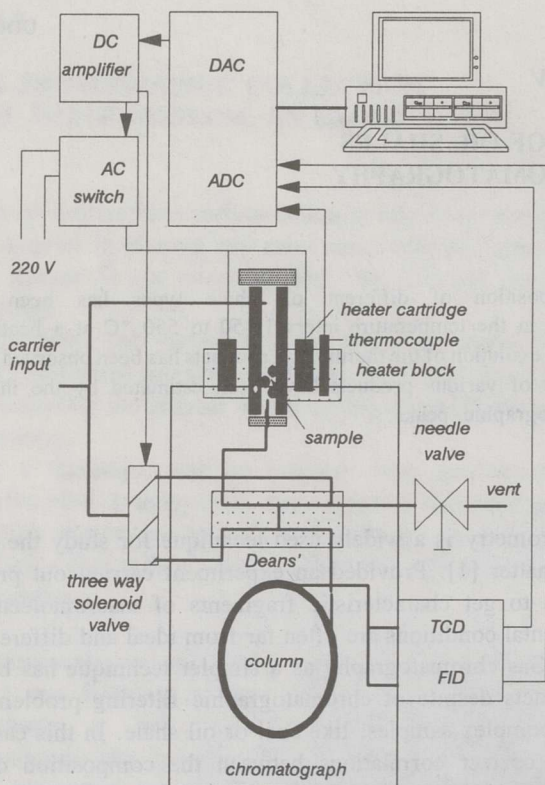


Fig. 1. Scheme and flow chart of the experimental device used: DC - electrical flow switching, AC - reactor heating control, ADC - analog to digital converter, Deans - flow switch, TDC - thermal conductivity detector, FID - flame ionization detector

The factors limiting possibilities of the experimental procedure used in this study are as follows:

- (i) Highly polar and high-boiling compounds cannot be detected by gas chromatography due to the trapping in the column.
- (ii) Most chromatographic peaks are overlapping ones.
- (iii) Quantitative calibrations could be performed only in case of the identified products where the response of the detector is known. Therefore the peak areas have been given in arbitrary units only. However, the different values of the same peak area can be compared within a given series of experiments.
- (iv) Similarly to the other techniques for thermal decomposition studies, the evolving products may be subjected to secondary transformation reactions.

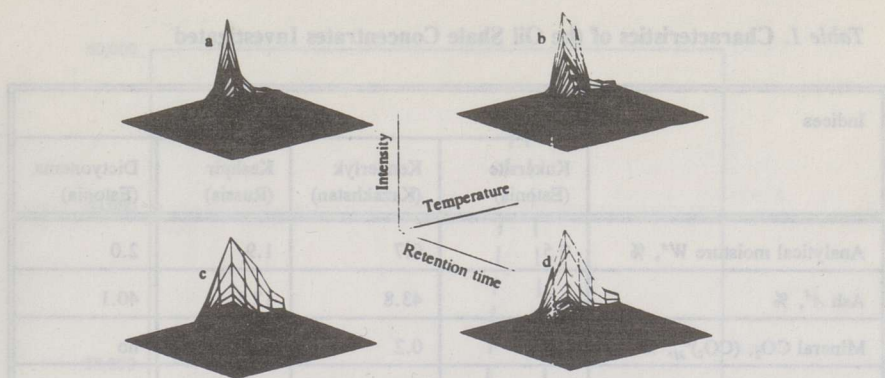


Fig. 2. Thermochromatograms of oil shale concentrates samples:
a - Kukersite, b - Kenderlyk shale, c - Kashpir shale, d - Dictyonema shale

