A study of sulfur functionalities in fossil fuels using destructive- (ASTM and Py–GC–MS) and non-destructive- (SEM–EDX, XANES and XPS) techniques[☆]

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Abstract

A set of Spanish coals and oil shales were studied using destructive and non-destructive techniques to identify the functionalities of the sulfur compounds. The selected samples included organic-sulfur-rich Spanish lignites mined in the Mequinenza, Utrillas and Calaf basins; calcareous source-rocks from Organyà and sulfur-rich oil shales from Ribesalbes. Using analytical pyrolysis coupled to gas chromatography–mass spectrometry, we estimated the ratio S_{org}/C in these coals and oil shales, and compared them with those obtained by the ASTM method D2492. Also, a scanning electron microscope (SEM) coupled to an energy-dispersive X-ray spectrometer (EDX) allowed the direct determination of organic sulfur content in coals. Two major non-destructive techniques, XANES and XPS, were used to investigate sulfur functionalities, such as pyritic, sulfidic, thiophenic, sulfoxide, sulfone, sulfonate and sulfate forms. The study shows that sulfur characterization in coal is not without difficulties and no method is exempt from problems and the introduction of possible artifacts. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Sulfur is ubiquitously present in fossil fuels but amounts vary from traces to more than 10% and it is bound in a variety of chemical forms. The problem of acid rain caused by the atmospheric release of sulfur dioxide from the combustion of sulfur in fossil fuels is a major environmental concern. Hence, the sulfur content in fossil fuels must be reduced to acceptable levels, particularly in high sulfur crudes and coals. Removing sulfur economically from such fuels raises serious technological challenges and economic burdens. A fuller understanding of the structures of sulfur-containing compounds present in fossil fuels, their thermal stability and reactivity is important for improving the available processes for removing sulfur or for devising new schemes.

Sulfur in fossil fuels is present in both inorganic and organic forms, with the latter mostly structurally integrated in the macromolecular organic matrix of the fuels. Thus, the organic forms are usually difficult to characterize. Often, a combination of several methods was used for determining organic sulfur, including the ASTM standard test method D2492 and Py–GC–MS. One problem in using the standard ASTM method is that the content of the organic sulfur form is determined by difference using wet-chemistry techniques, and, as a result, the value is subject to accumulated errors in estimating sulfate- and pyrite-sulfur [1]. Furthermore, some sulfur moieties that escape acid attack due to encapsulation within organic matrix may not be accounted. Py–GC–MS, on the other hand, provided information at the molecular level, particularly the presence of thiophenic forms [2,3]. Scanning electron microscopy (SEM) coupled to energy-dispersive X-ray (EDX) analysis, a conventional technique used earlier for studying coal, allows quantification of organic sulfur and its distribution by focusing on small areas of the sample free of mineral matter [4]. A major

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limitation of this method is that it cannot give specific structural information about organic sulfur functionalities that may be very important for processing coal.

X-ray absorption near-edge spectroscopy (XANES) has successfully given quantitative information on the presence of different sulfur forms in sediments, coals and petroleum asphaltenes [3–10]. This technique compared to many common methods (1) provides simultaneously qualitative and quantitative information about all the different forms of sulfur present, and, (2) allows measurements on whole untreated samples. Another frequently used method is X-ray photoelectron spectroscopy (XPS) which reveals information on the sulfur forms in the outermost layers (1–5 nm) of a solid sample. While XPS is a surface-restricted technique, XANES gives averaged bulk estimates of the sulfur composition of a sample exposed to X-rays. Thus, these techniques offer complementary information about sulfur speciation.

In this study, we combined a suite of techniques to characterize the different sulfur forms, especially the organic ones, in Spanish coals and oil shales characterized by a high content of sulfur. Large coal reserves in Spain are an important source of energy. Thus, the combustion of these coals can cause serious environmental effects due to the release of SO_x . More efficient and environmentally sound coal combustion for electrical power generation requires the removal of sulfur prior to or during combustion. For this reason, identifying sulfur forms in fossil fuels is of special interest. The ultimate goal is to gain new insights into the speciation of sulfur to better understand the potential problems for their desulfurization in fossil fuels.

2. Experimental

Table 1 shows the designation, origin, and different kerogen types in our samples.

