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ROCK EVAL PYROLYSIS AS A TOOL FOR CHARACTERIZATION OF ORGANIC MATTER IN SOIL SAMPLES

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Abstract:
Rock-Eval (RE) pyrolysis was designed for petroleum exploration to determine the type and quality of organic matter in rock samples. The aim of our work was to present new fields of application of the RE pyrolysis for assessing the proportion of the organic components of different thermal stabilities, and also to apply this method for characterization of organic matter dynamics in polluted sediments, soil and paleosoil profiles.

Keywords:
Rock-Eval pirolysis, organic matter dynamic, paleosoil

1. INTRODUCTION

The geological organic matter is present in the atmosphere, in the water, in the soil, in the recent sediments and in the rocks equally. Organic matter of sediment rocks is studied comprehensively, but we have less knowledge from geochemical of organic matter in soils and recent sediment, although it should be justified because of mass and the important role in the global carbon cycle.

SOM plays a significant role in the CO_2 content of atmosphere and in controling of global earth temperature. Wearing-away of rocks and pedogenesis processes are influenced by SOM. Adsorption characteristic of organic matter in soils and recent sediments determine the mobility of organic and inorganic pollution thus effects the quality of water in surface and groundwater.

SOM is not homogenous but is a mixture of many organic matters with different chemical compositions and physical qualities. This chemically and kinetically heterogeneous material comprises a mixture of plant and microbial residues of various compositions and with different decomposition rates, as well as their transformation products, in addition to refractory, long-residence-time macromolecular organic substances (kerogen, black carbon). Humification of biopolymers is determined by those environmental parameters (relief, climatic conditions), which define soil types too.

RE pyrolysis was designed for petroleum exploration to determine the type and quality of organic matter in rock samples. Nevertheless, this technique can be used for bulk characterization of the immature organic matter in soil samples and recent sediments.

Either aim of our work was to examine the soil conditions of an archeological site. This study is restricted to introduction of new investigation methods in paleosoil examination, using the example of the Neolithic archeological site. For determination of the original soil type of the examined area we adopt sedimentological, micromorphological and pedological investigations as a first step. For supplement this we made an attempt to apply a new method for characterization the soil organic matter.

2. MATERIALS AND METHODS

Samples were collected from the A and B horizons of chernozem braun forest soil from West-Hungary and we analyzed buried paleosoil samples from an archeological site from North-Eastern Hungary. The development of the soil horizon was finished in the Neolithic Age, when the soil was covered so the evolution of the soil horizon broke off. After this period the soil transformed a transition form of soil and sediment. Accordingly reconstruction the original type of the soil is possible only by complex analysis.

We described the soil profile, measured the content and distribution of grain size, the content and relative proportion of organic matter and carbonate. For sedimentological analysis the composition and distribution of grain size we applied Micromeritics SediGraph 5000ET X-ray sedimentograph. Applied method for measure content of organic matter and carbonate was Dean-method the "loss on ignition" [1]. The measured parameters were depicted on profile diagrams for evaluation purposes.

The Rock Eval data of the soil samples were determined with Delsi Oil Show Analyzer (Hetényi et al., 2005). The following parameters can be obtained from one single measurement: **S1** amount of thermovaporized free hydrocarbons - present in the rock as free or adsorbed compounds - expressed in mg HC/g of rock. **S2** the current potential of a rock sample, represents the total amount of oil and gas a source rock can still produce during subsequent complete thermal maturation in an open system. (expressed in mg HC/g of rock). **T_{max}** the temperature (°C) which is recorded for the maximum of the S2 peak varies as a function of the thermal maturity of the organic matter. **TOC** (total organic carbon) content (expressed in weight %) is defined as the sum of the pyrolysed organic carbon content and organic carbon residue content. **HI** (hydrogen index) is defined as carbon normalized S2 and expressed in mg HC/gTOC. **PI** (production index) S1/S1+S2.

