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Subtractive-FTIR spectroscopy to characterize organic matter in lignite samples from different depths

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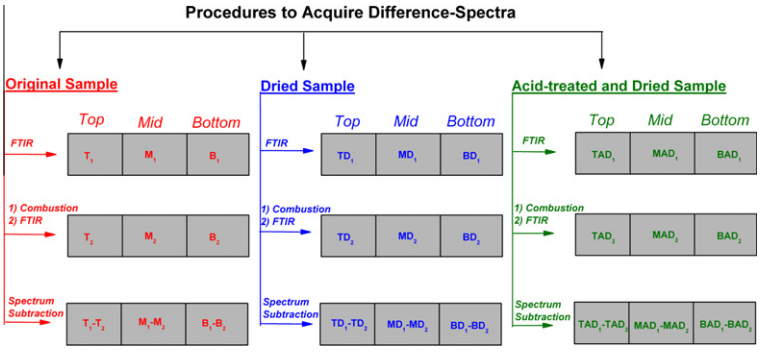
HIGHLIGHTS

- We propose a simple and virtually solvent-free methodology based on spectrum-subtraction.
- Representative FTIR spectra were acquired through combustion and spectrum-subtraction procedures.
- The methodology made it possible to evaluate FTIR spectra by subtracting bands related with inorganic matters.
- FTIR spectra were found to be changed depending on the depth.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic matter present in lignite samples collected from different depths (i.e. *top*, *mid* and *bottom*) of lignite source, Ilgın, Konya province, was examined by using subtractive-FTIR-ATR spectroscopy. FTIR spectra were recorded on (i) original samples, (ii) the samples dried at 105 °C and (iii) the samples acid-treated and dried. After a combustion process performed for each sample at 650 °C for 15 min, the spectra of samples were recorded and subtracted from the spectra of untreated samples. Hence, a software-based subtraction made it possible to acquire a representative spectra related with organic matter. As the contribution of the bands related with inorganic constituents in lignite samples were eliminated after spectrum-subtraction procedure, difference-spectra led analyzing the spectra related with organic matter in lignite samples, reasonably. Furthermore, the bands related with acidic functional groups, aromatic and aliphatic structures were analyzed on the basis of difference-spectra, easily. From the difference-spectra it was shown that an acid-treatment process under mild conditions caused shift in some specific bands related with carbonyl groups of carboxyls so that the band at around 1710 cm^{-1} arisen, while the intensity of the band at around 1420 cm^{-1} was diminished. Through the acid-treatment process, acidic groups in lignite samples from different depths were thought to be turned into similar forms by protonation and/or stripping of metal ions originally bonded. Difference-spectra acquired for acid-treated samples made it possible to evaluate the form of carboxylic acid groups present in the studied samples under specific environmental conditions. Hence, a facile and environmentally-friendly methodology was used to analyze organic matter in lignite by using FTIR spectra, and valuable information was acquired about the aliphatic, aromatic and acidic character of the studied lignite samples collected from different depths. The proposed methodology seems to be promising in acquiring approximate representative spectra for lignite organic matter by using little or no chemicals.

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1. Introduction

Lignite is a young coal in the intermediate stage of the transformation from wood to coal, and oxygen-containing functional groups present in the structure abundantly [1]. Despite its low calorific value, it is mainly used as a fuel source. In addition, lignite can be used as a source of organic matter to improve soil productivity, owing to humic substances present in its structure [2]. So, lignite should not be considered as a fuel only but also as a raw material for production of some chemicals [3]. In all cases, it is important to know characteristics of organic matter present in lignite. Therefore, it is necessary to isolate organic matters by using solvent extraction before the analysis [4]. However, it is, usually, difficult to extract all the organic matters via a uni-type solvent system. Usually, different solvent systems, which yield various fractions of organic matters present in lignite, are used for this purpose. Such an extraction process is time-consuming, labor-intensive and cost-effective and requires high volume of chemicals. For this reason, alternative, environmentally-friendly and practical approaches are needed to get information about organic matter present in lignite.

Fourier Transformed Infrared (FTIR) spectroscopy has an increasing popularity in routine analysis of solid, liquid, and gaseous samples, because of its simplicity and flexibility as well as short analysis time required. In characterization of organic matter present in lignite, FTIR has been applied, successfully [3]. However, bands arising from inorganic matter in lignite, sometimes, shield the bands related with organic matter. Hence, in a FTIR analysis to be directly performed on raw lignite, it is usually difficult to acquire the bands related with organic matter purely. Also, the content of inorganic matter present in lignite, and accordingly corresponding FTIR spectra, may vary from source to source, and this complicates the analysis of FTIR spectra directly recorded on raw lignite sources.

