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PARTIAL THERMAL ANALYSIS OF KEROGEN OXIDATION PRODUCTS

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A method is proposed which, in principle, permits resolution of complex TG curves into elementary curves. The method is based on appropriate preheating of the substrate. In fact, the method represents partial differential thermogravimetric analysis (PDTG). In this paper it was used, together with IR spectroscopy, for analysis of the precipitated acids obtained by partial oxidation of the kerogen from an oil shale. The precipitated acids were found to consist of five components, characterized by similar thermal properties. General qualitative and quantitative characteristics of the individual components are suggested.

The precipitated acids obtained by stepwise oxidative degradation of kerogen, one of the main structural fragments of Aleksinac (Yugoslavia) shale, were recently studied by thermal analysis [1]. The application of this method was found to be very valuable, since the use of most other instrumental methods was rather limited, the precipitated acids being insoluble in both organic and inorganic solvents.

Significant differences were observed in the weight losses and the shapes of the TG curves of the precipitated acids from various degradation steps, indicating their structural differences and the heterogeneity of the kerogen. The DTG curves of the kerogen and the precipitated acids were found to consist of two distinct parts: a low-temperature (250–450°) and a high-temperature (450–700°) part. The IR data suggested that the low-temperature part corresponded to thermal changes in aromatic structures, and the high-temperature part to those in aliphatic structures [1]. Hence, a combination of thermal and IR analyses proved to be very useful.

However, the DTG curves of the kerogen and the precipitated acids were found to have rather complex structures. Closer analysis of the overall curve into elementary curves did not give unique mathematical solutions, and thus it was not possible to obtain the "number" of simpler chemical constituents. Partial

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thermogravimetric analysis (PDTG), in combination with IR analysis, was therefore suggested as being necessary for a detailed study of the chemical nature of the present compounds.

Consequently, in this paper PDTG was used to examine the precipitated acids. The analysis was aimed at determining the chemical components in the precipitated acids with similar thermal properties. The IR spectra of the residues of precipitated acids subjected to PDTG were also analysed, and attempts were made to correlate the individual peaks with possible chemical changes in the precipitated acids. In this way, a better structural characterization of the precipitated acids, and consequently of the precursor kerogen, was found to be possible.

PDTG method

Two basic problems arise in the decomposition of DTG curves into elementary components:

1) the shapes of the elementary curves;
2) the number of the elementary curves.

The shape of an elementary curve depends on: a) the type of the process (degradation, evaporation, desorption), b) the mechanism of complex thermokinetic reactions (parallel, consecutive, independent, diffusion), and c) the type of the thermokinetic processes (isothermal, nonisothermal).

In the simple case of two components only, for a given type of processes the shapes of the elementary curves are assumed first, and in the next step the overall curve is decomposed mathematically into elementary curves. Even in such a case the result obtained may be ambiguous, since good agreement between elementary and experimental curves can be achieved in several different ways, e.g. by appropriate choice of the reaction order, of the degree of interdependence, etc. In more complex cases, in systems containing more than four elementary components, especially when the effect of diffusion may also be involved, theoretical assumptions are practically impossible. The most often used Gaussian function is the worst choice in this case, as it does not correspond to any of the thermokinetic processes. The choice of the Gaussian curve as the function for an elementary shape is justified only when a great number of very close and overlapping processes are concerned.

For the number of elementary curves determined with the described procedure, irrespective of their shape a unique mathematical solution can not be obtained. In principle, a greater number of elementary curves leads to better fitting with the complex experimental curve. However, in order to avoid ambiguity, additional restrictive conditions have to be introduced. One usually takes the number of elementary curves as the smallest number of elementary curves which fit well with the experimental curve. Finally, it is also assumed that the number of elementary curves is equal to the number of elementary processes. Both conditions are often wrong or cannot be checked experimentally. PDTG is an experimental method which permits determination of the shapes of elementary curves without any previous presumptions and then mathematically the number of curves. As it is a result of a combination of experimental work and mathematical analysis, the obtained number of elementary curves is always unique.

