

PIXE - A NEW ANALYTICAL TECHNIQUE FOR THE
ANALYSIS OF COAL AND COAL DERIVED FUELS

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ABSTRACT

A new technique, PIXE - particle induced x-ray emission scanning, for analyzing concentrations of sodium through uranium with detection limits in the order of ppb and ppm is explained in this paper. The accuracy of scan is $1 \mu\text{m}$ and the target can be moved over a distance of 8 inches in any direction for surface or depth analysis. PIXE is performed by scanning the target, in increments ranging from 1 to 8 mm adjustable diameter of proton beam, line by line, using a computer controlled Deadal motor driven linear translation stage in the needed directions.

The experimental results obtained from a number of coal and ash samples, using PIXE technique are presented. The degree of accuracy of the PIXE technique relative to other techniques is also discussed. The technique is very useful for coal and ash analyses, deposit analysis, and analyses of corroded and eroded surfaces using coal and coal derived fuels. PIXE is a unique technique which provides quantitative data on concentration of inorganic constituents, its oxidation state and depth simultaneously. Total analyses time in this technique, including sample preparation, varies from 8 - 10 minutes per sample.

INTRODUCTION

Coal is a heterogeneous assembly of macerals and minerals schematically shown in Fig. 1 {1}. This figure is similar to Schlosberg of Exxon. A number of investigators; Given {2}, Wisner {3} and Larsen {4} etc. have attempted to formulate a model for the organic components of coal (Figures 2,3 & 4) based upon the cumulative experimental results. The experimental results were obtained through different experimental techniques and using wide variety of analytical tools. In this regard a substantial understanding of coal structure has been obtained. However, these structures still do not provide clues to the solution of many engineering problems experienced due to coal utilization. Some of these problems may be attributed towards the poor understanding of chemical, thermodynamic and kinetic reactivity of coal in the process of combustion or conversion. The resolution to the engineering problems; deposits, corrosion, erosion, slag formation, NO_x , SO_x , and particulate emission, with the use of coal in industry can be achieved if multidimensional properties of coal are studied simultaneously. Industrial experience with coal {5} indicates that coal can be best analyzed for its structure (organic, inorganic, trace elements, porous and petrographic structure) under two main methods of study: Direct and Indirect.

In the Direct method, coal can be analyzed for its gross characteristic such as elemental composition, petrographic composition, Btu value, calorific value, etc. using conventional analytical tools. The results obtained through the Direct methods do not provide reasons for two coals exhibiting different chemical behavior although possessing similar gross characteristics and vice versa. Indirect methods, on the other hand, provide the core information most essential to the understanding of reaction mechanism and cause of many industrial problems {5}. Under Indirect methods controlled conditions may be used to obtain the recognizable chemical units of coal (representative of whole coal) without altering the chemical nature of coal. It is only through the Indirect methods that the composition of inorganic and organic constituents can be established {6,7}.

Inorganic constituents of coal and coal products are analyzed by a number of techniques. These techniques are reviewed in references {8 & 9} by Weaver and Fuller. The analytical techniques used are AAS, NAA, ICP, DCP, XRF, SEM, etc. Some of the techniques used are time consuming, some possess lower detection limits and some do not provide multi-elemental detections with depth profile. The PIXE (particle induced x-ray emission) technique overcomes the above mentioned difficulties. This technique even differentiates between the oxidation state of ions. According to Khan and Crumpton {10}, the PIXE technique is reliable and repeatable. PIXE technique has been widely used in the study of biological tissue {11}, meteoritic samples {12}, rain and snow {13 & 14}, and environmental samples {15} to analyze concentrations of trace elements sodium through uranium in ppb. In this paper, PIXE technique is reviewed and preliminary results on coal and coal ash using PIXE are presented.

