EPR study of some Mongolian coals

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Монгол орны нүүрсний ордууд болох Алагтогоо, Алагтолгой, Багануур, Нарийнсухайт, Нүүрстхотгор, Налайх, Шарын гол, Тавантолгой, Хартарвагатай, Хөшөөтийн нүүрсний электроны парамагнитын резонансын (ЭПР) туршлагын үр дүнг дэлгэв. ЭПР спектрийн гол параметрүүд болох ЭПР шугамын өргөн, g-фактор болон ЭПР шугамын өргөн ба эрчим микродолгионы хэмжээнээс хэрхэн хамаарахыг үзүүлэв.

I. INTRODUCTION

Coal is the most abundant fossil fuel resource in the world. Mongolia has about hundred and forty coal deposits and coal manifestations of Permian, Jurassic and Chalky age. The potential uses for coal are broader, nowadays coal is widely used by the power generation industry as a combustible, as a feed stock for liquid fuels and chemicals. New, more efficient and environmentally sound technologies for coal utilization will be required in the future, and these will arise from more detailed fundamental knowledge of coal structure and reactivity.

The existence of free electrons in coals' natural state offers a great attraction for Electron Paramagnetic Resonance (EPR) analysis to aid in the study of the structure and composition of coal. This method is one of direct and non-destructive approaches to coal analysis. Our approach utilizes the naturally occurring unpaired electrons in coal as "observation posts" from which to analyze surrounding molecular structures. These unpaired electrons have always offered an attractive route to the non-destructive study of coal structure.

Coal is highly aromatic and unpaired electrons delocalize over many carbons. This good coverage of the atoms in coal, together with a reasonably uniform distribution of unpaired electrons throughout all maceral components and the exceptional sensitivity of electron paramagnetic resonance spectroscopy (10^3 times the sensitivity of ^{1}H NMR) makes the paramagnetic spins very attractive natural observation posts from which to non-destructively analyze coal molecular structure.

The paper focuses on the EPR measurement results of a selection of ten Mongolian coals with different ranks ranging from 72.38 % to 88.91% carbon concentration. The nature of paramagnetic centres in the coals has been studied.

II. SAMPLE PREPARATION

Fresh coal samples collected from active ten different coal mines in the territory Mongolia. More than fifty particle coal samples were prepared from each deposit burden with different masses. Mass difference did not influence the results significantly. The representative samples were supplied in small sealed quartz vials under room temperature in the presence of air. Each vial contained about several tens to hundred milligrams of coal.

Content of carbon in the coals is determined by method X-ray microanalysis (see. Table 1).
X-ray microanalysis is made on scanning electron microscope (EO1455VP, Carl Zeiss, Germany) using energy dispersion SiLi-detector («Rontec», Germany). Oxygen enriched coal surface is bombed by rays with 20 keV electron energy (penetration depth of electron up to 10 mkm). Hydrogen atom is not registered by this method.

***Table 1** Carbon content of coals.*

Coal sample		C, mass %
1	Alagtogoo	75.90
2	Alagtolgoi	82.93
3	Baganuur	72.38
4	Narynsukhait	82.36
5	Nuurskhotgor	82.30
6	Nalaikh	81.76
7	Sharyn gol	43.67
8	Tavantolgoi	81.05
9	Khartarvagatai	77.42
10	Khushuut	88.45