The experimental conditions of Rock-Eval pyrolysis were chosen that all of the hydrocarbonaceous compounds yielded by soil organic matter are recorded as one single peak. Pyrograms of our samples can be described by a combination of four elementary Gaussian components: F1, F2, F3 and F4. These four components are related to major classes of organic constituents differing in origin and their resistance to pyrolysis: labile biological constituents (F1), resistant biological constituents (F2), immature non-biotic constituents (F3) and a mature refractory fraction (F4). F1/F2 ratio illustrate the relative evolution of the two '"bio-macromolecule" classes. The log[(F1+F2)/F3] index quantify the degradation of immature OM [2].

3. MATHEMATICAL DECONVOLUTION

In an immature organic matter, like soil, a wide range of components may be present simultaneously and each of them is represented by a Gaussian curve on the pyrogram (S2 peak) with characteristic mean (M) and standard deviation (σ) values. Each pyrogram is a complicated overlap of several normal distributions curves. In order to define discrete components of the multicomponent mixture, the pyrogram has to be decomposed mathematically. The well-known normal distribution curve is symmetric to the mean having one inflexion point on each side. A composite curve, may exhibit complicated shape with several inflexion points along it. It can be assumed, that in case of this special class of composite curves a mean value of at least one component falls within the interval of the two smallest inflexion points. This feature was utilized during the recursive decomposition algorithm applied in the project.

The first step is smoothing the originally rough pyrogram using moving average method. Moving the window and calculating the means over the whole temperature range result in a smooth data distribution of equal density. After several loops a 5°C interval was found large enough to get pyrogram without unrealistic peaks and ditches.

In the second step of the procedure numerical derivation was fulfilled twice to get the inflexion points of the smoothed composite curve. Without using an effective smoothing algorithm, there is no chance to get inflexions of real meaning. Afterwards, the two smallest inflexion points ($T_{i,1}$, $T_{i,2}$) were chosen, which surround the mean (M_i) in question. In the next step a two-dimensional search of (M_i, σ_i) was carried out using a Monte Carlo type simulation by computing numerous data pairs so that

$$M_i \in (T_{i,1}, T_{i,2}), \text{ and} \tag{1}$$

$$\sigma_i \in (1/(S2T_{i,1}\sqrt{2\Pi}),), (1/(S2T_{i,2}\sqrt{2\Pi}),), \tag{2}$$

where $S2T_{i,j}$ denotes S2 values at $T_{i,j}$ temperatures.

Finally, each (M_i, σ_i) pair was used for calculating model S2 curves, and a least square best-fit algorithm is applied to get the best M_i and σ_i among them. Best model curve is determined when ε is minimized so that

$$\varepsilon=\Sigma(S2_{observed} - S2_{calculated})^2, \tag{3}$$

where summation goes from 180°C up to $T_{i,1}$ in each case.

After subtracting the model curve from the original S2 composite curve, the process was repeated recursively to the residuum from the second step (numerical derivation) [3].

4. RESULTS AND DISCUSSION

T_{max} values of approximated Gauss curves belong three category: original biopolymers (180-340°C), partially docomposed biopolymers (340-420°C), humic substances (420-600°C). Calculated values are in accord with measured series of stepwise Rock-Eval analyses. Consequently, we can estimating the poportion of original biopolymers well.

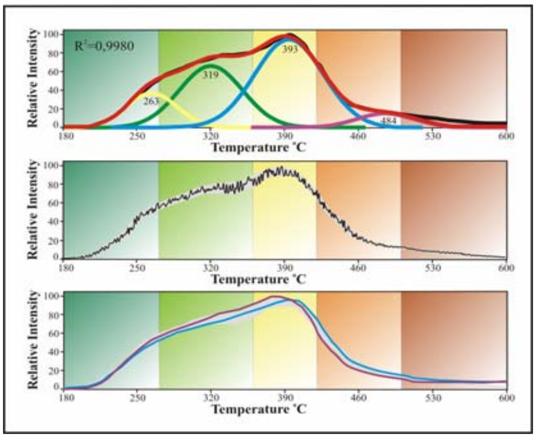

Figure 1. Steps of SOM "fingerprint" analysis

We use a modified application of Rock-Eval pyrolysis approach for estimating the proportion of the components with different thermal stability and the measure of humification. On a pyrogram each unique organic matter is represented by a normal distribution curve with characteristic mean and standard deviation. As a consequence, a pyrogram is a sum of numerous single Gauss curves what can be decomposed using a proper algorithm. In order to calculate possible composite curves, first the uncertainty of mean and standard deviation of RE measurement was determined by 20 independent runs. On this basis using a Monte Carlo type simulation 1000 different realizations were calculated. The envelope of all these curves defines the stripe what is the typical "fingerprint" of the SOM in question. We examined four chernozem-brown forest soil samples. We accepted that the unknown sample belongs into the specified soil type if it's pyrogram concide 90% with the soil type's envelope (Fig. 1). This method should be suitable for define soil type of „unknown" samples [4].

