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Sulfur Functionalities in Fossil Fuels: A comparison of XANES, XPS and GC-MS Techniques

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Beamline(s): X19A

Introduction: Sulfur is ubiquitously present in fossil fuels but amounts vary from traces to more than 10%, and it is present in both inorganic and organic forms. Because the organic sulfur mostly is structurally integrated in the macromolecular organic matrix of the fuels, it is usually difficult to characterize. Widely used gas chromatographic methods have limited utility because they detect only compounds that are amenable to be separated in the gas phase. On the other hand, spectroscopic techniques, such as sulfur XANES, allow the detection of all the different forms on whole untreated samples.

Methods and Materials: A set of Spanish coals and oil shales were studied using spectroscopic (XANES, XPS) and chromatographic techniques (pyrolusis GC-MS) 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 GC-MS, we estimated the ratio Sorg/C in these coals and oil shales, and compared them with those obtained by the standard ASTM method D2492. XANES spectra were collected using a Lytle fluorescence detector at the X-19A beamline.

Results: The ASTM method is very simple but it gives only superficial information on sulfur speciation in coal. 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. XANES results show the presence of both oxidized and reduced forms of sulfur in all the samples. Sulfate (+6 oxidation state) was the dominant oxidized sulfur form. The other major oxidized sulfur was the sulfonate functionality. Minor amounts of other oxidized sulfur forms, such as sulfoxides were found in all samples except in rocks from Organyà. Sulfones were exclusively detected in one sample whose origin could be attributed to oxidation of other sulfidic forms. Among the reduced sulfur forms, pyrite was found in significant amounts in all rock samples.Although earlier XANES studies suggested that elemental sulfur occurs in some coals, both our XANES and SEM-EDX results do not indicate its presence. Generally, the XANES technique is a sensitive technique to qualify and quantify sulfur speciation in fossil fuels.

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