



The spectrometric characterization of lipids extracted from lignite samples from various coal basins



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ABSTRACT

Lipids were extracted from seven different lignite samples and subsequently characterized using spectrometric methods. Excitation–emission matrix (EEM) or total luminescence spectrometry was here used for the first time to study lipids extracted from lignites more extensively. Spectrometric characterization showed that lipids differ from each other depending on the origin of the lignite in which they occur. EEM spectra can be used as fingerprints not only for distinguishing between lipids but also lignites. Lipids contain fluorophores, which participate in the total fluorescence of lignites; some of these also participate in the fluorescence of humic substances. The typical maxima (260–275/370–440 nm) of EEM lipid spectra lie within the A' region, which can be ascribed to aromatic ring systems and steroids. Lipids from South Moravian lignite also contain maxima in the H (255/305 nm) and V (430/475 nm) regions, in contrast to other samples. The first could be related to single aromatic systems and substituents such as carboxyl and carbonyl and the latter is probably the result of intramolecular charge-transfer states.

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1. Introduction

Lignites are low-rank coals which are formed from original phytomass by peatification followed by coalification and are considered as intermediate forms between peat and bituminous coal. According to one model, coal may be considered a three-dimensional cross-linked macromolecular structure in which relatively lower molecular weight compounds are trapped. These small molecules have been defined as the mobile component in coals and are extractable using organic solvents (Iino, 2000). Another model assumes that coal consists only of coal molecules forming huge associates through non-covalent interactions. An extraction yield of more than 50% can be achieved by using a suitable solvent mixture including an additive for some bituminous coals. General consensus suggests that the structure of lignite is better described by the first of these models (often called a two-phase model) (Iino, 2000). In non-energy applications, lignites have been studied mainly as raw materials for the sorption of toxic elements (Doskočil and Pekař, 2012), for the production of small compounds (Doskočil et al., 2014), and for agricultural purposes (Chassapis et al., 2009; Doskočil et al., 2015).

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A considerable part of lignite is formed by humic substances (traditionally divided into humic acid, fulvic acid, and humin), of which humic acids predominate (Doskočil and Pekař, 2012). Humic substances are naturally occurring biomolecules ubiquitous, not only in sediments (peat, coal, Leonardite) but also in water and soil, and are the subject of intense research.

In contrast to humic substances, lipids represent only a minor component of coals. They can be defined as organic substances that are effectively insoluble in water but extractable with non-polar solvents such as chloroform, hexane, benzene, and toluene. Clearly, this broad definition encompasses a wide variety of compound classes (such as fatty acids and their derivatives, waxes, terpenes, steroids etc.). It should be noted that geochemists sometimes use the term bitumen as a synonym for lipid (Lesueur, 2009). Lipids or bitumens are commonly extracted from coals by a variety of different methods including Soxhlet extraction (Papanicolaou et al., 2000), accelerated solvent extraction (Životić et al., 2008), and extraction in an ultrasonic bath (Fabiánska, 2004), using a solvent or solvent mixtures such as dichloromethane, chloroform, isohexane/acetone, and dichloromethane/ethanol. Most coals commonly have lipid contents ranging from 2 to 10 wt.% of the coal (Papanicolaou et al., 2000; Stefanova et al., 2011; Havelcová et al., 2012; Fabiánska and Kurkiewicz, 2013). The extracts comprise a complex mixture of nonpolar compounds with potential contributions from compounds produced by living organisms as

well as the degradation products of those compounds. The characterization of these extracts on the molecular level by means of gas chromatography coupled to mass spectrometry largely reveals the presence of *n*-alkanes, fatty acids, sesquiterpenoids, diterpenoids, non-hopanoid triterpenoids, hopanoids, and steroids (Stefanova et al., 2002, 2011; Fabiańska, 2004; Životić et al., 2008; Havelcová et al., 2012; Stojanović and Životić, 2013).

Ultraviolet–visible (UV–Vis) and Fourier transform infrared (FTIR) spectrometry are the most frequently used tools in spectroscopic characterization and can be very useful in the study of organic matter (Fuentes et al., 2006). A similarly reliable technique is fluorescence spectrometry, which provides important information on the structural nature of organic substances (e.g. functional groups, polycondensation, aromaticity) based on variances in the positions, shifts and intensities of fluorescence peaks. In addition, it is a simple, rapid, sensitive and non-destructive method requiring only a small volume of sample at a low concentration. In the literature, several fluorescence techniques have been applied to the study of coal extracts – from conventional emission spectrometry (emission scan fluorescence) to more recent and comprehensive methods such as synchronous fluorescence spectrometry and total luminescence spectrometry (or excitation–emission matrix, EEM) (von der Dick and Kalkreuth, 1986; Mille et al., 1988; Kashimura et al., 2004). Of these fluorescence techniques, synchronous fluorescence spectrometry is probably the most widely used in the study of extracts of raw coals and modified coals (preheating, oxidation, demineralization etc.), coal liquefaction, and tar (von der Dick and Kalkreuth, 1986; Mille et al., 1988; Kister and Pieri, 1996; Kashimura et al., 2004). This technique has been successfully applied in the determination of polyaromatic hydrocarbon families or certain polyaromatic hydrocarbons (Kister and Pieri, 1996; Matuszewska and Czaja, 1996).