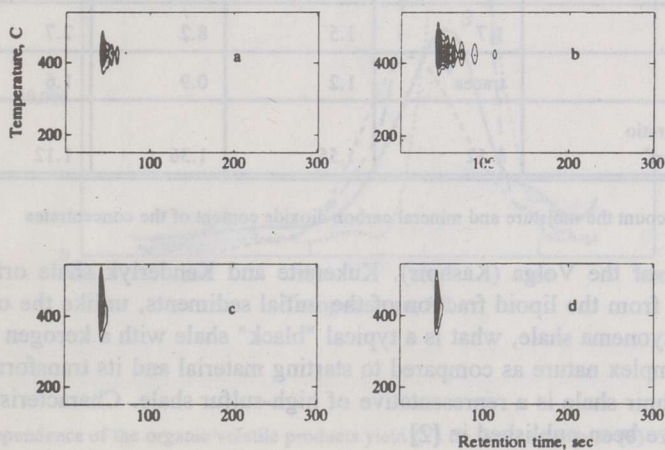


Fig. 3. Contour plots of thermochromatograms. For a, b, c, d, see Fig. 2

Data on the samples investigated have been given in Table 1. The oil shale concentrates have been prepared by centrifugation of the pulverized shale suspensions in aqueous calcium and zinc chloride solutions of different density. The samples under study represent various types of shales originating from different regions of Estonia (Dictyonema shale and Kukersite), Kazakhstan (Kenderlyk) and Russia, the

Table 1. Characteristics of the Oil Shale Concentrates Investigated

Indices	Oil shale			
	Kukersite (Estonia)	Kenderlyk (Kazakhstan)	Kashpir (Russia)	Dictyonema (Estonia)
Analytical moisture W^a , %	0.5	0.7	1.9	2.0
Ash A^d , %	6.3	43.8	12.1	40.1
Mineral CO_2 , $(CO_2)_M^d$, %	0.3	0.2	0.2	no
Organic matter [$100 - A^d - (CO_2)_M^d$], %	93.4	56.0	87.7	59.9
Ultimate analysis, %:				
Carbon C^a ,	69.3	42.7	53.7	50.2
Hydrogen H^a ,	8.8	5.6	6.3	4.9
Sulfur S^a ,	1.7	1.5	8.2	2.7
Nitrogen N^a ,	traces	1.2	0.9	1.6
Atomic H/C ratio of organic part*	1.52	1.55	1.36	1.12

*Taking into account the moisture and mineral carbon dioxide content of the concentrates

middle reaches of the Volga (Kashpir). Kukersite and Kenderlyk shale originate preponderantly from the lipid fraction of the initial sediments, unlike the organic part of the Dictyonema shale, what is a typical "black" shale with a kerogen which is of a very complex nature as compared to starting material and its transformation ways. The Kashpir shale is a representative of high-sulfur shale. Characteristics of these shales have been published in [2].

Results and Discussion

The thermochromatograms of the four oil shale samples investigated are presented in Figs. 2 and 3. These graphs can be treated as fingerprints of the samples and can be used to identify the shale type. But this is not the only value of ThGC as it can provide more useful information to better understanding the degradation process.

The rate of evolution of the volatiles from the decomposition of samples is relatively low mainly below 350 °C dominated by water and carbon dioxide release, seen clearly on the TCD signal recording. Below 400 °C the rate of volatiles evolution depends strongly on the nature of the organic matter of the starting shale.

The active thermal decomposition of shale and the formation of volatile substances take place between 350 and 500 °C where most chromatographic peaks exhibit maximum intensity.

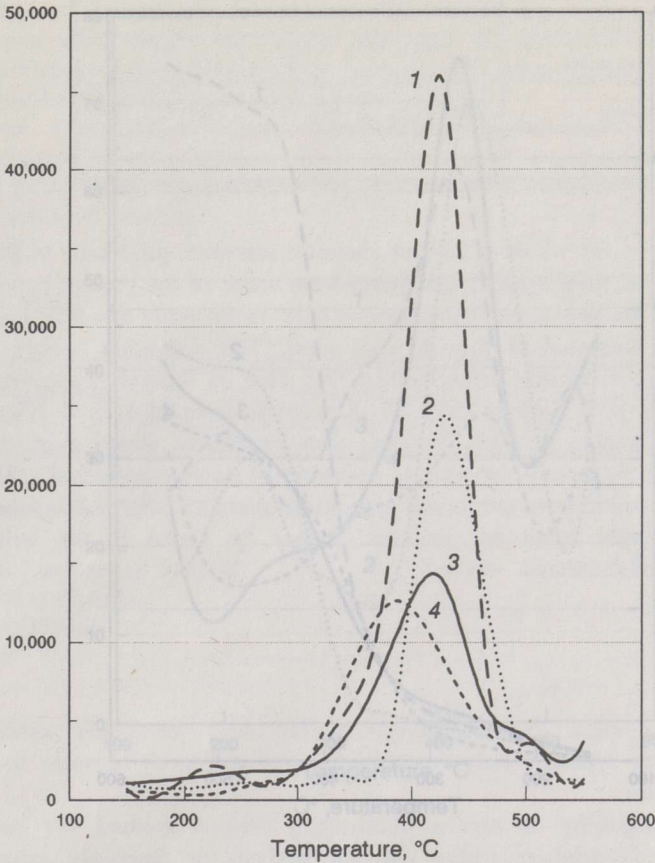


Fig. 4. Dependence of the organic volatile products yield (Y) on the temperature (T): 1 - Kukersite, 2 - Kenderlyk shale, 3 - Dictyonema shale, 4 - Kashpir shale

