Characterization of humic acid from leonardite coal: an integrated study of PY-GC-MS, XPS and XANES techniques

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Abstract

We studied the humic-acid fraction isolated from a Spanish leonardite coal (Torrelapaja, Cretaceous basin belonging to the Utrillas facies) using a suite of chromatographic and spectroscopic techniques to characterize the structure of the carbon skeleton and the nature of the sulfur-containing compounds. In particular, analytical pyrolysis coupled to gas chromatography-mass spectrometry was used to gain detailed molecular information on the organic structures. Pyrolysis in the presence of a methylating agent (tetramethyl-ammonium hydroxide, TMAH) was used to characterize polar moieties. We employed non-destructive techniques, XANES and XPS, to investigate the composition of the sulfur functionalities (such as sulfide, polysulfide, thiophene, sulfoxide, sulfonate and sulfate). The combination of these different approaches allows a more complete understanding of the organic sulfur structures in the leonardite coal. In agreement with previous studies, our results show that oxidized sulfur functionalities, such as sulfonate and sulfate, represent the major forms of sulfur in leonardite coal. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The organic matter in coals contains significant amounts of oxygen, sulfur and nitrogen heteroatoms incorporated in various functionalities (e.g. carboxylic group), which vary in abundance depending on the specific conditions of the coal-beds. The characterization of the humic acid fractions from low-rank coals was shown to be useful for obtaining information about the structure and reactivity of the macromolecular organic matter [1,2]. Leonardite is a highly oxidized coal found in superficial strata related to oxidized environments. There has been much interest in understanding the structure of organic moieties in such coals because of the potential role of the oxidized functionalities to bind many heavy metallic ions through complexation. This binding ability could be exploited to eliminate inorganic pollutants and organic microcontaminants from waters or gases.

Most past studies on structural characterization of humic matter employed destructive (e.g. pyrolysis, chemical degradation) as well as non-destructive approaches (e.g. NMR, ESR, IR and X-ray absorption spectroscopy) [3–6]. The destructive pyrolysis techniques have proven valuable for obtaining detailed molecular information; the thermal degradative products can be related to the original molecular moieties in the macromolecular organic matter. The pyrolysis of polar macromolecular materials is well known to produce volatile polar products, only some of which can be chromatographed; very polar products remain attached to the column, undetected and unquantified. Pyrolysis with tetramethyl-ammonium hydroxide (TMAH) derivatizes polar compounds to less polar products, which are more amenable to chromatographic separation. This procedure avoids decarboxylation and produces methyl esters of carboxylic acids and methyl ethers of hydroxyl groups [7,8]. The technique previously was used to analyze humic acids, greatly enhancing product yields and producing some products not previously observed by conventional pyrolysis [7,9–11]. The mechanism of TMAH-induced pyrolysis has been described in detail [7,8].

In this paper, we also use non-destructive spectroscopic methods X-ray Absorption Near-Edge Structure (XANES) and X-ray Photoelectron Spectroscopy (XPS) to characterize sulfur species in leonardite coal, complementing the structural details obtained by Py-GC-MS (both with and without TMAH). XANES was particularly successful in identifying sulfur species [12–15] it is sensitive to the electronic structure, oxidation state and the geometry of the neighboring atoms, and provides characteristic fingerprint information. It was shown that XANES spectroscopy is better than other common techniques (e.g. chromatography) for sulfur speciation in sediments because (a) it provides simultaneous qualitative and

quantitative information on all the sulfur forms present (sulfide, sulfoxide, sulfonate and sulfate) and (b) has the ability to analyze whole samples [12,13]. In recent years, several researchers used XANES and XPS to identify and quantify organic sulfur in coals and various other organic materials [14–17]. XPS is a surface-restricted technique that provides quantitative information on forms of sulfur in the outermost 1–5 nm of a solid. The information from XPS is complementary to that of XANES, also identifying chemical forms of sulfur in coals [14].