The Mequinenza coal-bearing sequence is included in the Los Monegros Lacustrine System (SE Ebre basin) deposited during late Oligocene (ca. 30 Ma). Evaporitic facies developed mainly in the marginal lacustrine zones, while carbonate and lignite deposits dominate inner lacustrine areas [11]. Utrillas facies belonging to the Maestrazgo Basin located between the Iberian mountain chain and the outer

sector of the Catalan Coastal Range in NE Spain contain leonardite [12]. The humic substances of leonardite have been used to bind heavy metals at nuclear power plants [13], and to remove organic pollutants [14]. Lignites were deposited during the middle Albian (Lower Cretaceous, 105 Ma) in the proximity of a delta estuary [15]. Calaf lignite belongs to La Segarra Lacustrine System (Eastern Ebre basin) deposited during the early Oligocene (ca. 35 Ma) [16] in a lacustrine basin. Samples from Organyà basin (Southern Pyrenees) are included in a completely inverted basin in which a calcareous and marl sequence, 5000 m thick approximately, was deposited during the Lower Cretaceous rifting phase. Their maturity is high because they have expelled a significant percentage of petroleum [17] and the samples are kerogens extracted from calcareous rocks. Finally, Ribesalbes oil shales were deposited during the Middle Miocene (Serravallian) [18]; they are immature and calcareous in origin.

Method ASTM D2492-90 is the most frequently used method for quantifying sulfur forms in coal. Wet treatments are used to directly determine pyritic and sulfate forms. Total sulfur is assessed by elemental analysis in an elementary analyzer (Carlo Erba 1106). However, the content of the organic sulfur form is indirectly calculated by the difference of the other forms and, consequently, all the errors in determining the three remaining forms are reflected in the estimate of the organic sulfur fraction. Additional problems, frequently cited in the literature, derive from the poor reactivity exhibited by different sulfur compounds [4].

Analytical pyrolysis (Py–GC–MS) was performed in a Curie-point pyrolyzer (Horizon Instruments Ltd) coupled to a Varian Saturn 2000 GC–MS, using a 30 m $\times$ 0.25 mm DB-5 column (film thickness 0.25 μm). Approximately, 100 μg of a finely divided sample was deposited on a ferromagnetic wire, inserted into the glass liner and immediately placed in the pyrolyzer. The sample was pyrolyzed by keeping it at 40 $^{\circ}\text{C}$ for 1 min, raising temperature to 610 $^{\circ}\text{C}$ at a rate of 6 $^{\circ}\text{C}/\text{min}$, and holding it there for 20 min. The injector was equipped with a liquid-carbon-dioxide cryogenic unit, and programmed to follow the temperature profile from –30 $^{\circ}\text{C}$ (1 min) to 300 $^{\circ}\text{C}$ at 200 $^{\circ}\text{C}/\text{min}$. The GC–MS interface was kept at 300 $^{\circ}\text{C}$. The different chemical compounds in the outlet gas from the pyrolyzer were identified by gas chromatography (GC) and mass spectrometry (MS).

Scanning electron microscopy (SEM) was carried out with a microscope ISI DS-130 coupled to a solid-state detector Si/Li Kevex and a SUN SparcStation 5 for acquiring and processing energy-dispersive X-rays (EDX) spectra. Powder samples were converted into flat pellets and coated with a thin graphite layer to prevent the accumulation of static charge derived from the electron beam.

Total sulfur in the samples was determined by focusing on large sample areas using low SEM magnifications. The peak/background ratio was used to quantify sulfur using pyrite as a standard. In the spectra acquired from large

Table 1
Selected samples and types of kerogen for this study

Samples	Basin	Kerogen type
8-Me	Mequinenza	III-S
Cañizara	Utrillas	III
L-12	Utrillas	III
Salomé	Utrillas	III
Calaf	Calaf	III
O-7	Organyà	II-S
O-13	Organyà	II-S
Rib-3	Ribesalbes	I-S
Rib-7	Ribesalbes	I-S

sample areas other chemical elements besides S were detected, such as Si, Al, K, Ca and Fe associated with particles of mineral matter. Organic sulfur was determined from the peak/background ratio in EDX spectra acquired from small sample areas using very high SEM magnifications. In this case, the absence of significant amounts of cations in the EDX spectrum implies that the detected sulfur is in the organic form. Usually, the distribution of organic sulfur in samples is highly inhomogeneous, especially if the pyrite content is high; therefore, the mean of at least 10 measurements was taken as the true concentration of organic sulfur.