The evolution of organic products (and combustible gases such as H_2S , etc.) at different temperatures, evaluated by using FID is shown in Fig. 4. The yield of products is given in arbitrary units per weight of the initial sample. The shales investigated differ not only in products yield, but also in the maximum temperature of their formation. In the high temperature domain of the decomposition (above 500 °C) there is the low evolution of volatiles and the number of components is smaller.

The integrated curves for the organic volatiles formation have been shown in Fig. 5.

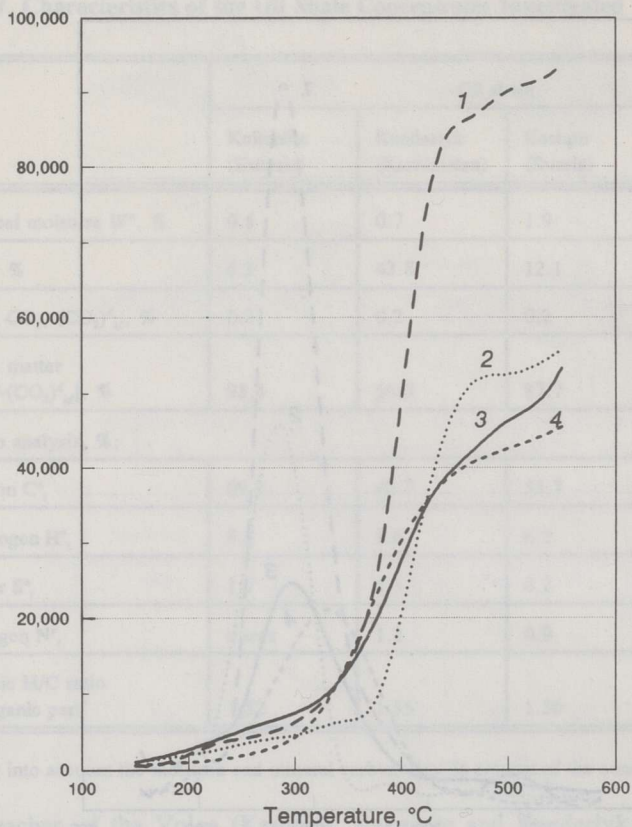


Fig. 5. Cumulative total yield of the organic volatile products (Z) on the temperature (T). For 1, 2, 3, 4, see Fig. 4

The evolution of inorganic destruction products (registered as a difference between TCD and FID signals) takes place over a wide range of temperatures and the pattern of their formation is unique for each of the shales under study (Fig. 6). This is especially pronounced in the case of the inorganics evolving from Kukersite and Kashpir shale showing maximum also at 340 °C.

The characteristic temperatures (beginning and maximum of volatiles evolution) have been presented in Table 2, while the temperature corresponding to 10 % of total evolution has been taken as the beginning of decomposition. These temperatures seem to be typical for different kerogens.