2. Material and methods

2.1. Description and extraction of selected samples

The geological Cretaceous formations of Torrelapaja Basin (Aragon, Spain) belonging to the Utrillas Facies contain leonardite. The Utrillas Facies are part of the Maestrazgo Basin located between the Iberian mountain chain and the outer sector of the Catalan Coastal Range in NE Spain. Lignites were deposited during middle Albian (Lower Cretaceous, 105 Ma) in the proximity of a delta estuary [18]. They have a total sulfur content of 4.6%. The humic-acid fraction of leonardite was extracted with NaOH according to the method of del Río and Hatcher [19]. The humic acid content was 79%. The organic matter in humic substances was characterized by elemental composition (47.8% C, 3.0% H, 0.8% N, 2.4% S and 38.1% O). Like their parent coals, the O and S content of the humic acids from Torrelapaja leonardite is relatively high.

2.2. Curie-point flash-pyrolysis-gas chromatography-mass spectrometry

The pyrolysis was performed with a Varian Saturn 2000 GC-MS, using a 30 m $\times$ 0.25 mm DB-5 column (film thickness 0.25 μ m), coupled to a Curie-point pyrolyzer (Horizon Instruments Ltd.). Approximately 100 μ g of a finely divided sample was deposited on a ferromagnetic wire, then inserted into the glass liner and immediately placed in the pyrolyser. The pyrolysis was carried out at 610°C. The temperature of the chromatograph oven was programmed to rise from 40°C (1 min) to 300°C at a rate of 6°C min⁻¹; the final temperature was held for 20 min. The injector, equipped with a liquid carbon dioxide cryogenic unit, similarly was programmed from -30°C (1 min) to 300°C at 200°C min⁻¹, while the GC-MS interface was kept at 300°C. The compounds were identified by comparing the mass spectra (obtained at 70 eV) with those of the Wiley and NIST computer libraries and by retention times given in the literature [20].

For the pyrolysis-methylation, ~100 μ g of a sample in finely divided form was deposited on a ferromagnetic wire and mixed with ~0.5 μ l TMAH (25% w/w aqueous solution). The wire then was inserted into the glass liner, which was subsequently placed in the pyrolyser. Pyrolysis was carried out as described above.

2.3. X-ray absorption near edge structure

XANES spectra were collected using a Lytle fluorescence detector at X-19A beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The X-ray beam was diffracted by a double-crystal Si (111) monochromator which passes a narrow energy band to the sample. The monochromator was detuned by $\sim 70\%$. The sample chamber was continuously flushed with He to prevent the X-ray beam attenuation by air. Vairavamurthy et al. [21] have described details of the beam-line setup. The spectrum was recorded so that the scanning procedure yielded enough pre-edge and post-edge data for a precise background-signal correction. Sulfate was used for calibration using 2483.1 eV for the peak position.

The data were processed using the Origin program (Microcal). Typically, a spectrum was deconvoluted into a series of Gaussian peaks and an arctangent function that represents the transition of the photoelectron to the continuum. The peak position was used to indicate the form of sulfur. The relative peak areas gave quantitative information on the different types of sulfur [22].

2.4. X-ray photoelectron spectroscopy

The XPS data were obtained on a FISON ESCALAB 200R system equipped with an hemispheric detector using an X-ray source of MgK with 120 W. The spectrometer was run at an analyzer pass energy of 10 eV. A correction for binding energy was made to account for sample charging based on the C1s peak at 284.9 eV. The S2p peak was curve resolved using a mixed Lorentzian-Gaussian line shape. Peak assignments are based on the binding energy positions measured for sulfur containing compounds. The model compounds were the following: polyphenylensulfide, benzodiphenylensulfide (a model for thiophene) calcium sulfate and a sulfonate compound [23].

2.5. Results and discussion

Figs. 1 and 2 show the results of the pyrolysis (both in the absence and presence of TMAH) of the humic acids (HAs) isolated from the leonardite. Conventional pyrolysis of the HAs produced only small quantities of volatile products. As shown in Fig. 1(A), a large peak of sulfur dioxide together with sulfur monoxide and carbon dioxide were released with low amounts of aromatic compounds (benzene, toluene, phenol and naphthalene). Organosulfur compounds (thiophene, methylthiophene, benzothiophene) were also identified as free products in HA by conventional pyrolysis suggesting that sulfur might be incorporated into the HA structure in the early stages of coalification. This finding agrees with that of others who identified sulfur compounds in HA isolated from peat and lignite [24]. In Fig. 1(B), a series of *n*-alkanes ranging from C₈ up to C₃₀ also were released albeit in lower amounts when compared with aromatic compounds.