In their study of extracts, Mille et al. (1988) reported that it is possible to clearly elucidate the differences among coals of different ranks using fluorescence spectrometry. However, it is not clear whether fluorescence spectrometry can also be used to fingerprint extracts (such as lipids) from various lignites, due to the paucity of available experimental data. The utilization of total luminescence spectrometry for the analysis of coal extracts is of marginal interest (von der Dick and Kalkreuth, 1986), in spite of the fact that EEM provides a global and complete view of fluorescence spectra from substances in the form of three-dimensional contour plots of fluorescence intensity as a function of excitation and emission wavelengths (Rodríguez et al., 2014).

The goal of this work was to extract and characterize lipids from different lignites by means of rapid and relatively simple spectroscopic methods. In the present work, excitation–emission matrix (EEM) spectrometry was used for the first time to extensively study lipids extracted from lignites and to show that this approach is a valuable source of new knowledge relating not only to lipids but also to lignites and their major components (i.e. humic acids).

2. Materials and methods

Seven lignite samples from different coal basins were selected for the extraction of lipids. The selected basins were Chucurovo and Maritza East (Bulgaria), Krepoljin 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 (2013). Detailed characteristics of all the lignites, including their geochemical and petrographic descriptions, have been published elsewhere (Stefanova et al., 1995, 2002, 2005; Havelcová et al., 2012; Fabiańska and Kurkiewicz, 2013; Stojanović and Životić, 2013; Doskočil et al., 2015).

The lignite samples were finely milled (to a grain size of under 0.2 mm) and ca. 40 g were then placed in a cellulose thimble and Soxhlet extracted for 36 h using trichloromethane as a solvent. The lipid fractions isolated from the lignites were collected and concentrated by a rotary evaporator and the resulting dark brown extracts were dried in a desiccator with Na₂SO₄.

Elemental compositions of the extracted lipid fractions 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.

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 were blanked against chloroform.

FTIR spectra from lipids were obtained in Attenuated Total Reflection (ATR) mode using a Nicolet iS50 spectrometer. Samples were dissolved in chloroform at a concentration of ca. 120 mg/l. All spectra were recorded over the range 4000–400 cm⁻¹ at 4 cm⁻¹ resolutions and were the averages of 128 scans. The spectrum for air on a clean dry ATR diamond crystal was used as the background for the infrared measurements. Thermo Scientific Omnic spectroscopy software was used to obtain the spectra and Advanced ATR algorithm corrections were applied to band intensity distortion, peak shifts, and non-polarization effects.

For fluorescence measurements, lipids were dissolved in chloroform at a concentration of 75 mg/l. All spectra were performed on a Fluorolog fluorescence spectrophotometer with a scan speed of 600 nm/min, using excitation and emission slit bandwidths of 5 nm. 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. The sample cell with lipid 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 (2006).

Table 1

Lipid yields, results of elemental analysis, and calculated ratios.

| Origin of lipid | Lipid yield (wt.%) | Elemental analysis (at.%) | | | | Atomic ratios | | FTIR intensity ratios | |
|------------------|--------------------|---------------------------|------|-------------------|------|---------------|------|---|---|
| | | H | C | O ^{diff} | N | H/C | O/C | I _{CH₂/CH₃} ^a | I _{Ar} /I _{Al} ^b |
| SML ^c | 2.1 | 58.4 | 37.0 | 4.6 | 0.00 | 1.58 | 0.12 | 2.11 | 0.12 |
| Chucurovo | 9.0 | 54.0 | 39.3 | 6.8 | 0.00 | 1.37 | 0.17 | 1.47 | 0.55 |
| Maritza East | 7.8 | 56.7 | 35.1 | 8.1 | 0.04 | 1.62 | 0.23 | 2.52 | 0.10 |
| Kostolac | 1.0 | 62.1 | 33.7 | 4.1 | 0.03 | 1.84 | 0.12 | 3.06 | 0.09 |
| Krepoljin | 3.4 | 54.7 | 37.6 | 7.8 | 0.00 | 1.46 | 0.21 | 1.60 | 0.20 |
| K1 | 2.3 | 62.9 | 33.1 | 4.0 | 0.01 | 1.90 | 0.12 | 5.19 | 0.05 |
| L2 | 3.8 | 61.1 | 35.2 | 3.7 | 0.01 | 1.74 | 0.11 | 3.83 | 0.06 |

^a FTIR ratio calculated as ratio of intensity at 2918 cm⁻¹ to intensity at 2955 cm⁻¹.

^b FTIR ratio calculated as ratio of intensity at 1510 cm⁻¹ to intensity at 2918 cm⁻¹.

^c SML, the abbreviation for South Moravian lignite.

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