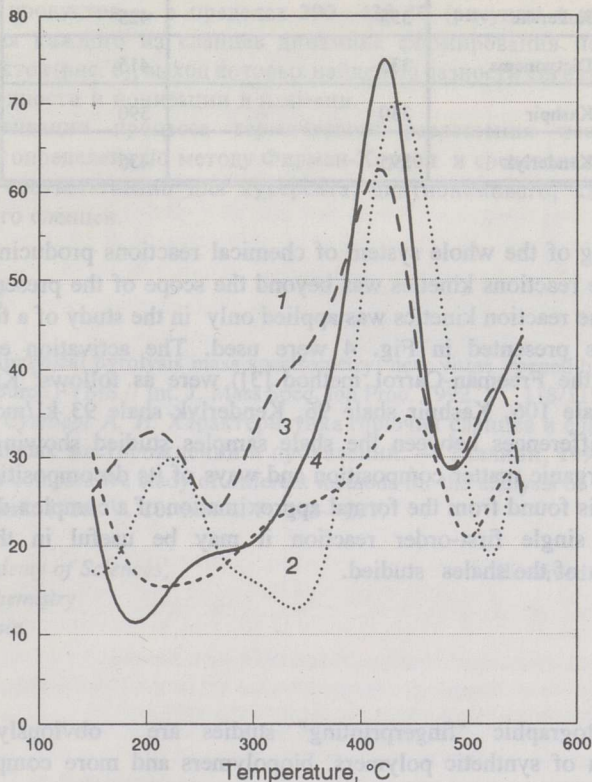


Fig. 6. Dependence of the inorganic volatile products yield (Y) on the temperature (T). For 1, 2, 3, 4, see Fig. 4

A comparison of the evolving curves gives evidence of the differences between the samples and points to temperature regions where different decomposition processes take place. The chromatographic information obtained likewise reflects specificities of various shales. The most pronounced example is an intensive formation of aliphatic hydrocarbon series in case of Kukersite and Kenderlyk shale being less intensive for the other shales. The formation of light hydrocarbon products is due evidently to the paraffinic groups decomposition in the polymeric structures but they may also originate from the hydrocarbons trapped in the microporous structures of shales. These light compounds afford sharp peaks of regular shape and peak maxima at about 425 °C on the evolution curves.

Table 2. Characteristic Temperatures of Kerogen Thermolysis, °C

Oil shale	Beginning of volatiles evolution	Maximum of evolution
Kukersite	355	425
Dictyonema	335	415
Kashpir	330	390
Kenderlyk	395	435

The modelling of the whole system of chemical reactions producing volatiles in respect to these reactions kinetics was beyond the scope of the present paper. The evaluation of the reaction kinetics was applied only in the study of a total evolution and the curves presented in Fig. 4 were used. The activation energy values calculated (by the Freeman-Carrol method [3]) were as follows: Kukersite 138, Dictyonema shale 106, Kashpir shale 96, Kenderlyk shale 93 kJ/mol. There are considerable differences between the shale samples studied showing by this the difference in organic matter composition and ways of its decomposition. Although this parameter is found from the formal approximation of a complex decomposition process by a single first-order reaction it may be useful in the numerical characterization of the shales studied.

Conclusions

Thermochromatographic "fingerprinting" studies are obviously useful for characterization of synthetic polymers, biopolymers and more complex bio- and geomacromolecules.

Thermochromatography is also a challenging on-line method for complex macromolecules degradation studies and for analysis of thermally extractable compounds desorbed from complex matrices. The chromatographic characteristics of the products of thermal decomposition/extraction at slow heating rates and the kinetics of volatiles evolution are of the highest interest.

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ИССЛЕДОВАНИЕ ГОРЮЧИХ СЛАНЦЕВ МЕТОДОМ ТЕРМОХРОМАТОГРАФИИ

Резюме

Концентраты органического вещества кукерсита (Эстония), кендерлыкского (Казахстан), кашпирского (Россия, Поволжье) и диктионемового (Эстония) сланцев (табл. 1) исследованы методом термохроматографии, в котором программированный в отношении температуры пиролиз сочетается с быстрым газохроматографическим анализом летучих продуктов. Полученные на

сконструированной в Институте химии АН Эстонии установке (рис. 1) термохроматограммы специфичны для каждого из сланцев (рисунки 2 и 3), они характеризуют состав их керогена и особенности его термоллиза.

Начало термического разложения (за него принята температура, по достижении которой выделяется 10 % летучих веществ от их общего количества) колеблется в пределах 330—395 °С (табл. 2), максимальная скорость выделения летучих органических продуктов — в пределах 390—435 °С (рисунки 4 и 5). Особенно характерна для каждого из сланцев динамика формирования неорганических летучих продуктов (рис. 6), выход которых найден по разности сигналов детекторов по теплопроводности и ионизации в пламени.

Энергия активации процесса термического разложения исследовавшихся концентратов определена по методу Фирман-Кэррол и составляет 138, 106, 96 и 93 кДж/моль соответственно для кукерсита, диктионемового, кашпирского и кендерлыкского сланцев.

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