On buried soil's study we have to pay attention to the processes which passes off after the coverage of soil. Soil life breaks off; ventilation stops or decreases and the accumulated sediments increase the pressure. These processes are able to change the original properties of the soil therefore only time-independent, steady-state characteristics are adequate for pedological-morphological description. These are texture, type of soil structures, fabric and porosity. We applied Rock-Eval Pyrolysis to get new details of soil organic matter, which can indicate the soil type. Mathematical decomposition of the S2 peaks was used to determine the rate of partially decomposed biopolymers, humic substances. The rate of organic carbon accumulation and decomposition rate of biopolymers were interpreted as function of environmental effects.

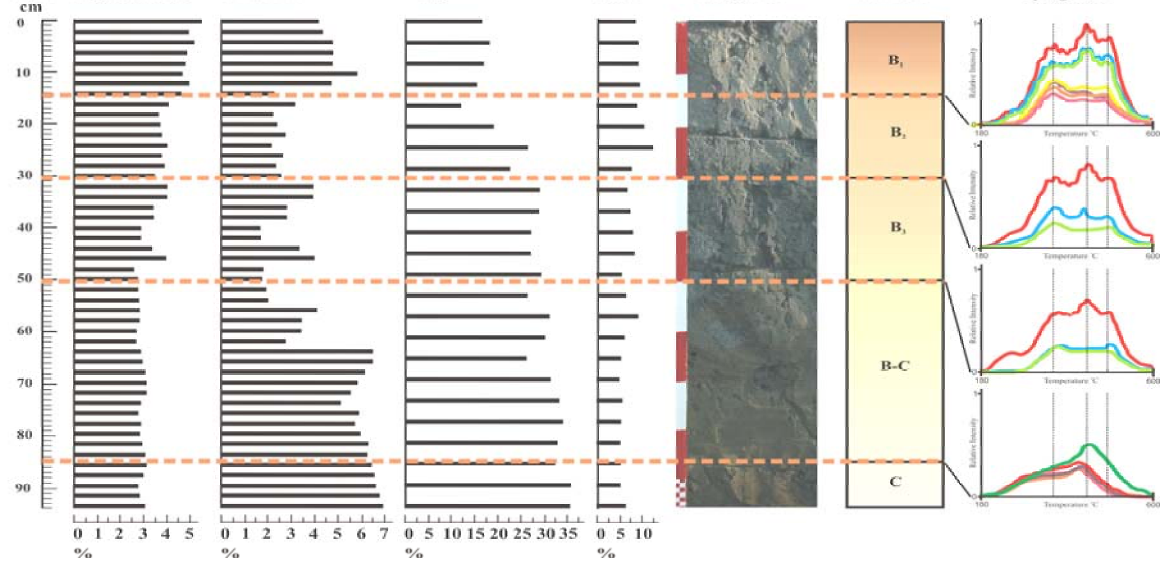

Figure 2. Profile of the monolith and the measured parameters

All measured parameters from RE Pyrolysis and pedological analysis were depicted on profile diagrams for evaluation purposes (Figure 2). The results of the analysis indicate an obvious mobilisation process, which worked downwards the profile, and leads to the formation of a clay accumulation zone within the profile. This shows strong hydromorphic effect in the soil. According to relationship between (a) stabile bio-macromolecules (F2) and immature geo-macromolecules (F3); (b) labile bio-macromolecules (F1) and refractory geo-macromolecules (F4); (c) relationship between components F1, F2, F3 and (d) F1+F2, F3 and F4 components three zones can be well separeted. Consequently the horizons prognosticated by pedological description are identifiable from RE details as well.