Together with technological improvements in their equipments, powerful software packages, which are able to perform many graphical analyses and processes, have been supplied in today's FTIR systems. Hence, different FTIR spectra can easily be subtracted from each other, and the techniques based on this feature are sometimes called *subtractive-FTIR*. The technique has been applied to forensic analysis of soil organic matter [5] and paint samples [6], and analysis of proteins in aqueous solution [7]. The method proposed by Cox et al. [5] applies a subtractive-FTIR technique for forensic analysis of soil organic matter. In the method, soil to be analyzed is subjected to a thermal treatment by which organic matter present in the soil is combusted, leaving the inorganic matter. By subtracting the FTIR spectrum recorded after combustion process from that of untreated soil, it could be possible to acquire so-called FTIR spectrum related with organic matter present in soil. The method is simple and promising in routine analysis of organic matter in different organomineral samples, and it can be adapted to lignite analysis as well. In this way, a good representative FTIR spectrum for organic matter in lignite can be acquired without a supplementary solvent extraction step used to isolate organic matter from inorganic matter in lignite. This point of view can be useful for rapid and facile characterization of organic matter in lignite, comparison of different lignite sources and their quality, etc. FTIR spectrum of organic matter can be further fulfilled to estimate the quality of lignite under consideration as a fuel and/or co-fertilizer. The studies dealing with characterization of organic matter in lignite by using different techniques have a lack of information on the applicability of subtractive-FTIR spectroscopy technique in characterization of organic matter present in lignite samples collected from different depths. Hence, the present study is believed to be useful to point out the efficiency of the technique in lignite-organic matter analyses. By comparing the difference-spectra, differentiations in macromolecular structure of organic matter present in different depths of the lignite source were discussed. Thus, the study criticizes effect of drying and acid-treatment processes on the difference-spectra, and thus proposes a practical guide to evaluate characteristics of organic matter in lignite samples collected from different depths.

2. Experimental

2.1. Chemicals

Little or no chemicals were used throughout the experiments. Lignite samples were treated with 1.0 $molL^{-1}$ HCl solution which was prepared from stock HCl (Merck). Double-distilled water was used in the experiments.

2.2. Lignite samples

Lignite samples were kindly supplied from GLİ-Ilgın (Konya province, Turkey) Lignite Management of General Directorate of Turkish Coals, Turkey. The samples collected from different depths were named as *top* (collected from ~34 ± 2 m depth), *mid* (collected from 40 ± 2 m depth) and *bottom* (collected from 46 ± 2 m depth) samples. Lignite samples grounded in a porcelain mortar were sieved from 63 μm sieve (−63 μm), and used throughout the experiments. The samples were combusted in a temperature controlled oven using porcelain crucibles.

2.3. Instruments

FTIR spectra of grounded lignite samples (−63 μm) were recorded on a Perkin–Elmer Spectrum BX-II instrument with an ATR (*Attenuated Total Reflectance*) accessory at a resolution of 4 cm^{-1}. Spectral analyses and subtraction processes were performed by using the software Spectrum® (Version 6.3.5.0176). Thermogravimetric analyses were performed by using SII Exstar 6000 TG/DTA 6300 model instrument within the temperature range 30–1000 °C on platinum pans with 10 °C min^{-1} increments under dry air atmosphere.

2.4. Method

To understand general character of the FTIR spectra of organic matter in the studied lignite samples, different methodologies were followed. Each methodology includes a combustion process where the lignite samples are subjected to a thermal treatment at 650 ± 5 °C for 15 min [5]. The difference in the methodologies is the previous form of the lignite samples before the combustion process:

(i) Original samples (without a drying process),
(ii) Samples dried at 105 °C for 2 h, and
(iii) Samples treated with 1.0 $molL^{-1}$ HCl for 1 h and afterwards dried at 105 °C for 2 h.

Spectra recorded after combustion process were subtracted from their respective original spectra. For example, the FTIR spectrum of original sample collected from the top region of the lignite source was recorded, and then the spectrum of the same sample subjected to combustion process was recorded. By subtracting the last spectrum from the first one, representative spectrum related with organic matter in top lignite sample was acquired. In the second part of the experiments, lignite samples were dried