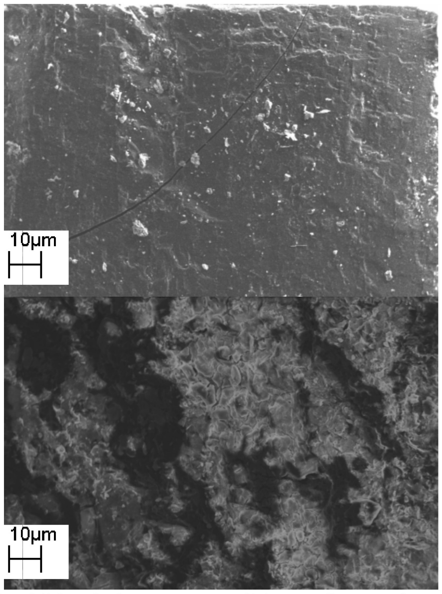

***Fig. 1** Morphology images of Tavantolgoi coal as an example: coal surface in view and close look*

III. ELECTRON PARAMAGNETIC RESONANCE

The EPR spectra were obtained in the solid state at room temperature (300 K) in quartz tubes. A Radio PAN SE/X 2543 spectrometer was used operating at a frequency of 9.3 GHz (X-band), with a 100 KHz modulation frequency, 0.1 mT modulation amplitude and ≤ 70 mW microwave power. For the check of the property of microwave cavity Q or quality factor, which indicates how efficiently the cavity stores microwave energy, is defined as: Q = (2p(energy stored))/(energy dissipated per cycle), where the energy dissipated per cycle is the amount of energy lost during one microwave period, there was used crystal ruby Al_2O_3:Cr, which was fixed on the wall of rectangular shape H_{102} cavity, as an adjustment of phase modulation of magnetic field and calibration of H_1 − component of ultrahigh frequency radiation. Ultrahigh frequency field was measured by frequency meter and magnetic field – by the sensor of nuclear magnetic resonance. Modulation amplitude and time constant of EPR registration (10 min) were chosen from well-known requirements for undistorted registration of first derivative resonance absorption signal by magnetic induction [1, 2]. Registered EPR spectrums as a first derivative resonance absorption signal of microwave radiation of studied coals in the magnetic field. The parameters of the EPR spectra: g-factor, linewidth (ΔB) and integral intensity were evaluated. g − Factor was determined as $g = \frac{h\nu}{\beta B_r}$, where h − is the Planck constant, a − the Bohr magneton, ν − the microwave frequency, and B_r − is the resonance magnetic induction. The influence of microwave power on the width and amplitude of the EPR spectra was studied. Coal free radicals were detected and quantified using the approximation: intensity $\cdot\, \Delta B^2$.

IV. RESULT AND DISCUSSION

In EPR signals of coals, important properties are EPR signal intensity and line form, line width and g-factor value [3].

Singlet, isotropic EPR signal was recorded for all coal samples which has value of g-factor is far close to the g-factor of free electron. EPR parameters of the coals are listed in the table 2.

Table 2 EPR parameters (EPR line width ΔB and g-factor) of coals under study.

Coal sample		EPR parameters	
		ΔB, mT	*g-factor*
1	Alagtogoo	0.62	2.0037
2	Alagtolgoi	0.77	2.0037
3	Baganuur	0.54	2.0039
4	Narynsukhait	0.62	2.0033
5	Nuurskhotgor	0.32	2.0036
6	Nalaikh	0.79	2.0036
7	Sharyn gol	0.79	2.0038
8	Tavantolgoi	0.69	2.0041
9	Khartarvagatai	0.32	2.0032
10	Khushuut	0.57	2.0031

The determination of g-parameter reflects most accurately the content of heteroatoms in the sample. The greater g-factor may explained from its character value for bituminous coal of oxygen containing radical influence in which is unpaired electron localized on the oxygen atom with a great extent [4]. The lowest g-value 2.0031 corresponds to that of free radicals with condensed aromatic system, containing high percent of C, H and low percent O atoms. The highest g-factors 2.0036-2.0041 for paramagnetic centres with the broad and narrow lines indicate existence of nitrogen, oxygen or sulphur free radicals in the simplest aromatic structures in the analysed coal samples. The large (2.0031-2.0041) g-factor variation indicates big difference of coals and high inhomogenity of the analysed coals structural unit.

The EPR spectra width were between 0.32 – 0.79 mT.

Dependences of EPR spectra width and intensity on the microwave powers are shown on figures 2, 3 below for each coal sample. A measurement of the EPR spectra width and amplitude in broad range of microwave powers and analyzing the differences in dependences can be established separated paramagnetic centers. Due to the work [5] the differences in microwave saturation of EPR lines are helpful for separation of the components of the EPR spectra of coal and macerals. The complex character of the coal spectrum is often visible for the higher microwave powers, when some components became partly saturated and the intensities of the others relatively increased.

Dependence of the EPR spectra width on the microwave power values is variable for each coal because of fluently different characteristics of studied coals.

Legibly increasing EPR spectra width is depending on the microwave powers increasing (see. Fig. 2 Dependence − 1, 2, 6, 8) for coals Alagtogoo, Alagtolgoi, Nalaikh, Tavantolgoi which corresponds to all possible orientations of radical. Nalaikh and Tavantolgoi have the saturation tail at highest microwave powers. EPR spectra width value is varied between 0.60-0.85 mT. The increase of the width of the EPR spectra shows coals high ability of reactions such as oxidation, which diminishes the exchange interactions between the unpaired electrons in different polycyclic aromatic systems.