Every measured parameters (all measured and calculated values from Rock Eval pyrolysis and pedology routine) were fed into SPSS 11.0 programme. The Factors were composed of strong correlated parameters. As following step we depicted these ones versus depth (put back in the original soil profile). Factor 1 involves clay, S1, S2, T_{max} and organic matter (measured by Dean method); Factor 3 contains sand and HI values (Figure 3). We can separate three point set in this way, which correlate with the pedological details.

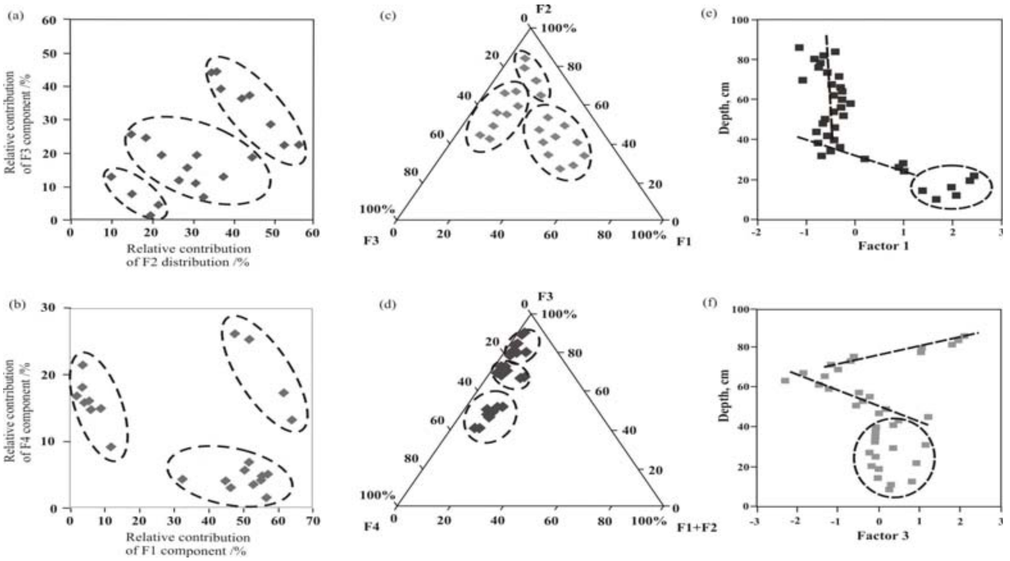

Figure 3. Functionalities of the four constituents (a), (b), (c), (d) and diagrams factors versus depth. (Ellipces do not represent confidence intervals, but are for guidance.)

We compared pedological details with the results of Rock-Eval analysis. Consequently we can state, that the soil formed in an environment in which the effect of cyclical fluctuating water could influent the soil development. This phenomenon suggests determination the paleosoil as Fluvisol. We established Rock-Eval pyrolysis is suitable to soil classification. We found, it is able to provide new details to explanation paleosoil horizons.However results varied between comparatively wide limits (6.1-29.5 mg/g), presence of nitrate was general; nitrate was detected in every examined tobacco product. One cigarette's average content was 10 mg nitrate. Concentrations of cigar and pipe tobaccos were similar to the cigarettes' results. The results are summarized in Figure 4.

5. CONCLUSIONS

Rock-Eval pirolysis proved to be suitable for efficient examination of soil organic matter and estimation the measurement of humification. Further advantages, slight sample need to measure (0.1 g), doesn't require preparation (if the sample is carbonate-free), fast measure (25 min.), and we can detect six parameters from one single measurement (S1, S2, TPI, TOC, Tmax, HI) which we can use perfectly in evaluations. We can escape the lengthy and many chemicals requiring laboratory separates.

Rock-Eval pyrolysis is useable new method for determination paleosoil type, supplements the routinish classical measurement techniques. The method gives us excess-informations compared to traditional organic matter measure. In the course of known type paleosoil pyrolysis can provide new details according to the former details. Rock-Eval pyrolysis is capable define parameters, which help determination of unknown paleosoil type and allow identify minor occurences within genetical horizons. Statistical evaluation of details assists the complex explanation of the measured values, accordingly determination of paleosoil type.

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