INORGANIC ELEMENT FUNCTIONAL GROUP DATABASE ON PULVERIZED COAL SURFACE BASED ON XPS METHOD

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ABSTRACT

The research results of coal characterization using the XPS method are summarized. Microsoft Visual Studio.net is utilized to build a database functional group characterization for coal, which contains over 1000 records including the kind of functional group, binding energy value, coal specie, producing area, sample preparation, and literature information. The database can be used to search and analyze XPS data for coal conveniently and is also of significance to support further coal research using XPS.

Keywords: XPS, Functional groups, Coal, Database

1   INTRODUCTION

X-ray photoelectron spectroscopy (XPS), also known as ESCA (electron spectroscopy for chemical analysis), is a method for solid materials surface analysis. When a sample is bombarded with X-rays, photoelectrons are ejected from the sample surface. Because each element has a characteristic set of binding energies, element identification can be made by measuring the binding energies of photoelectrons. XPS can be also utilized to distinguish several different chemical environments, valence states, or functional groups of the same element simultaneously by the chemical shift. The chemical shift is the change of energy in a photoelectron line caused by an element being in a chemical environment different from the pure element. It can offer much micro-chemical information for material surfaces and is widely used in many domains. Because of the advantages stated above, XPS can determine much information about coal that other analytical methods can not obtain, for instance, element composition of the coal surface, existing forms of elements, evolution of elements, etc. Consequently, the XPS method is widely applied in the study of coal. An example of XPS complete spectra of typical coal is shown in Figure 1.
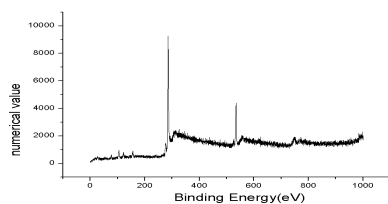
Figure 1. XPS complete spectra of typical coal[1]

Frost[2] et al. at first applied the XPS method in a functional group characterization of coal surfaces in 1974. The forms of C, O, and S in several coals and their typical inorganic minerals were analyzed, and the direct quantification method was discussed. Later, Brown[3], Wallace[4], Burchill[5], Bartle[6], Kelemen[7, 8], Hittle[9], Perry and Grint[10] studied forms of C, O, N, and S and their functional groups in coal respectively. Chen[11, 12], Liu[13, 14], and Dai[15] studied typical Chinese coals using the XPS method. Journals reporting XPS studies on coal and coal-like substances number more than 200. This demonstrates that XPS as an analytical method is playing a more and more important role in the study of coal.

Coal is a complex substance containing many compounds with functional groups of C, O, N, and S whose binding energies may be close to each other or even overlap. Thus it is difficult to resolve peaks for different kinds of elements and to determine the binding energy of sub-peaks. At the same time, the experimental results of different investigations on the same functional group of the same element may be a little different because of differences in experimental apparatuses, energy calibrations, coal species, producing areas, sample preparations, and other aspects. All of these induce problems of identification of sub-peaks, determination of binding energies, and further quantification. Though existing XPS databases such as NIST are widely used in research on coatings, sensors, catalysts, biomaterials, electronic materials, ceramics, polymers, thin films, and composite materials to find XPS data of various elements and functional groups, in many situations they are difficult to use directly for a functional group analysis of coal.

In order to use the binding energy data of various kinds of functional groups efficiently, an approach using XPS to probe functional groups of coal surfaces is reviewed in this paper. Together with the author's data, the classification and basic characterization of inorganic element functional groups (C, O, N, S, etc.) on the surfaces of various coals from different production areas are summarized. A functional group characterization database has been established, which includes the kind of functional group, binding energy value, coal specie, producing area, sample preparation, and literature information. It can be used to find and analyze XPS data for coal and also help new coal research with XPS. Because of the intrinsic complexity of the structure and composition of coal, some model compounds have previously been studied by other researchers. These are also embodied in this database.

2   DISCUSSION

Microsoft Visual Studio.net is used to build a database about inorganic element functional groups on the surface of pulverized coal based on the XPS method (short for CXPSDB). The database contains primary data about the element, spectral line, functional group, and binding energy as well as detailed information about coal specie, producing area, sample preparation, experimental apparatus, excitation source, energy calibration, energy analysis mode, author, references, and journals. The opening screen of CXPSDB is shown in Figure 2. The

CXPSDB involves data compilation, GUI design, search strategy, and implementation.
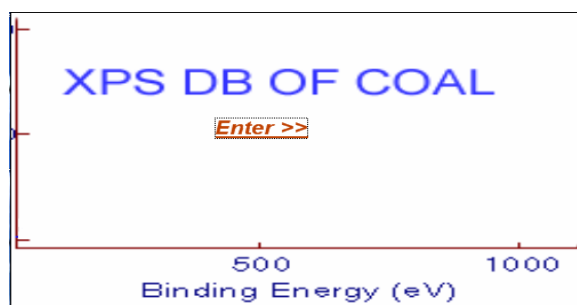
Figure 2. Start-up interface of XPS DB of coal

