



## Full Length Article

## Spectral characterization and comparison of humic acids isolated from some European lignites



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## ABSTRACT

Humic acids isolated from seven lignite samples from six European coal basins were characterized using spectral methods and elemental analysis and compared with each other. X-ray photoelectron spectroscopy and fluorescence spectrometry are not commonly used for the investigation of lignite humic acids, although they may provide relevant information. Comparison of the examined lignite humic acids shows that they are very similar to each other in chemical nature regarding the at least degree of aromaticity, molecular weight, and the distribution of functional groups. Fluorophores of lignite humic acids lie within the A region with typical maxima centred in the range 255–265/460–510 nm. EEM spectra have the character of fingerprints for humic acids, and lignites (as the starting material). In this work, the capacity of lignite as a parent source of humic acids for agricultural applications is appreciated mainly on the base of extractability and ash content.

## 1. Introduction

Lignites are low-rank coals formed from original phytomass during peatification followed by coalification, and are considered as intermediate forms between peat and bituminous coal. Lignites are mainly used as fuel and for energy production, even though they have low calorific values and high amounts of water, oxygen, and ash. In this respect, the sorption of hazardous species [1], the production of small compounds (e.g. malonic acid, succinic acid) [2], and use in agricultural practice [3] may be regarded as more suitable ways of processing these immature coals.

Lignites represent heterogeneous systems composed of numerous components in various portions. For example, lipids represent a minor part ranging from 1 to 10 wt%, being extractable with non-polar solvents such as chloroform and hexane [5]. In contrast, a considerable proportion of lignite is composed of humic substances traditionally divided on the basis of their alkaline and acid solubility into three classes: humic acids, fulvic acids, and humin. Humic substances are naturally occurring molecules, ubiquitous not only in sediments (peat, coal, leonardite) but also in water and soil. Humic acids are insoluble under acidic conditions (pH 1–2), but become soluble and extractable in alkaline solutions. Lignites are the most abundant fossil fuel, which are rich in humic acids and can be regarded as their major source [4]. Lignite humic acids may be used effectively as natural fertilizer and soil conditioner to remediate soil structure and to improve plant growth [6–9]. The active and positive role of humic acids in soil is related to

their slow release of plant nutrients, cation exchange capacity, pH-buffering alkalinity, water-holding capacity, and interaction with metal ions and xenobiotic organic molecules [3,10]. For agricultural purposes, the chemical properties of lignite humic acids should be optimal, i.e. as similar as possible to the humic acids commonly present in soils. To improve the properties of these natural products, different treatments have been applied, so-called regeneration and modifications, using oxidizing agents (oxygen, nitric acid, hydrogen peroxide etc.) and different cross-linking reagents like formaldehyde [11–13]. Unfortunately, lignitic humic acids are the subject of less interest compared to humic acids originating from other sources. Lignite humic acids contain various functional groups (e.g. carboxylic, hydroxyl groups) and moieties (aliphatic chains and aromatic rings) which characterize their composition and properties [14]. They are characterized by higher carbon content, lower oxygen and nitrogen content, more aromatic moieties, and less carboxylic groups in comparison with humic acids from soil and peat [11,15,16]. The recognizable differences between soil, peat, and coal humic acids can mainly be related to varying degrees of maturity [16]. From a molecular standpoint, lignite humic acids are characterized by the presence of methylene and ethylene bridges between the aromatic rings [2]. Grasset et al. [17] showed that low rank coal humic acids contain intact lignin monomers of predominantly gymnosperm origin. In contrast to soil humic acids, lignite humic acids were shown to contain saturated long chain alkanic acids with a strong predominance of even numbered homologues [16].

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Elemental analysis and spectrometric methods including ultraviolet-visible (UV–Vis) and Fourier transform infrared (FTIR) spectrometry are often used in the characterization of coal humic acids. Advanced techniques such as fluorescence spectrometry and X-ray photoelectron spectroscopy (XPS) are applied to a lesser extent, even though they can provide a more coherent picture of this molecular system with coal provenance. Furthermore, the paucity of available experimental data in the literature makes comparison between lignite humic acids and humic acids of different origins difficult. Nuclear magnetic resonance (NMR) and pyrolysis–gas chromatography combined with mass spectroscopy (pyr–GC–MS) are very helpful techniques in investigating the structure of humic acids and their aromaticity [18,19]. The disadvantage of this approach is the lack of availability of such equipment.

The present study is focused on the characterization and mutual comparison of humic acids from different origin, i.e. seven lignite samples from various European basins. The analysis was based on a multiple-technique approach including traditional and commonly available methods (elemental analysis, FTIR, UV–Vis spectrometry) and advanced methods (fluorescence spectrometry, XPS). Of the various fluorescence spectrometry methods available, excitation-emission matrix spectroscopy (EEM) appears to be particularly useful for the investigation of different lignite humic acids, inasmuch as EEM spectra can be used as fingerprints.

## 2. Materials and methods

### 2.1. Sample preparation

Seven lignite samples from different coal basins in Central and Eastern Europe were selected for the extraction of humic acids. These basins included Balsha and Maritza East (Bulgaria), Dragačevo (Tijanje deposit) and Kostolac (Serbia), Konin (Poland), and the South Moravian Coalfield (the northern part of the Vienna basin in the Czech Republic). Two lignites from the Kazimierz (sample K1) and Lubstów (sample L2) mines belonging to the Konin basin were also subject to extraction; the sample codes (K1 and L2) correspond to the designation used in Fabiańska and Kurkiewicz [20] for these coals. Detailed characteristics of all the lignites, including their geochemical and petrographic descriptions, have been published elsewhere [20–24].