The slow increase of the width of the EPR spectra is accompanied saturation for the coal from Baganuur deposit (see. Fig. 2 dependence 3). On the average values of the microwave powers Baganuur coal has signal widening.

Observed EPR spectra width definite narrowing with the increase of microwave power values dependences 5 and 9, where the coal samples taken from the deposits Nuurstkhotgor and Khartarvagatai. The narrowing EPR lines at higher microwave powers are possible for distant paramagnetic centres, which results from strong exchange phenomena.

In the EPR spectra of the coal from Narynsukhait (see. Fig. 2 dependence 4) may have the most interesting linewidth dependence on microwave powers. At microwave attenuation 3 dB and 15 dB it has ΔB value maximum.

Observed a considerably weak increase of ΔB value at low microwave powers, is being accompanied by itself saturation and strong increase at high microwave powers in the signals Sharyn gol and Khushuut coals.

EPR spectra width dependences on microwave powers can be enveloped as following: EPR spectra is widening with increase of microwave power for the coals Alagtogoo, Alagtolgoi, Baganuur, Nalaikh, Sharyn gol, Tavantolgoi and Khushuut and is narrowing for the coals Nuurst-khotgor, Naryin-sukhait and Khartarvagatai. The absence of broadening in spectra with an increase of the microwave power is characteristic for the majority of carbonic materials. However, as can be seen from figure 2, the insignificant broadening of spectra with an increase of the microwave power is observed for the studied coals. This can be connected with the partial localization of paramagnetic center on the hydrocarbon radicals, to a considerable degree of those subjected to the thermal fluctuations (rotations).

The amplitude of EPR spectra dependence of studied coals on microwave powers is shown in fig 3.

The amplitude of EPR spectra saturation is more clearly expressed for coals from Alagtogoo, Baganuur, Khartarvagatai and Khushuut deposits (see. Fig. 3 dependences 1, 3, 9 and 10). The saturation characterizes relatively long spin–lattice relaxation time of the nature paramagnetic centers in coals.

Tavantolgoi coal amplitude of the EPR spectra passes the saturation at low value of the microwave powers and goes up at the highest microwave power.

The dependences of the amplitude of EPR spectra on microwave powers of the coals from Narynsukhait and Nalaikh can be the superposition of two dependences (see. Fig. 3 dependences 4 and 6): increasing part and a part with clearly expressed saturation. This can testify about the presence of different nature in the paramagnetic center of the bituminous coal or paramagnetic center locating in the substantially different conditions (for example, with respect to interaction with the atmospheric oxygen) [6].

As one can see, the EPR spectra amplitude of the Nuurstkhotgor (see. Fig. 3 dependence 5) coal is linearly increasing with increasing the used microwave power. Accordingly the coal owns the specificity property that having paramagnetic centers with the short relaxation time.

The dependences of coals Alagtolgoi and Sharyn gol are shown in fig. 3 (dependences 2 and 7). The amplitude of the EPR spectra of the both coals strongly was decreased at low microwave powers and then increased steadily for the Alagtolgoi coal and increased strongly for the Sharyn gol coal.

V. CONCLUSION

The first derivative of absorption spectrum for studied coals is singlet and symmetrical. The EPR spectra parameters such as amplitude, width, g-factor are not associated to the content of carbon in the coals. The data on the EPR spectra amplitude and width dependences on microwave powers is confirmed the existence of several paramagnetic centers in studied coals.