2.1 Data compilation

The current CXPSDB contains data originating from scientific papers published between 1974 and 2006, including English and Chinese papers. The data compilation process involves the following several steps: first, a literature search of published papers identified by keywords such as "X-ray photoelectron spectroscopy and coal" or "XPS and coal" in Engineering Index, Elsevier SDOS, ACS, and CNKI databases; second, review of the identified papers and selection of those that have adequate information on energy calibrations and excitation sources as well as adequate information on preparation of the specimen material; third, checks for data consistency and entry of the data into the database; and finally, data verification from checks of all numerical data , chemical information, sample information, and citation information. More than 100 papers are cited in this CXPSDB containing about 1000 records.

2.2 Graphical user interface (GUI) design, search strategies, and implementation

GUI design, search strategies, and implementation are introduced together because they are closely interrelated; GUI for searching is shown in Figure 3. Because the CXPSDB focuses on the main inorganic element functional groups in coal, only the information for C, O, N, and S is recorded, while the information for Si, Al, and Cl is neglected. Based on the needs of the XPS analyst, mainly the identification of elements from observed spectral features and the determination of chemical state and functional groups from small energy shifts of photoelectron, the following search options are provided:

    1. Identify binding energy and functional group by elementary spectral line.

    2. Identify functional group and unknown spectral line by binding energy.

Figure 3. GUI for searching

2.2.1 Identify binding energy and functional group by elementary spectral line

When searching by elementary spectral line, a user first chooses the element type, then selects spectral lines, and at last submits to obtain the results shown in Figure 4. Element, spectral line, functional group or chemical bond, binding energy and its shift are provided in the results which can be arranged according to the magnitude of binding energies. If the scope of the binding energy of the element in the functional group is known, a user can enter it in the binding energy option for the secondary search to shrink the scope of the unknown functional group and obtain a better result. Additional detailed information (Figure 5) is also provided through the symbol "+" in Figure 4. The detailed information associated with the determination of this functional group and its binding energy is provided, such as author, journal, reference, volume, year, sample, coal specie, production area, sample preparation, experimental apparatus, excitation source, energy calibration, and energy analysis. If more than one record in Figure 5 corresponds to the same binding energy of the same functional group in Figure 4, it demonstrates that several authors obtained the same result under the condition of different samples and experimental apparatuses, which is useful for comparison and analysis.
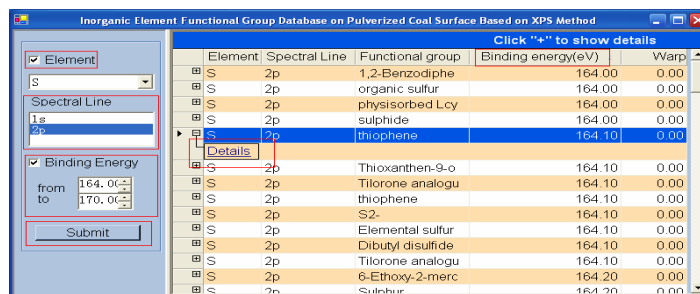

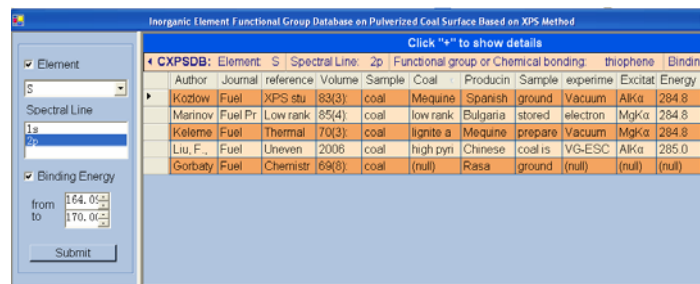**Figure 4.** GUI of identify binding energy and functional group

Figure 5. GUI of detail information

2.2.2 Identifying functional group and unknown spectral line by binding energy

When searching by binding energy, a user chooses that option and enters a range of binding energies which displays results as in Figure 5. Composition search is similar. If the binding energy fluctuates by not very much, it can be identified easily; otherwise other information should be considered to determine a match. Detailed information can be obtained in Figure 4.
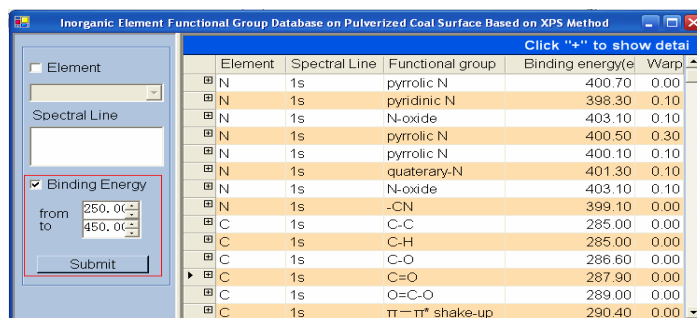
Figure 6. GUI of identify functional group and unknown spectral line

