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ANALYSIS OF ORGANIC MATTER FROM WITWATERSRAND BASIN (SOUTH AFRICA) BY OTA AND Py-GC-MS
Preliminary results

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Abstract

Oxyreactive Thermal Analysis (OTA) and pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) have been performed on highly matured, uraniferous samples.

Organic matter investigated by OTA gives two exothermic peaks on DTA curves. The dominant peak appearing at temperature higher than 500°C, confirm the high maturity of the organic matter. Results of analysis by Py-GC-MS complement the OTA results. The organic matter in all of the samples shows the same general pyrolysis characteristics. The pyrograms are dominated by low molecular mass aromatic hydrocarbons. The samples differ in relative abundances of the compounds.

The changes in temperature and intensity of the lower-temperature peak in OTA method and differences in relative abundances of aromatic hydrocarbons were used to investigate differences in thermal maturity of the organic matter.

Keywords: organic matter, pyrolysis-GC-MS, thermal analysis, Witwatersrand

Introduction

Thermal analysis methods have already proven to be efficient in a wide range of problems emerging in investigation of a variety of fossil organic matter, that differs in thermal maturation. The potential of thermogravimetric analysis (TG) alone or coupled with either Fourier Transform Infrared Spectrometer (FTIR) or with mass spectrometry was reported in the literature [1–4]. The TG results are comparable with commonly used methods. Huang *et al.* [5] noticed a strong correlation between the derivative of a TG curve maximum and vitrinite reflectance, which enabled estimation of coal rank with high precision by TG analysis. A comparative study of TG and NMR results suggests a possibility to elucidate a mineral matter effects on organic material [2].

A differential thermal analysis (DTA), which is related to TG, conducted in air atmosphere is less popular, probably because the obtained results often seem problematic or difficult to explain (e.g. [6]). Those problems are overcome by a modified DTA, called Oxyreactive Thermal Analysis (OTA). OTA provides reproducible re-

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sults, applicable in characterization of solid materials, if the oxidative conditions are strictly maintained [7].

A thermal oxidation of organic matter results in exothermic reactions indicated by sharply defined peaks on the DTA curves. The number of reactions, their temperature and the amount of evolved heat are characteristic and structure dependent features of the combusted material [7, 8].

The OTA method has successfully been used in studies of organic matter in rocks. The OTA enables to estimate the degree of thermal maturity of the investigated material and distinguishes between different types of organic matter [8, 9].

In this study a Py-GC-MS (pyrolysis – gas chromatography – mass spectrometry) was complement by OTA. The Py-GC-MS is commonly used to determine fossil organic structure [10, 11]. In the Py-GC-MS method, pyrolysis causes the thermal disintegration of a macromolecule into smaller components. A gaseous fraction of pyrolysis products is analyzed by GC-MS. Therefore a direct, though fragmentary data about the organic matter composition is obtained. The method, however, cannot directly determine the nonvolatile components.

Combination of the results obtained by OTA and Py-GC-MS may help to better understand the investigated material.

Samples description

Seven samples (coded CL) from the Paleoproterozoic Witwatersrand Basin (South Africa) and one sample (L 1) of pyrobitumen from slightly younger (2143±143 Ma [12]), Franceville Basin (Gabon) were used in the present study. The Witwatersrand organic matter is highly mineralized, mainly in U and Au. It occurs as layers, commonly 1–2 cm thick, which often shows a columnar fibrous-like texture perpendicular to the bedding plane.

Chemical analyses and Raman spectroscopy of a representative suite of organic material from a number of Witwatersrand mines by Landais *et al*. [13] suggest that the organic material is mature (catagenetic zone) and highly aromatic. H/C and O/C atomic ratios vary from 0.423 to 0.550 and from 0.030 to 0.074, respectively. Coal in the layers is classified as semi-anthracitic and anthracitic [14]. More details about the organic matter from Witwatersrand can be found in [15] and [16].