Fig. 1. Partial chromatograms (A–B) of the thermal degradative products obtained after pyrolysis of the Spanish leonardite coal in the absence of TMAH. In the chromatogram (A), the letters indicate the following: B, benzene; TP, thiophene; TO, toluene; MT, methylthiophene; F, phenol; N, naphthalene; BT, benzothiophene. Arabic numbers in chromatogram B indicate the number of carbons in the *n*-alkanes.

Pyrolysis in the presence of TMAH produced a markedly different pattern. High proportions of long-chain fatty acid methyl esters were released, as well as phenolic derivatives and aromatic acid methyl esters. Table 1 lists the identities of some of the major compounds.

These compounds are thought to represent structural components of the humic macromolecule, as suggested by several authors [26]. The extent of the presence of high aromatic and aliphatic acids in the structure of leonardite HA, measured by pyrolysis, only become apparent after methylated protection of the carboxyl and phenolic groups. Taking these data into account, in agreement with other authors [24,26] it is apparent that a structural model for humic substances based on only conventional pyrolysis would be incomplete. The aliphatic acids released after pyrolysis in the presence of TMAH consisted mainly of C_{10} – C_{26} monocarboxylic acids (Fig. 2). The bimodal distribution of fatty acids, with strong even over odd predominance and maxima at C_{16} and C_{26} , reflects the contribution of the waxes of higher plants. The aliphatic acids may be chemically bound to the matrix in a form similar to that suggested by Schnitzer and Neyroud [25].

Fig. 2. Total ion chromatogram of thermal degradation products obtained after pyrolysis of the humic acid fraction from leonardite, in the presence of TMAH. The peaks are identified in Table 1. Fatty acids identified as methyl esters are labelled as C_n where n indicates the number of carbons of the chain.

Different phenolic derivatives with lignin-related structures also were released during TMAH pyrolysis of leonardite HA, including benzenecarboxylic acids with p-coumaryl, guaiacyl skeletons. Specific compounds (2) 4-methoxybenzenecarboxylic acid methyl ester and (5) 3,4-dimethoxybenzenecarboxylic acid methyl ester (Fig. 2) and benzenepropenoic acid methyl ester (11) were detected here, but not from conventional pyrolysis of HA fractions because of decarboxylation reactions (Fig. 1).

Peat accumulations require anaerobic conditions to preserve enough organic matter for coal formation. Under such conditions, the lignin in peat HA probably remains relatively unaltered. The release, by pyrolysis-methylation, of high amounts of methoxylated benzenecarboxylic acids from the leonardite HA suggests that the lignin moiety is oxidized upon coalification. The locations of the carboxyl and carbonyl groups in the lignin-derived products (Table 1) indicate that such oxidative alteration affects the 3-carbon side-chain of the lignin. The presence of carbonyl and carboxyl groups at the α -carbon of lignin monomeric units, previously described in the structural model for low rank coals proposed by Hatcher et al. [27], is solely derived from the oxidation of lignin. Benzenepropionic acid with a carboxyl group located at the γ carbon previously was shown to be produced in the

Table 1

Identification and relative abundance of the compounds released after pyrolysis-methylation (TMAH) of leonardite humic acids where +, ++, +++ indicate low, medium and high relative abundances, respectively