EXPERIMENTAL THEORY

PIXE (particle induced x-ray emission) in general involves bombardment of elements with any particles: alpha, beta, gamma, electron, proton, etc. In the present study, however, the instrument generated a proton beam to excite electrons of K and/or L shells of atoms. The spectra of K and K x-rays and L and L x-rays are sufficient to detect even heavy elements. Proton beam with the energy strength of 4 MeV bombards K and L shells of electrons of an element {15,16}. The electrons after absorbing the proton energy migrate to higher energy levels and leave the vacant spots in K and L orbits. The transition of electrons from higher energy "allowed" orbitals takes place to fill the vacant spot in the K and L orbits. The transition of electrons from higher energy to lower energy orbits accompanies with the emission of electromagnetic radiations. The emitted radiation carries an amount of energy equivalent to the energy difference between two shells of the electron transition. These emissions correspond to K and L x-ray radiations. The wave length of the produced radiations are characteristic of the elements and varies from element to element. The corresponding K and L x-ray intensities are recorded in the form of a spectrum. Since these x-rays are characteristic for each element, the fingerprints of the x-ray emission attributes to the elemental identification. The area covered under a peak in the spectrum directly relates to the concentration of individual elements. The principle of PIXE and the development of PIXE is explained in great detail by Johansson and Johansson {17}.

EXPERIMENTAL METHOD

The experimental program was conducted in three steps. The first step was involved with the generation of the homogeneous beam of protons with a given intensity. The second step dealt with the preparation of samples and exposing the samples to the beam of protons. The third step was carried out to obtain the elemental x-ray spectra and compare it with that of standard elements.

Homogeneous beam of protons, with the energy of the order of 4 MeV, is generated using Tandem/Van de Graff accelerators. This energy is sufficient to detect heavy metals. The beam of protons travels a long way before it hits the coal sample. The proton beam passes through a diffuser foil, several collimators and finally through a 25 μm diameter Kapton window. The purpose to pass the beam through a number of obstacles was to scatter the beam to obtain uniformity and subsequently to refocus it to obtain homogeneity. The homogeneity of the beam was checked by using known standard element. The test section where the sample was introduced was filled with helium. The beam when projected on a sample covered an estimated diameter of 8 mm. The Kapton window in the set up was changed every 12 hours so as to avoid pick up of any interaction effects in the final spectra. The Faraday cup was used to integrate the charge. This cup was mounted downstream of the sample. The detection was done by the Ge Princeton Gamma Tech. detector. This detector possessed energy resolution of 150 eV at the Mn 5.9 KeV K line.

Several other protective measures were taken in the PIXE set-up to maintain the sensitivity of the experiment. The sample slides were mounted in a slide projector. The insertion and the removal of the slides was controlled automatically.

Coal and ash samples were analyzed as a thin slide on kimfol film. Samples were mixed with an appropriate binding agent and the mixture was then transferred on to kimfol film slides. Binding agent used for coal was cellulose acetate (Polystyrene) in toluene where as ash samples were mixed with 6F HNO₃ doped with 100 ppm yttrium. Coal and ash samples were mixed with their appropriate binding agent in the ratio of 300 mg to 300 μ l of this mixture were deposited on the kimfol film slides and irradiated directly. Kimfol is a polyvinyl very thin material, easy to handle, resistant to chemical attack and can withstand high proton beam currents.

The concentration of an element in a sample was determined by comparing the area of the K (or L) peak of the element of interest with that of a reference element that contained Argon, Rhodium or yttrium as the internal standard. The standard reference spectra were obtained from bombarding high purity atomic absorption standards in a matrix of boric, perchloric, nitric, and hydrofluoric acid under the same conditions (i.e. target thickness, type of backing and its thickness, integrated charge, and current) as the samples. This normalization procedure removed uncertainties due to x-ray absorption and x-ray production cross sections. The data acquisition system and the slide projector are automatically controlled by a PDP 11/44 computer [16]. The thickness profile is obtained by bombarding the sample with variable proton energies that can pass through the sample. The stopping power of proton (depth penetration) is a function of its energy and the thickness of the sample under study.