3   SAMPLE APPLICATION

New XPS photoelectron spectra are obtained using an XSAM800 ESCA spectrometer (made by KRATOS Company) equipped with MgKα (1253.6ev), the excitation source being operated at 12.5KV and 16ma. The analysis mode of FRR is used; the vacuum in the analysis chamber is always better than 5×10^{-7}Pa. A correction for binding energy is made to account for sample charging based on the C1s peak at 284.6eV. Coal is ground to pass a 100 mesh screen. Raw coal is dried in 80°C for 3 hours and then is put into a desiccator before use. The functional groups of C, O, N, and S in each coal sample are analyzed. The Proximate and Ultimate analysis of a coal sample is shown in Table 1.

Table1. Proximate and Ultimate analysis of a coal sample

NO.	PROXIMATE ANALYSIS (WT %)				ULTIMATE ANALYSIS (WT %)					QD (MJ.KG^{-1})
	M	V	A	FC	C	H	O	N	S	
Coal sample	1.28	21.76	16.19	60.77	70.68	5.52	4.02	1.68	0.63	33.34

By identifying binding energy and functional group by elementary spectral lines in the CXPSDB, the result is obtained that C in coal mainly presents as graphite, hydrocarbon, hydroxyl or ether, carbonyl, carboxyl or ester, and π－π* shake up, while the C-N in coal is so weak that it can be neglected. Once corrections for binding energies of all these records in this CXPSDB are standardized at 284.6ev, the binding energies of various functional groups can be attained (from small to large): graphite (284.4±0.3); hydrocarbon (285.0±0.3eV); hydroxyl or ether (286.1±0.2eV); carbonyl (287.6±0.3eV); carboxyl or ester (288.6±0.4eV); and π－π* shake up (291.2±0.2eV), which can be used for peak-splitting and further quantification. The C1s spectral line and the result of peak-splitting of coal are shown in Figure 7. The data of sub-peaks can be used for further study. Of course the functional groups of O, N, and S and their quantification can be obtained in a similar way. This is shown in Figure 8, Figure 9, and Figure 10.
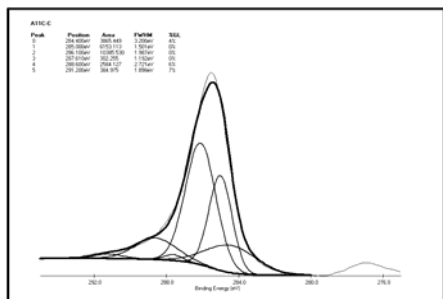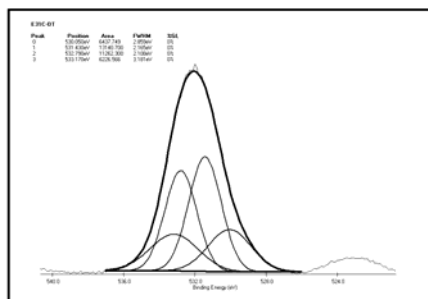
Figure 7. C1s spectral line of one coal

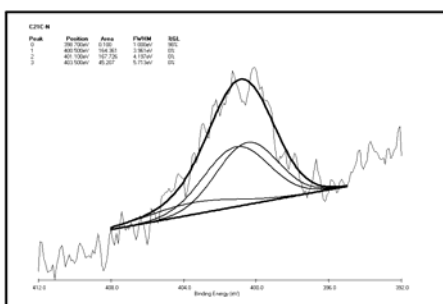**Figure 8.** O1s spectral line of one coal

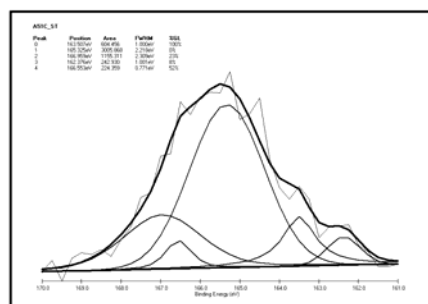**Figure 9.** N1s spectral line of one coal

Figure 10. S2p spectral line of one coal

4   CONCLUSIONS

A database of XPS data of inorganic element functional groups in coal has been made. It will be updated with additional XPS studies of coal. The next step is to make it into a Web-based database, available, free of charge, on the Internet.

The building and application of this CXPS DB is of significance for searching for experimental data about coal conveniently and precisely as well as to help further research and analysis of these XPS data.

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