The functionality of sulfur in coal was assessed by X-ray absorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS). XANES spectra were collected using a Lytle fluorescence detector at the X-19A beam-line, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The X-ray beam diffracted by a double-crystal Si (111) monochromator irradiated the sample. The monochromator was detuned by ca. 70%. The sample's chamber was continuously flushed with He to prevent the attenuation of the X-ray beam by air. Vairavamurthy et al. [19,20] described details of the beam-line setup. The spectrum was recorded at optimized conditions so that pre-edge and post-edge data allowed a precise background correction. The white-line maximum for sulfate was assigned at 2483.1 eV, and was used to calibrate the spectra. Speciation information was derived by deconvoluting a XANES spectrum into a set of Gaussian peaks and an arctangent function representing the transition of the photoelectron to the continuum. The peak position depends on sulfur functionality thereby allowing the assignment of different sulfur forms: 2472.6 eV for pyritic, 2473.3 eV for sulfidic, 2474.7 eV for thiophenic, 2476.8 eV for sulfoxide, 2480.4 eV for sulfone, 2481.7 eV for sulfonate, and 2483.1 eV for sulfate. The relative peak area revealed the relative abundance of the different sulfur forms [21].

The XPS spectra were obtained on a FISON ESCALAB 200R system equipped with an hemispheric detector using an X-ray source of MgK of 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 corresponding S2p peak was curve resolved using a mixed Lorentzian–Gaussian line shape. Sulfur functionality in coals is assigned from the observed shifting of the binding energy (BE) of the level S2p for different organic sulfur compounds taken as models listed in the literature: 158.7–159.6 eV pyritic, 161.2–162.5 eV sulfidic, 163.7–164.0 eV thiophenes, thioethers and mercaptanes, 166.0 eV sulfoxide, 168.0 eV sulfone, 169.2 eV sulfonate, and 174.8–175.8 eV sulfate [22].

3. Results and discussion

Table 2 shows the quantitative results for sulfur forms

Table 2

Percentages of different forms of sulfur content (pyritic, sulfate, organic, total and atomic ratio of sulfur versus carbon) and percentages of carbon content of raw coals and oil shales (d.a.f) obtained according ASTM (n.d.: not determined)

Samples	%S _{pyritic}	%S _{sulfate}	%S _{org}	%St	%C	%(S/C) _{at}
8-Me	0.5	0.7	12.2	13.4	60.6	8.3
Cañizara	2.0	0.3	3.1	5.4	73.2	2.8
L-12	3.3	0.8	2.7	6.8	70.6	3.5
Salomé	1.9	0.8	3.9	6.6	70.0	3.5
Calaf	1.7	7.6	5.8	15.1	53.1	10.7
O-7	0.4	0.3	0.3	1.0	1.2	0.3
O-13	0.5	0.1	1.7	2.4	2.1	0.4
Rib-3	0.3	0.5	2.0	2.8	15.2	4.7
Rib-7	n.d.	n.d.	n.d.	0.3	10.3	1.2

obtained by the ASTM method. The total sulfur concentration is very high (>10%) in samples 8-Me and Calaf but the forms are varied. While sample 8-Me is almost entirely organic (91%), the Calaf sample contains about 62% inorganic S. The Utrillas coals (Cañizara, L-12 and Salomé) have intermediate sulfur concentrations, with about 50% together being pyritic and sulfate sulfur. The total sulfur concentration in the remaining samples is relatively low (<3%), although the distribution of sulfur species among them is somewhat similar.

The organic sulfur content was indirectly estimated by Py–GC–MS through the thiophene ratio (TPR). This parameter is defined as [2,3-dimethylthiophene]/[1,2-dimethylbenzene] + non-1-ene} ratio [2] obtained from the relative area of their respective peaks in the chromatogram of the pyrolyzer's outlet gas. For example, Mequinenza coal (8-Me) contains the highest amount of alkylthiophenes in the pyrolysis products and, consequently, it has the highest TPR calculated value (3.43) of all coals studied (Table 3). By comparing this value and the Cañizara TPR value (0.92) detected with a mass spectrometer with that obtained for the same coal sample by Sinninghe Damsté et al. [23] who used a FID detector, we arrive a factor of 0.5. All parameter values in Table 3 are multiplied by this factor, and the corrected values, designated TPRc are also included in this table.