EXPERIMENTAL RESULTS, DISCUSSION AND CONCLUSIONS

The characteristics of coal samples analyzed by PIXE methods are shown in Table 1.

TABLE 1
COAL AND ASH SAMPLES

<u>Sample #</u>	<u>Origin</u>	<u>Rank</u>	<u>% C dmmf</u>	<u>% MM Dry</u>
1. Coal - PSOC 95	(Washington)	HVA	84.39	23.75
2. Coal - PSOC 124	(W. Virginia)	HVA	83.48	9.71
3. Coal - PSOC 245	(No. Dakota)	Lignite	73.39	15.38
4. Coal - PSOC 251	(Kansas)	HVA	83.73	19.99
5. Coal - Low Temp. Ash	From coal sample #1			
6. Coal - Low Temp. Ash	From Coal sample #3			

Inorganic constituents in coals are detrital and authigenic. Minerals which are formed as a result of coalification process consists of montmorillonite, chlorite, kaolite, pyrite, gypsum, hematite, siderite and calcite. The detrital constituents include monmorillonite, quartz, plagioclase, alkali feldspar, biolite, chlorite, volcanic glass and rock fragments. Na, Mg, Al, K, Ca, Ti, Fe, Sc, V, Cr, Mn, Co, Ni, Zn, As, Se, Ru, Ag, Cd, Sb, Cs, Ba, Sm, La, Ce, Eu, Yb, Th, U etc. are the inorganic elements responsible for the formation of the mineral matter in coals. Major mineral matter which is not bonded with the organic structure of coal is widely known and can be taken out in the cleaning processes by physical or chemical means. However, this is cumbersome, expensive and time consuming process and changes the chemistry of whole coal. These are some of the reasons why direct use of coal is encouraged.

In the present investigation, powder form of coal samples was used. Therefore, the PIXE analysis of coal samples presented contain elemental concentration of total mineral contents. Fig. {5} through {10} illustrates the concentration distribution of various major elements in the sample. Some of the peaks are not seen on

plots due to scaling. These hidden peaks represent the elemental concentration the order of one ppm. In between the adjoining peaks, there are also elements less than 1 ppm which have not been identified due to presence of one of the elements in far excess compared to others and which controlled the vertical scale. Detection of the elements below 1 ppm concentration may be possible in future work. Since it is a preliminary investigation, it provided us an input to set up scales for future work on the coal mineral and ash investigation. Nevertheless, it was the first effort to analyze coal using the PIXE technique.

Presence of Na, Al, Si, K in large quantities also interfered with the Ar - standard used to identify trace elements. Fe, Ca, Al, Na, Si, K, Mg, Ba, etc. are not trace elements (concentration range is higher). These elements come from pyrite, silicates and quartz incorporated into coal during the coalification process. Mn, Co, Ni, V, Zn, Sr, Cr, As, Se, Sm, Pb, Cu, Th, U etc. are the trace elements. Concentration of these elements vary from few ppm to below hundreds.

Results of PIXE analysis are summarized in Table 2. The identified elements and their concentration levels match with the ones obtained from other methods given in references 7, 9 and 18, which demonstrates the accuracy of the method.

TABLE 2
GENERAL TREND IN
CONCENTRATION OF ELEMENTS (PPM)

Coal Sample	Concentration of Elements Na, Ca, Mg, Fe, Al, Si, K, Ba	Concentration of Elements Se, V, Ti, Co, Zn, Sc, Cr, As, Pb, Cu, Cd, Sr, Sb, Cs, Sm, Th, U
Washington HVA	Hundreds	Under One
W. Virginia HVA	To	To
Kansas HVA		
North Dakota LIGNITE	Thousands ppm	Under Hundred ppm
Coal Ash		
Coal Ash		

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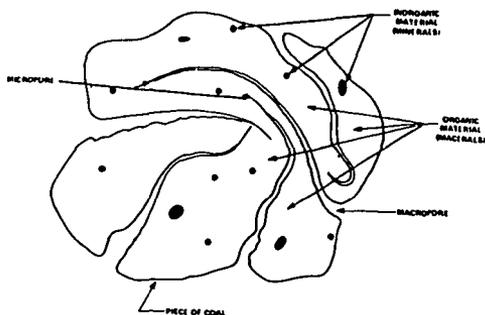


Fig. 1: Heterogeneous Assembly of Macerals and Minerals with Pores in a Piece of Coal.