Samples investigated during this study were collected in the Carbon Leader placer, mined in the Carletonville Gold Field at depth between 1500 and 4000 m below surface.

A sample from the Franceville Basin is an unmineralized pyrobitumen with macroscopically visible degassing bubbles. H/C atomic ratio of the sample is 0.47.

Methods

Organic matter was hand-picked after crushing the sample. To avoid oxidation or fractionation phenomena, the organic matter was not chemically treated. The purity of the organic matter was checked under a binocular microscope.

Oxyreactive Thermal Analysis

OTA was performed using a derivatograph Q 1500, system Paulik–Paulik–Erdey (MOM, Hungary) in a dynamic air atmosphere with air flow of 1.9 cm^3 min^{-1}. The heating rate was 10°C min^{-1} over a temperature range 20–600°C. All samples were ground with Al_2O_3 at the 1:3 ratio to a grain diameter less than 0.3 μm. Multiplate sample holders with sets of 4 platinum plates were used. The sample mass was 0.045g (0.180 g of sample and inert material) for samples from Witwatersrand Basin. The pyrobitumen sample (L 1) masses 0.010 g (total 0.040 g). Fundamentals and details of the OTA method are described by Cebulak and Langier-Kuzniarowa [7].

To inspect the possibility of mineral matter influence on the OTA curves, powdered samples were divided into to portions:

1. One portion of each sample was prepared as described above and analyzed.
2. The second portion of organic matter was first purified using a method described by Rouzaud *et al.* [17]. The method is based on a phenomenon that carbonaceous matter is readily wet by organic solvent while minerals are wet by water. The samples were mixed with water and the mixtures were stirred with toluene. Organic matter concentrated in toluene. After evaporation, the purity of the concentrated organic material was first checked by X-ray powder diffraction and then analysed by OTA.

Comparison of the two obtained sets of curves assures, that all mass changes are due to combustion of the organic matter.

Flash pyrolysis–gas chromatography–mass spectrometry

A Curie-point Pye-Unicam pyrolyser, type: 795050, working in 770°C was coupled to a Hewlett Packard gas chromatograph with a HP-1 column (60 m×0.32 mm i.d.), coated by 0.25 μm stationary phase film. The experimental conditions were as follows: carrier gas – He, temp. program: 50°C, heating rate to 175°C–10° min^{-1}, to 225°C–6° min^{-1} to 300° min^{-1}, final temperature 300°C. The mass spectrometer was operated in the electron impact ionization mode at 70 eV. Data were acquired in a full scan mode and processed with the Hewlett Packard Chemstation software. Compounds were identified by their mass spectra. Their retention times were compared to standard compounds and literature data

Results and discussion

Py–GC–MS

The pyrogram of all samples is dominated by CO_2 peak, which is thought to be at least in part artificial. The CO_2 can partially originate from O_2 absorbed on the sample so it cannot be used in evaluation of the oxidation stage of the pyrolyzed organic material. Only the increase in the baseline of the pyrogram enables identification of several components (Fig. 1).

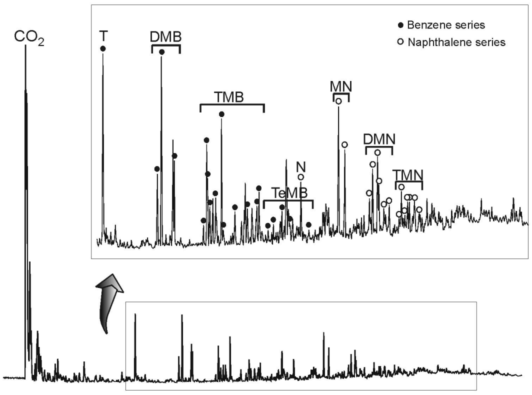

Fig. 1 Pyrogram of a mineralized sample at full scale and on an expanded scale where components of benzene and naphthalene series are shown. Peak labeled T is toluene, DMB are dimethylbenzenes, TMB – trimethylbenzenes, TeMB – tetramethylbenzenes; N is naphthalene, MN are methylnaphthalenes, DMN – dimethylnaphthalenes, TMN – trimethylnaphthalenes

The mineralized samples are dominated by low molecular mass aromatic hydrocarbons with toluene being the most abundant. The benzene series is best developed, up to the C_4-alkylbenzenes. Similarly, the naphthalene and indene series are detected up to C_3 alkyl substitution. The more alkylated aromatic compounds appear in lower concentration than compounds which aromatic rings are alkylsubstituted to a lesser extend (Fig. 1). This feature is typical for all of the mineralized samples but there are differences in relative abundances of the compounds between the samples.