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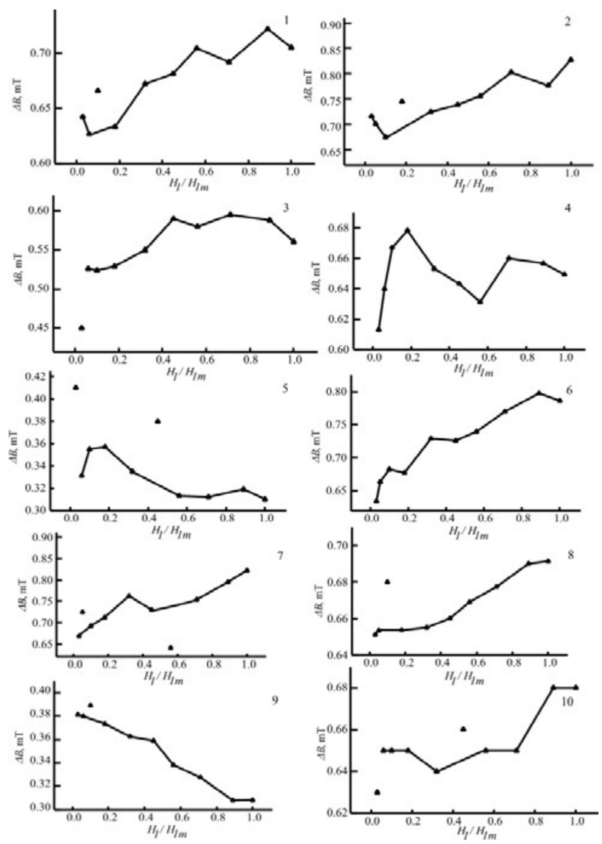

Figure 2 *EPR spectra width dependence on microwave powers for coals from: 1 − Alagtogoo, 2 − Alagtolgoi, 3 − Baganuur, 4 − Narynsukhait, 5 − Nuurstkhotgor, 6 − Nalaikh, 7 − Sharyn gol, 8 − Tavantolgoi, 9 − Khartarvagatai, 10 − Khushuut deposits.* H_{1m} *− amplitude of the* H_1 *− components of magnetic field in the resonator is at the maximum power (70 mW).*

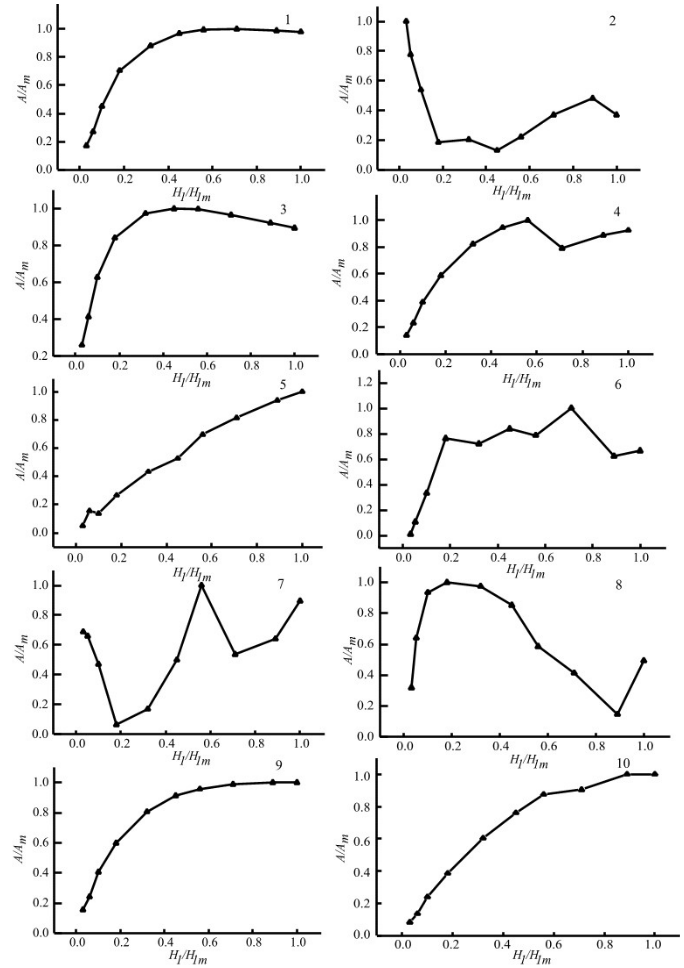

Figure 3 *EPR spectra amplitude dependence on microwave powers for coals from: 1 − Alagtogoo, 2 − Alagtolgoi, 3 − Baganuur, 4 − Narynsukhait, 5 − Nuurstkhotgor, 6 − Nalaikh, 7 − Sharyn gol, 8 − Tavantolgoi, 9 − Khartarvagatai, 10 − Khushuut deposits.* H_1 *− amplitude of the* H_{10} *− components of magnetic field in the resonator is at the maximum power (70 mW). Dependence is calibrated to the maximum amplitude* A_m*.*