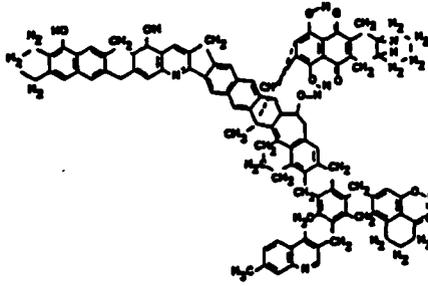


Fig. 2: Hypothetical Chemical Structure of Coal Molecule by Given.

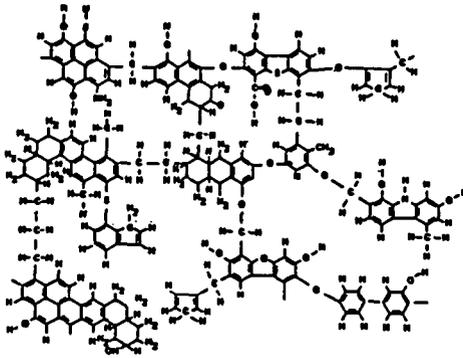


Fig. 3: Schematic Representation of Chemical Structure of Coal by Wiser.

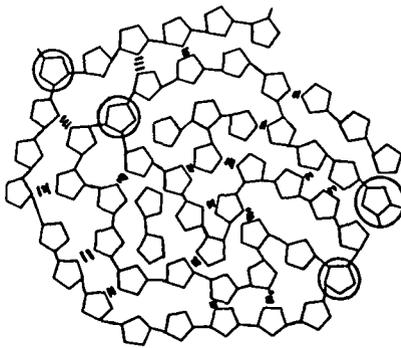


Fig. 4: Macromolecular Structure of coal by Larsen.

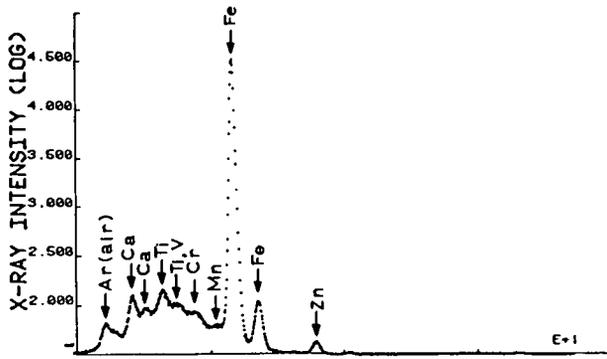


Fig. 5: X-Ray Spectra of Coal Sample 1.

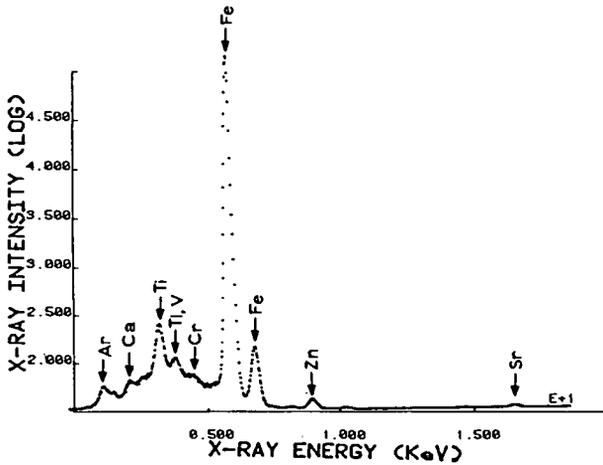


Fig. 6: X-Ray Spectra of Coal Sample 2.