Experimental

Preparation of samples of precipitated acids

The precipitated acids were obtained by alkaline permanganate degradation of the kerogen from Aleksinac (Yugoslavia) oil shale. The kerogen concentrate was oxidized at 75° in 15 steps with 0.50 g portions of $KMnO_4$, according to the procedure described previously [1–3]. In the first step, 3.3448 g of the kerogen concentrate (2.4216 g of kerogen) was dispersed in 100 cm^3 1.6% KOH heated to 75° and the first portion of permanganate was added. After the reduction of the permanganate, the alkaline solution was separated by centrifugation and the following degradation products were isolated: neutral and basic products, ether-soluble acids and precipitated acids [2]. The solid residue was then oxidized with a new portion of permanganate. The same procedure was repeated in a total of 15 steps. Alkaline solutions from some of the degradation steps were combined (from steps 2 and 3; 4–6; 7–9; 10–12; and 13–15). The precipitated acids isolated were denoted PA–2, PA–3, PA–4, PA–5 and PA–6, respectively. The precipitated acids from the first degradation step were denoted PA–1. Two samples of these precipitated acids were studied in this paper: PA–3 and PA–6.

Thermogravimetric analysis

Thermogravimetric analyses (20–700°) were carried out on a DuPont 951 thermogravimetric analyser.

The ambient atmosphere was nitrogen at a flow rate of 15 cm^3/min. 10 mg samples and a heating rate of 5 deg/min were used.

The preheated samples were prepared by heating the samples (PA–3 or PA–6) under nitrogen. The samples were heated in the thermogravimetric analyser (5 deg/min) until the given temperature was reached. They were then cooled to room temperature. These samples were subjected to standard thermogravimetric analysis.

IR spectra

IR spectra were obtained on a Carl-Zeiss Specord 75. The preheated samples of precipitated acids prepared for PDTG analysis were used for IR analyses as well.

Computer and programming

Functional analysis of thermogravimetric curves was carried out on an HP-86B computer. A home-made program written in Basic was used.

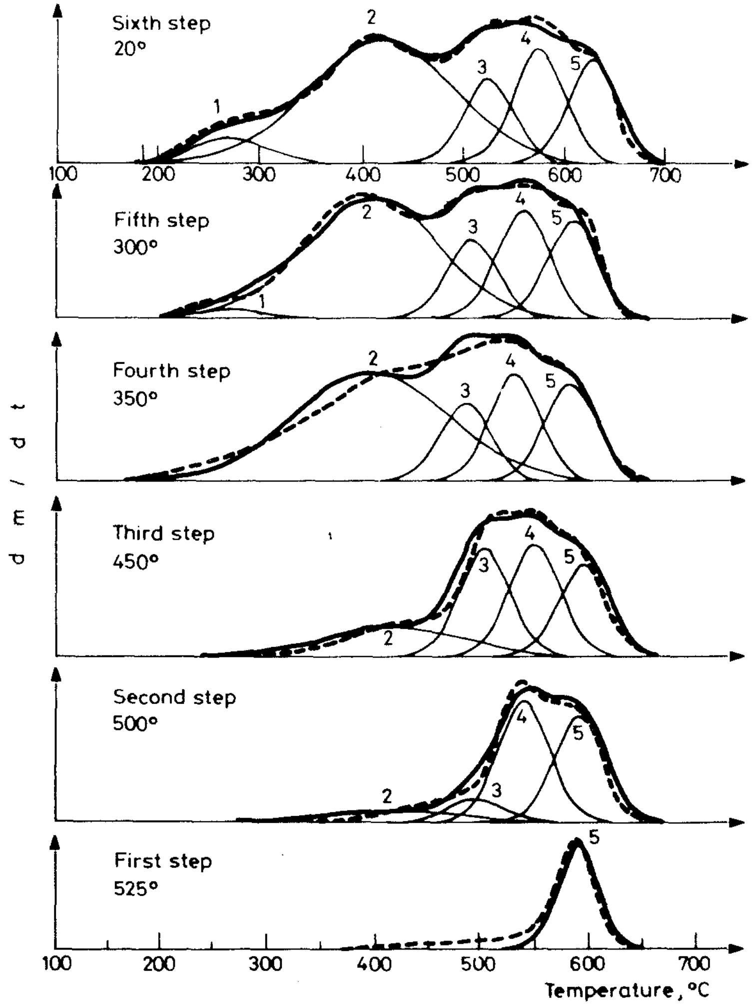

Fig. 1 PDTG analysis of PA-3 from mild kerogen oxidation: DTG experimental curve (full thick line). Gaussian curves (full thin lines). Sum of Gaussian curves (dotted line)