By plotting the corrected parameter TPRc versus S_{org}/C as

Table 3

Values of thiophene ratio (TPR), atomic relation S_{org}/C, thiophene ratio corrected (TPRc) and estimated relation S_{org}/C

Samples	TPR	S _{org} /C	TPRc	S _{org} /C estimated
8-Me	3.43	0.075	1.71	0.11
Cañizara	0.92	0.016	0.46	0.029
L-12	0.97	0.014	0.48	0.030
Salomé	0.85	0.021	0.42	0.026
Calaf	0.84	0.041	0.42	0.026
Rib-3	1.00	0.048	0.50	0.031
Rib-7	1.11	0.056	0.55	0.035

Table 4

Values of mineral matter as well as organic sulfur (S_{org}) (d.a.f) calculated by ASTM and organic sulfur measured in SEM–EDX technique

Samples	S_{org} ASTM	Mineral matter	S_{org} ^a ASTM	S_{org} SEM–EDX
8-Me	12.2	21.3	15.5	11.8
Cañizara	3.1	23.1	4.1	7.6
L-12	2.7	28.9	3.8	6.5
Salomé	3.9	30.4	5.6	4.9
Calaf	5.8	41.3	9.9	17.3

^a Organic sulfur (d.a.f) corrected by the presence of mineral matter.

determined by the ASTM method (Table 2) an apparent relation is found which suggests that the amount of thiophenes produced is correlated with the organic sulfur content in these samples as Eglinton et al. reported [2].

From the ASTM method, an S/C ratio of 0.075 for 8-Me coal was found, while the value from analytical pyrolysis is 0.11 indicating that the concentration of organic sulfur as deduced from the TPR parameter is slightly overestimated as suggested previously [2]. The ratio S_{org}/C is also overestimated for the remaining coals and oil shales. Consequently, the TPRc parameter from the Py–GC–MS test gives a rapid approximation of the S_{org}/C ratio in coals and oil shales. Hence, the TPRc parameter is suitable for approximate estimation of the S_{org}/C ratio in coals with almost all sulfur as organic sulfur, but it only can be taken as a rough indicator of the organic sulfur content if the concentrations of pyritic and sulfate forms are important.

Table 4 gives the organic sulfur measurements obtained directly by SEM–EDX. For comparison, the ASTM values

Fig. 1. Deconvolution of the XANES spectrum into several Gaussian and arctangent peaks to obtain the composition of various sulfur functionalities in (A) Utrillas (L-12) coal and (B) Ribesalbes oil shale (Rib-3).

Table 5
Percentages of several forms of sulfur calculated by XANES technique

Sample	Pyritic	Sulfidic	Thiophenic	Sulfoxide	Sulfone	Sulfonate	Sulfate
8-Me	5.1	9.4	35.3	12.8	–	14.2	23.4
Cañizara	9.3	12.0	32.4	10.4	–	11.9	23.9
L-12	4.4	12.5	33.1	8.7	–	–	41.2
Salomé	8.6	9.6	28.5	7.6	–	–	45.7
Calaf	7.3	13.3	18.7	0.4	–	–	60.2
O-7	9.9	7.0	–	–	–	–	83.1
O-13	22.7	18.7	–	–	14.3	–	44.3
Rib-3	7.3	20.0	12.8	3.4	–	–	56.2
Rib-7	6.7	17.7	20.6	13.5	–	–	41.5

and the corresponding ones corrected by the presence of mineral matter are included, since SEM–EDX determinations are calculated on a mineral matter free basis.

Differences between the S_{org} concentration obtained by the two methods are not significant in coals, such as 8-Me, in which most of the sulfur is organic. However, there are noticeable differences in Calaf coals with a significant content of inorganic sulfur. In such cases, the SEM values are substantially higher than the ASTM values, a pattern observed for all coals. The presence of small particles of calcium sulfate and/or pyrite embedded in the coal matrix probably overestimates the organic sulfur concentration because finding ‘clean’ regions for analysis is problematic.

The sulfur functionality in the coals has been assessed by XANES, and typical spectra from Utrillas (L-12) coal and Ribesalbes oil shale (Rib-3), respectively, are shown in Fig. 1A and B. The continuum background was subtracted from the XANES spectrum and the main signal deconvoluted into peaks with increasing energy, assigned to different sulfur functionalities: pyritic, sulfidic, thiophenic, sulfoxide, sulfone, sulfonate and sulfate forms. Table 5 shows the XANES results.

The areas of the deconvoluted peaks represent the abundances of the different chemical types of sulfur compounds. Sulfate (+6 oxidation state) was the dominant oxidized sulfur form in all samples, ranging from 23.4% in 8-Me to 83.1% in O-7 samples. Sulfate can be present as organic ester sulfate and/or inorganic sulfate, although XANES cannot differentiate between them. The other major oxidized sulfur was the sulfonate functionality which was particularly abundant in 8-Me (14.2%) and Cañizara (11.9%) coals. Sulfonates also were found in soils and sediments, together with significant amounts of ester-bonded sulfate [9]. A biological origin was suggested for sulfonates in natural organic matter [24]. Minor amounts of other oxidized sulfur forms, such as sulfoxides were found in all samples except in rocks from Organyà (samples O-7 and O-13). Sulfones were exclusively detected in sample O-13 (14.3%) whose origin could be attributed to oxidation of other sulfidic forms [10].