Humic acids were extracted from lignites using a modified procedure recommended by the International Humic Substances Society [25]. Briefly, the lignite samples were finely milled (to a grain size of under 0.2 mm) and demineralized with 0.1 M HCl in the ratio of 1:10 (sample:solution), and, after decalcification, the suspensions were washed with distilled water until almost neutral pH was achieved. All samples were shaken overnight with 0.1 M NaOH and 0.1 M pyrophosphate solution under N<sub>2</sub> in the ratio of 1:10 (sample:extractant). After centrifugation (4000 rpm, 30 min), humic acids were precipitated by acidification to pH < 2 with 6 M HCl, and further separated by centrifugation (4000 rpm, 20 min). Precipitated humic acids were treated with a mixture of 0.5 vol% HCl–HF for a period of 24 h and subsequently separated by centrifugation. The humic acids were purified and dialysed using a Spectrapore membrane (MWCO 3500) until free chloride ions were washed out, and finally freeze-dried. The samples were left to equilibrate in the ambient laboratory atmosphere at about 25 °C, which resulted in the final equilibrium moisture.

### 2.2. Sample characterization

#### 2.2.1. Elemental analysis

Elemental compositions of the humic acids were determined using a CHNS-O EA 3000 Elemental Analyzer. The % oxygen content was calculated by difference and the data obtained were corrected for moisture and ash content.

#### 2.2.2. UV–Vis spectrometry

UV–Vis spectra were obtained on a Hitachi U-3900H UV/Vis spectrophotometer by recording the absorption spectra between 200 nm and 900 nm. Samples were measured in a 10 mm quartz cuvette and with a phosphate buffer blank (NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>).

#### 2.2.3. FTIR spectrometry

FTIR spectra were obtained by means of a Diffuse Reflectance Infrared Fourier Transform (DRIFT) technique using a Nicolet iS50 spectrometer. Approximately 2 mg of powder was ground with 200 mg of KBr in an agate mortar and then transferred to the sample holder cup. The DRIFT accessory sample holder cup was filled with the mixture and the top was leveled off. All spectra were recorded over the range 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> and were the average of 128 scans.

#### 2.2.4. Fluorescence spectrometry

For fluorescence measurements, lignite humic acids were dissolved at a concentration of 10 mg L<sup>-1</sup> of organic carbon in phosphate buffer (NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>). All spectra were run on a Fluorolog fluorescence spectrophotometer with a scan speed of 600 nm min<sup>-1</sup>, using excitation and emission slit bandwidths of 5 nm. Emission spectra were collected in the ranges 330–600 nm and 390–600 nm with excitation wavelengths of 310 nm and 370 nm for the obtained biological fluorescence index (BIX) and fluorescence index (FI), respectively. The excitation-emission matrix (EEM) spectra were obtained by scanning the emission and excitation wavelengths over the range 250–600 nm, with the emission and excitation increment set at 5 nm. For the determined of Milori index [26] and humification index (HIX) or Zsolnay index [27], emission spectra were recorded over the range of 460–650 nm and 280–600 nm using excitation wavelengths of 400 nm and 254 nm, respectively. The sample cell with humic acid solution was kept at a temperature of 20 °C during each measurement. Primary and secondary inner filter effects were corrected. The fluorescence intensity values of samples (in counts per second, CPS) were corrected using the method devised by Lakowicz [28].

#### 2.2.5. XPS spectrometry

XPS spectra were measured with a Kratos AXIS Ultra DLD spectrometer using a monochromatic Al K $\alpha$  source operating at 150 W (10 mA, 15 kV). Milled samples were molded into a disc with a diameter of 10 mm. High resolution spectra were obtained using an analysis area of ~300  $\mu$ m  $\times$  700  $\mu$ m and 20 eV pass energy with a step size of 0.1 eV. The analyzer chamber pressure was less than 2.10<sup>-7</sup> Pa. The Kratos charge neutralizer system was used for all analyses. The spectra were corrected using the random hydrocarbon peak at 284.6 eV. Spectra were analyzed using CasaXPS software (version 2.3.15).

## 3. Results and discussion

### 3.1. Yields and elemental analysis

The yields and elemental analyses of lignite humic acids are summarized in Table 1. The yield of humic acids ranged from 3.0% to 11.4% depending on the type of lignite. The highest yields (11.4% and 11.1%) were obtained for humic acids isolated from South Moravian and K1 lignites. In contrast, the lowest yields (3.0% and 3.2%) were determined for humic acids extracted from Maritza East and Kostolac lignites. It is worth noting that yields depend on the selected methods of isolating and purifying humic acids, and therefore they reflect the degree of proportion of humic acids in lignite rather than the total content. Likewise, ash content of humic acids can depend both on the sample preparation procedure as well as on the origin of the source material. Extremely high ash contents were determined for humic acids originating from Kostolac and Balsha lignites. Lignites (e.g. Kostolac, Balsha) with high ash contents and low contents of humic acids appear

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