Results and discussion

PDTG of precipitated acids (PA)

The PDTG method was applied to investigate two samples of precipitated acid originating from middle and final steps of kerogen oxidation (PA–3 and PA–6, Figs 1 and 2, respectively). The principle of the method can easily be understood from

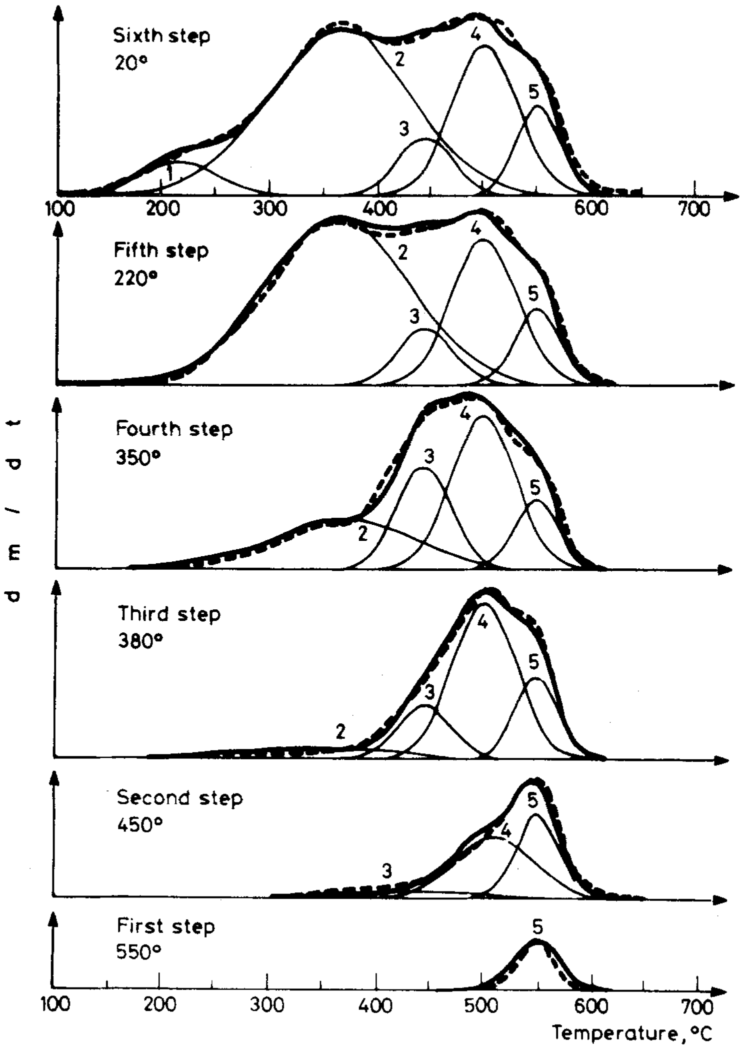

Fig. 2 PDTG analysis of PA–6 from kerogen oxidation: DTG experimental curve (full thick line). Gaussian curves (full thin lines). Sum of Gaussian curves (dotted line)

Figs 1 and 2. Two of the precipitated acid samples (PA–3 and PA–6) showed a complex structure at 20°. When aliquots of these samples were heated to 525° or 500°, then cooled and subjected again to simple DTG analysis, only the peak at 575° or 550° was observed (peaks "5", Figs 1 and 2). Mathematical analysis of these peaks was easy and gave unique solutions. For PA–3 and PA–6, the peaks had a Gaussian shape, especially the high-temperature half of the curve. The low-temperature half was somewhat above the Gaussian curve. This may be attributed to a small portion which belongs to the component represented by "peak 4". Both parameters, T_{max} and D, of the Gaussian curve corresponding to this peak can be obtained directly from the high-temperature half of "peak 5".