Number	Compound	Major (<i>m/z</i>) ^a	Abundance
1	3-methoxybenzenecarboxylic acid, methyl ester ^b	135, 166	++
2	4-methoxybenzenecarboxylic acid, methyl ester ^b	135, 166	++
3	1,2-benzenedicarboxylic acid, dimethyl ester ^b	194, 163	++
4	1,3-benzenedicarboxylic acid, dimethyl ester ^b	194, 163	+++
5	3,4-dimethoxybenzoic acid, methyl ester	165, 196	+
6	3-methoxybenzene-1,2-dicarboxylic acid, dimethyl ester ^b	193, 224	++
7	4-methoxybenzene-1,3-dicarboxylic acid, dimethyl ester ^b	193, 224	++
8	3,4,5-trimethoxybenzenemethanol, methyl ether	212, 181	+
9	1,2,4-benzenetricarboxylic acid, trimethyl ester ^b	221, 252	+
10	1,3,5-benzenetricarboxylic acid, trimethyl ester ^b	221, 252	+
11	3-(3,4-dimethoxyphenyl)-2-propenoic acid, methyl ester	191, 222	+
12	Benzenetricarboxylic acid, trimethyl ester	221, 252	++
13	5-methoxybenzene-1,3,5-tricarboxylic acid, trimethyl ester ^b	251, 282	+
14	1,2,3,4-benzenetetracarboxylic acid, tetramethyl ester ^b	279, 310	+
15	1,2,4,5-benzenetetracarboxylic acid, tetramethyl ester ^b	279, 310	+

^a Major *m/z* means major fragment ions in 70 eV mass spectra.

^b The positional isomers were tentatively assigned according to the relative retention times given by Schnitzer and Skinner [20].

early stage of coalification and with increasing coalification is subsequently oxidized and finally disappears [28].

We detected significant amounts of organic sulfur with both XPS and XANES spectroscopies. The XPS results indicate that the S in leonardite exists as 27% organosulfides and 73% exists as a sum of sulfoxide, sulfate and sulfonate sulfur (Fig. 3).

Similarly, significant values, 40.9% of sulfate and 23.2% of sulfonate were quantified by XANES. In an earlier study, sulfonates were shown to be present in humic acids isolated from leonardite by the Electronic Paramagnetic Resonance (EPR) technique [29]. The sulfate detected here in the leonardite coal by the XANES method probably represents ester-bonded sulfate and not the sulfate ion. Since, from 25 to 93% of the organic S in soils from various sampling depths were previously shown to be in the ester-bonded form [30]. Also, it has been independently shown that the humic materials extracted from soils contain significant amounts of ester-bonded sulfate and sulfonates [13].

The reduced and partially oxidized sulfur functionalities in leonardite quantified from XANES spectrum (Fig. 4) were 7.1% polysulfidic sulfur, 4.0% elemental sulfur, 20.1% thiophenic sulfur and 4.7% sulfoxide.

Because of the close juxtaposition of the XANES features for pyrite and reduced sulfur species, it is sometimes difficult to quantify pyrite from a sample's spectrum. In this study, although SEM-EDX suggested the presence of pyrite in leonardite,

Fig. 3. XPS S-2p spectrum of leonardite coal with binding energy (BE) given in eV.

Fig. 4. Deconvolution of the XANES spectrum into several Gaussian and arctangent peaks in order to obtain the composition of sulfur functionalities in leonardite.

the XANES analysis did not give clear evidence for it. It is possible that the XANES deconvolution significantly underestimated the proportion of pyrite and overestimated the proportion of organic sulfur [31]. Consistent with the high oxidation level of leonardite, a significant fraction of pyrite may have also become oxidized to sulfate and elemental sulfur.

3. Conclusions

Pyrolysis provides information on thiophenic sulfur functionalities in the humic acid structure of leonardite by detecting thiophene, methylthiophene and benzothiophene products. In contrast, Py-TMAH supplies data on oxygen functionalities, such as benzenecarboxylic moieties and phenol derivatives possibly from lignin sources, that are not detected by conventional pyrolysis. Whilst pyrolysis and pyrolysis-TMAH are powerful methods with which to study the chemical structure of humic acids from leonardite, they cannot differentiate among sulfur functionalities present in leonardite. To this end, XANES and XPS analysis can be used to qualify and quantify the composition of sulfur functionalities, such as sulfidic sulfur, as well as oxidized sulfur functions in leonardite. The XANES technique provides unambiguous information on the presence of sulfoxide, sulfonate and sulfate. The predominance of the oxidized forms of sulfur supports the view that leonardite coal is highly oxidized in nature.

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