To summarize the observed tendencies an alkylation index of Holliger et al. [18] was calculated:

$$\text{Alkylation index} = \frac{\text{benzene} + \text{toluene}}{\text{Sum of } C_0 + C_3 - \text{alkylbenzenes}}$$

A low value of the Alkylation index indicates more extensive alkyl substitution of benzenes (beyond simple methylation). A similar ratio can be calculated for naphthalenes and indenes, which show essentially the same trends.

The more fused-ring aromatic hydrocarbons which occur in low relative abundances include anthracene, phenantrene, pirene and their methylated variants.

The relative concentration of the heavier aromatic hydrocarbons influences a value of Aromatisation Index proposed by Holliger *et al.* [18]:

$$\text{Aromatisation index} = \frac{\text{Sum of all monoaromatic hydrocarbons}}{\text{Sum of all mono–, di–, tri– and tetraaromatic hydrocarbons}}$$

The Aromatisation index employs all the quantitated homologues of benzene, naphthalene, phenantrene, anthracene and pyrene. The benzene values are placed in numerator over the sum of all the aromatics, thus the ratio decreases when relative concentrations of the polynuclear aromatics increase.

Oxygen- and sulphur-bearing pyrolysis products were observed in the investigated samples. Concentration of thiophenes and methyl thiophenes is relatively low and similar for all samples. Samples CL 2, L 1 and to much lesser extend CL 6 are enriched in oxygen containing compounds, mainly in phenols and methyl phenols (Fig. 3).

Table 1 Parameters from Py-GC-MS data

Sample	Alkylation index	Aromatisation index	*n*-octene/ *m*+*p* xylene ratio
CL 1	0.19	0.56	0.11
CL 2	0.41	0.73	1.34
CL 3	0.26	0.64	0.01
CL 4	0.29	0.72	0.17
CL 5	0.30	0.45	0.03
CL 6	0.35	0.62	0.28
CL 7	0.38	0.47	0.20
L 1	–	–	3.44

The *n*-alkene/*n*-alkane homologues are present up to C_{22}. The samples show great variations in the abundance of aliphatic *vs.* aromatic hydrocarbons. An *n*-octene/ *m*+*p*-xylene ratio was chosen to highlight the observed differences [19]. The accuracy of the ratio is emphasized by unequal distribution of the aliphatic doublet. The *n*-alkane series represent detectable but minor fraction in almost all samples.

The calculated ratios are given in Table 1.

Oxyreactive Thermal Analysis

In general, the data obtained for all samples from Witwatersrand Basin are similar and confirm the high maturity of organic matter. Combustion of organic matter occurs in two stages, seen as two exothermic peaks on a DTA curve (Fig. 2). The major portion of the samples combusts at temperatures higher than 500°C. The high-temperature peak is dominant on both DTG and DTA curves, indicating very advanced stage of thermal maturation of organic matter [20]. The maximum temperature and shape of the high-temperature peak varies between samples (Table 2, Fig. 2).