The next step in the PDTG analysis requires heating of another aliquot of the sample to a somewhat lower temperature, at which, if possible, only two peaks are observed. Computer functional analysis of the new DTG curve is simple now, and also gives unique solutions, since the mathematical shape of one peak is already known from the previous step. The second, unknown peak, together with the first one which is known, should satisfy the PDTG experimental curve.

The second step required heating of PA–3 at 500° and of PA–6 at 450°. Very good agreement between the experimental curve and the sum of the elementary curves was obtained (the difference was less than 3%) when "peak 4" was also described as a Gaussian curve, of course with a set of corresponding parameters which differed from those for "peak 5". In this, as well as in the previous step, it was difficult to choose an adequate temperature, i.e. one at which only the required peak remained. However, it was important that at a least the high-temperature half of "peak 4" remained free of "impurities" from "peak 3", since one half of the curve was sufficient to calculate the characteristic parameters of the curve.

In the third step the procedure was repeated. This step was aimed at obtaining only three peaks, two of which were known from the previous steps. Thus, in a stepwise manner it is possible to come to a unique resolution of any complex curve into elementary curves.

It was finally shown that in both cases the PDTG curve consisted of 5 elementary peaks which could be described by Gaussian functions. In both cases the agreement between the experimental and the theoretical summed curves was better than 99%.

On the basis of PDTG analysis, it was also possible to determine quantitatively the contributions of the corresponding elementary components. The results are given in Table 1. In both samples the contribution from "peak 1" was minor, only 5%. "Peak 2", at 400°, contributed maximally, about 50% of the total surface area. Among the high-temperature peaks, 50% of the total surface area belonged to "peak 4", while the shares of the other two peaks ("peak 3" and "peak 5") were very close to each other.

Table 1 Quantitative analysis of the components of precipitated acids (PA–3 and PA–6)

Sample	Peak 1		Peak 2		Peak 3		Peak 4		Peak 5	
	T_{max}, °C	%	T_{max}, °C	%	T_{max}, °C	%	T_{max}, °C	%	T_{max}, °C	%
PA–3	265	5.3	415	50.6	520	12.3	570	16.6	626	15.2
	55.9				44.1					
PA–6	215	5.6	365	55.1	445	7.3	500	23.0	550	9.0
	60.7				39.3					

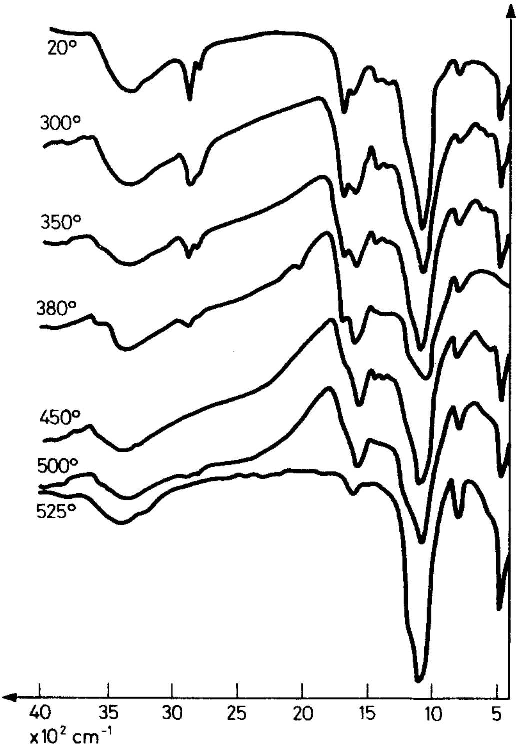

Fig. 3 IR spectra of PA–3 (original and preheated samples)