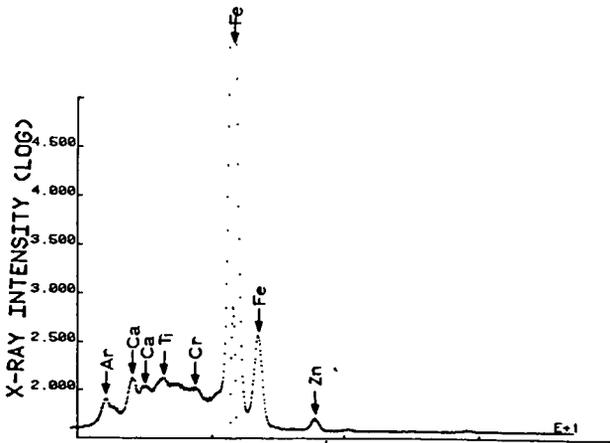


Fig. 7: X-Ray Spectra of Coal Sample 3.

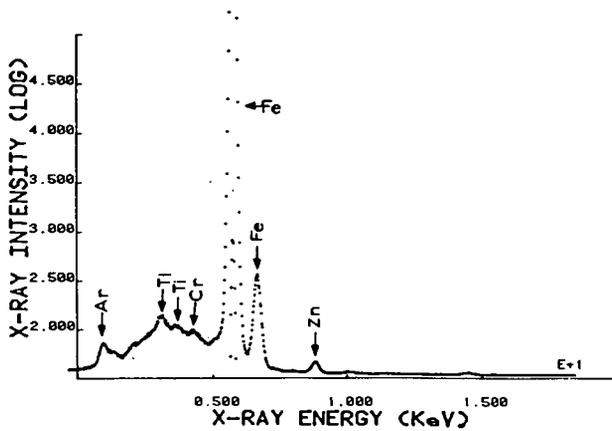


Fig. 8: X-Ray Spectra of Coal Sample 4.

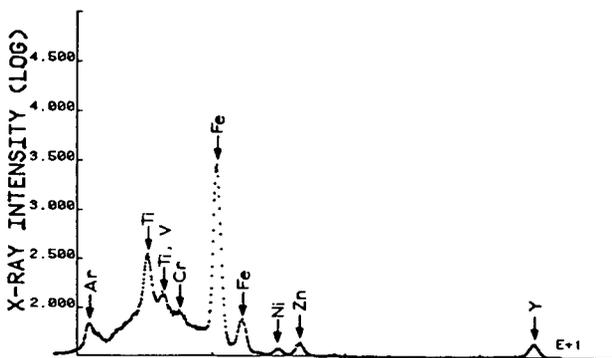


Fig. 9: X-Ray Spectra of Coal Ash Sample 1.

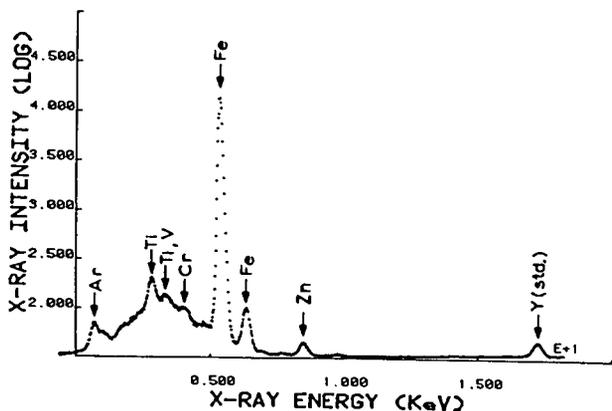


Fig. 10: X-Ray Spectra of Coal Ash Sample 2.