The low-temperature peak occurs at temperatures between 306 and 355°C. The amount of evolved heat roughly decreases with increasing temperature of the reaction. The peak is barely visible on the DTG curve due to small mass of organic matter involved in combustion at that temperature range. Despite the small mass consumed during the reaction, the peak on the thermal curve is relatively strong. This is illustrated by the behavior of sample CL 1, which is characterized by both the lowest temperature of the first peak and its highest intensity on the DTA curve. The small mass loss results only in a

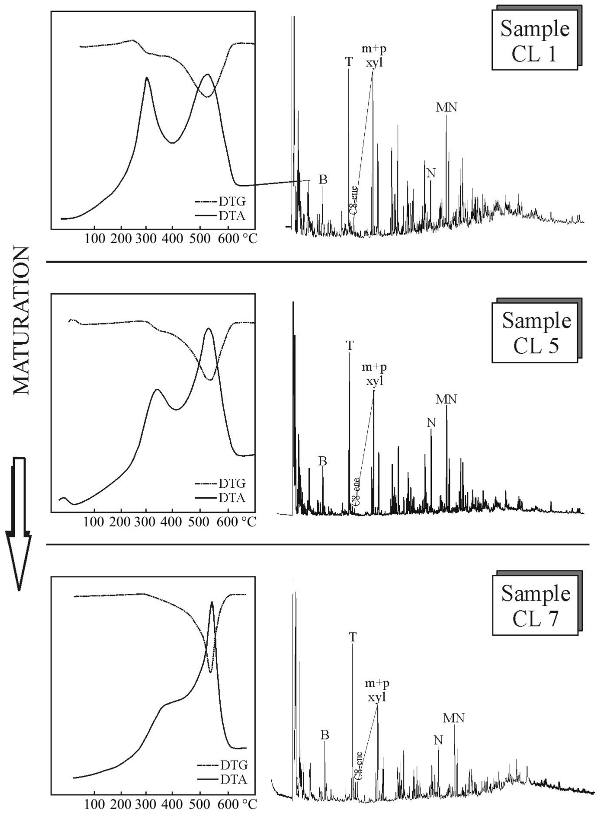

Fig. 2 DTA and DTG curves of CL 1 (top), CL 5 (middle), CL 7 (bottom) samples together with pyrograms of the samples. Peak labeled B is benzene, T – toluene, C8-ene – octene, *m* + *p* xylene – *meta* + *para* xylene, N – naphthalene and MN are 2- and 1-methylnaphthalenes

Table 2. Reaction characteristics from OTA

Sample	Peak reaction temperature/°C		End temperature/°C	Sample left/%
	I peak	II peak		
CL 1	306	528	620	11.1
CL 2	320	505	590	16.7
CL 3	322	540	630	17.8
CL 4	325	535	620	16.7
CL 5	335	535	625	22.1
CL 6	335	515	610	24.5
CL 7	~355	530	590	22.2
L 1	450		520	0.0

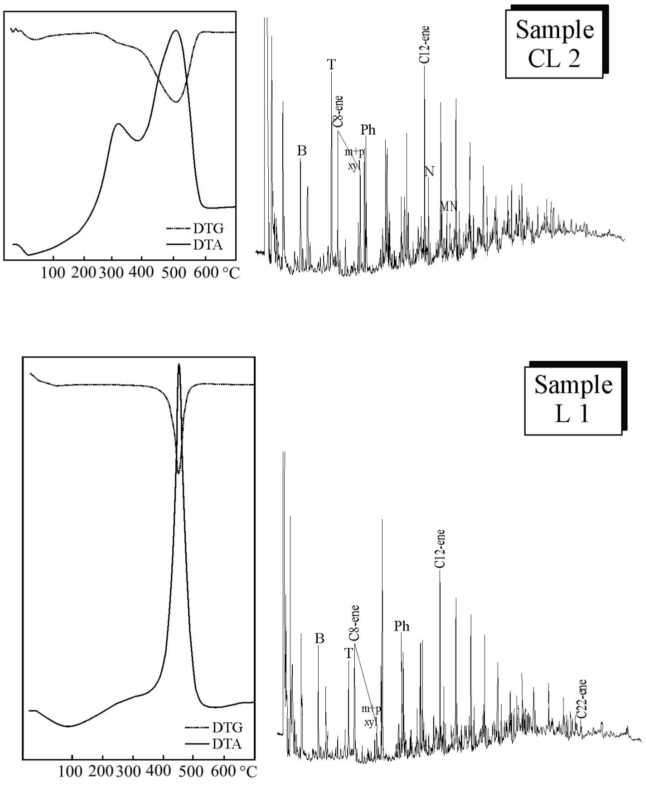

Fig. 3 DTA and DTG curves of samples CL 2 (top) and L 1 (bottom) together with pyrograms of the samples. Labels as in Fig. 2, the peak labeled Ph is phenol