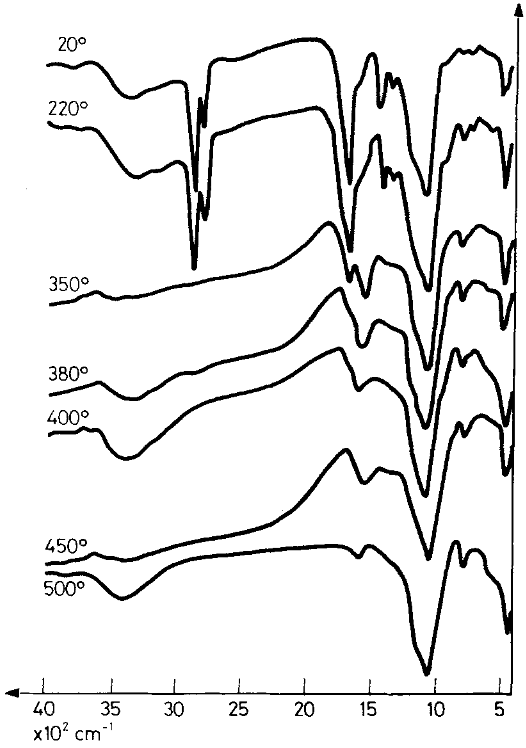

Fig. 4 IR spectra of PA–6 (original and preheated samples)

Possible structure of elementary PA components

The analytical approach to the determination of the structure of elementary components was based on IR analysis, as shown in Figs 3 and 4. Samples of the preheated precipitated acids used for IR analysis were the same as those for PDTG, i.e. they had an identical thermal pre-history. Differences in the IR spectra of PA–3 and PA–6 samples at 20° corroborated earlier observations [1]. During the oxidative degradation of the kerogen with alkaline permanganate, the aromatic portions were oxidized more easily than the aliphatic ones. Hence, the aliphatic/aromatic ratio was considerably higher in PA–6 (2.1) than in PA–3 (0.9).

The thermal stability was opposite to the oxidation stability. The PA–3 samples, preheated at 450°, did not show any traces of CH_3 and CH_2 stretching vibrations (2800–2900 cm^{-1}), indicating that both low-temperature peaks ("peak 1" and "peak 2") should correspond to aliphatic structures with lower thermal stability.

The share of the aromatic structures in the IR spectra (band at 1600 cm^{-1}) increased in proportion with preheating up to 450°, due to the decrease in the content of aliphatic structures. The carbonyl groups were the next in the order of increasing thermal stability. They partly disappeared, together with aliphatic structures, in the temperature range 380–450°, which corresponded to "peak 2" in the PDTG analysis. As aliphatic structures were not present at temperatures higher than 450°, "peak 3" and "peak 4" must have corresponded to aromatic structures with carbonyl groups. Carbonyl groups disappeared completely at higher temperatures and therefore "peak 5" corresponded to "pure" aromatic compounds, as aromatic bands were the only ones in the IR spectra of the sample preheated to 500–525°.

On the basis of the IR analysis, it may be concluded that PDTG analysis can be used for both specific qualitative and quantitative structural analysis.

At present, the structures of the carbonyl compounds ("peaks 3 and 4") remain an open question, requiring the analysis of volatile products.

References

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Zusammenfassung — Es wird eine Methode beschrieben, mit der es prinzipiell möglich ist, komplexe TG-Kurven in Elementarkurven zu zerlegen. Diese Methode beruht auf einem geeigneten Vorerhitzen des Substrates und stellt eigentlich ein partielles differentialthermogravimetrisches Verfahren (PDTG) dar, das in dieser Arbeit zusammen mit der IR-Spektroskopie angewendet wurde, um durch teilweise Oxydation von aus Kerogen eines Schieferöles gefällte Säuren zu untersuchen. Fünf Säuren, deren thermische Charakteristika einander ähnlich sind, konnten festgestellt werden. Es wurde eine allgemeine Charakteristik qualitativer and quantitativer Art der einzelnen Komponenten gegeben.

Резюме — Предложен метод, позволяющий в принципе разделять сложные кривые ТГ на элементарные кривые. Метод основан на соответствующем предварительном нагреве субстрата и в действительности является парциальным дифференьиальным термогравиметрическим анализом. Совместно с ИК спектроскопией метод был использован для анализа осажденных кислот, полученных частичным окислением керогена из сланцевого дёгтя. Установлено, что осажденные кислоты состоят из пяти компонент с близкими термическими характеристиками. Для индивидуальных компонент предложеные общие качественные и количественные характеристики.