Among the reduced sulfur forms, pyrite was found in significant amounts in all samples; its abundance was parti-

cularly high in sample O-13 (22.7%). SEM–EDX revealed the presence of pyrite in all samples [25]. It is possible that the values for pyrite from XANES may be underestimated because the spectral response of the reduced species usually are lower than those of oxidized species. Thus, the oxidized sulfur forms may be overestimated [2,20]. Most reduced sulfur forms in the coals detected by XANES correspond to thiophenic sulfur, with concentrations varying over a broad range (13–35%). Values for 8-Me coal (35.3%) are in good agreement with previous XANES studies by Brown et al. [26] and Huffman et al. [7]. They are the most stable sulfur forms in coals, and survive even at relatively high temperatures. The presence of sulfidic sulfur was revealed by thermogravimetric analysis, since their decomposition temperature is between 250 and 450 °C as it was reported by Bonet et al. [25] in samples from the same origin and similar properties to those analyzed in this paper. Although earlier XANES studies suggested that elemental sulfur occurs in some coals, both our XANES and SEM–EDX results do not indicate its presence.

Fig. 2 gives examples of typical XPS spectra of different coals. XPS S2p spectra usually appear as a single peak located at different binding energy (BE), except the

Fig. 2. Percentages of sulfate sulfur obtained by the XPS spectra at the level S2p, for Utrillas (L-12) and Calaf coals as well as Organyà (O-7) and Ribesalbes (Rib-7) oil shales. Binding Energy (BE) is given in electron volts.

Table 6
Percentages of several forms of sulfur quantified by XPS technique

Sample	Pyritic	Sulfidic	Thiophenic	Sulfoxide	Sulfone	Sulfonate	Sulfate
8-Me	–	–	74	–	–	26	–
Cañizara	–	–	–	–	100	–	–
L-12	52	–	–	–	–	16	32
Salomé	100	–	–	–	–	–	–
Calaf	–	–	–	–	–	15	85
O-7	–	100	–	–	–	–	–
O-13	–	100	–	–	–	–	–
Rib-3	–	100	–	–	–	–	–
Rib-7	–	100	–	–	–	–	–

spectrum of Utrillas sample (L-12), which appears split into three peaks. Because XPS is a surface technique, it may overestimate the presence of small particles mostly located on the large particles of coal. Additionally, XPS might overestimate the amount of oxidized sulfur forms, especially the sulfate form, due to the apparent propensity of pyrite in air to surface oxidation. Consequently, XPS in general terms may be considered as a complementary technique to XANES to reveal mostly the surface chemistry. However, XPS spectra are much less structured and considerably simpler than XANES spectra. Furthermore, the spectral energy and shape for a particular functionality may be affected because of charging effects depending on sample's composition. For example, the XPS results show a strong tendency to overestimate the presence of oxidized sulfur forms especially when mineral matter is abundant, probably because the charging effects that are unavoidable in studies of non-conducting samples. Although a more detailed differentiation into specific types is problematic, XPS can readily distinguish between reduced and oxidized sulfur forms. Quantitative estimates of the organic and inorganic forms based on peak is given in Table 6.

4. Conclusions

In this study, sulfur-rich kerogens such as type I-S oil shales, type II-S source rocks and III-S coals with outstanding organic sulfur contents have been characterized in their different types of sulfur forms, by using destructive and non-destructive techniques in order to characterize their functionalities. The ASTM method is very simple but it gives only superficial information on sulfur speciation in coal. SEM–EDX identifies the chemical species in the mineral matter and directly quantifies the organic sulfur and its distribution in the coal matrix. Problems appear when mineral matter is very abundant and/or distributed in small sized particles. The TPRc ratio allows an estimation of the organic sulfur content of fossil fuels. XPS is a suitable technique to qualitatively determine sulfur forms in coal, especially to differentiate between reduced and oxidized forms. However, because coal is non-conducting, XPS is prone to charging effects, thereby overestimating the

presence of oxidized species. Generally, the XANES technique is a sensitive technique to qualify and quantify sulfur speciation in fossil fuels.

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