hump on DTG curve contrary to the effect of the high-temperature reaction, which results in a distinct peak on the DTG curve during heating. Perhaps, the reaction at ~300°C is characterized by high specific heat and high oxyreactivity as a result of combustion of components with elevated H/C atomic ratio.

In other samples, the thermal effect of the first reaction diminishes and almost disappears as in sample CL 7. There is only a weak shoulder on DTA curve of sample CL 7 and DTG curve is featureless (Fig. 2).

Narrow reaction range and a single, very intensive peak with maximum temperature at 450°C are characteristic feature of sample L 1 (Table 2, Fig. 3).

At the advanced stage of thermal maturation, polyaromatic molecules dominate the structure of organic matter. While the structure is simple from a chemical point of view, it is difficult to investigate because of a limited number of techniques available. However, the relatively simple chemistry of organic matter investigated during this study enabled comparison of data obtained by OTA and Py-GC-MS methods.

The comparison of the two data sets reveals some dependences (Fig. 2). A linear correlation between temperature of the first peak on DTA curve and the value of the

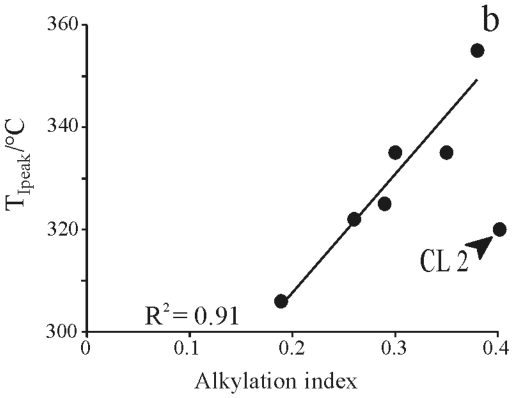

Fig. 4 Correlation of temperature of the first peak with Alkylation index. Sample CL 2 does not contribute to the R^2 value

Alkylation index in the mineralized samples is observed with the exception of CL 2 (Fig. 4). Probably it is the elevated oxidation state that cause sample CL 2 to differ from others. The increasing value of the Alkylation index and increasing temperature of the low-temperature peak which intensity decreases in the same time is interpreted here as an indication of an increasing maturation stage (Fig. 2).

A possible influence of oxygen-bearing compounds on OTA results was not evaluated during this study due to the complexity of that problem.

The Aromatisation index rather does not determine aromaticity of the organic matter as proposed by Holliger *et al.* [18]. With increasing transformation stage of the organic matter the pyrograms become simpler. Toluene predominates as the components other than toluene gradually disappear (Fig. 2). The low-temperature peak in the OTA method gradually diminishes.

In the L 1 sample the *n*-alkenes series dominates the pyrogram. The C_{12} *n*-alkene gives the largest peak, whereas benzene, toluene and naphthalene though readily detectable are much lower. The sample shows almost no alkylation of the aromatics and lack aromatic hydrocarbons larger than naphthalene. The specific character of the pyrogram of sample L 1 agree with the results obtained by the OTA. In this case the thermal behavior of L 1 also differs dramatically from other samples (Fig. 3).

Conclusions

The results of OTA prove useful in investigation of highly transformed solid residues and complement well the results obtained by Py-GC-MS in this case. The obtained results confirm the high aromaticity of the mineralized organic material and document differences in transformation stage.

Due to the simplicity of the results of data obtained by OTA it provides a general characteristic of the whole organic material and indicate a possibility of distinguishing between different organic types.

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